



**ADDIS ABABA UNIVERSITY**  
**ADDIS ABABA INSTITUTE OF TECHNOLOGY**  
**SCHOOL OF GRADUATE STUDIES**  
**SCHOOL OF CHEMICAL AND BIO ENGINEERING**

**Performance of Mg and Al mixed oxides derived from  
hydrotalcite for removal of fluoride from a solution**

**By Admasu Arega**

**Advisor Dr. Beteley Tekola**

**ADDIS ABABA UNIVERSITY**

**ADDIS ABABA, ETHIOPIA**

**October, 2015**



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**A thesis submitted to school of graduate of Addis Ababa  
University in partial fulfillment of requirements for the degree  
of Masters of Science in Chemical Engineering (Process  
Engineering)**

**ADDIS ABABA UNIVERSITY**

**ADDIS ABABA, ETHIOPIA**

**October, 2015**

**Addis Ababa University**

## School of Graduate Studies

This is to certify that the thesis prepared by Admasu Arega, entitled Performance of Mg and Al mixed oxides derived from hydrotalcite for removal of fluoride from a solution submitted in partial fulfillment of the requirements for the Degree of Master of Science in Process Engineering complies with the regulations of the university and meets the accepted standards with respect to originality and quality.

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## Abstract

Exploiting efficient and affordable treatment technology for fluoride removal via adsorption is highly desirable.

In this study, calcined hydrotalcites with different Mg/Al molar ratios were prepared. Layered double hydroxides calcined at 450 °C have been shown to recover their original layered structure in the presence of appropriate anions which may enhance its adsorption capacity. Uptake of fluoride ion from aqueous solution by CHT was investigated by batch experiments. The response surface methodology was applied to optimize the adsorption capacity by employing a 3<sup>3</sup> factorial design. The optimal pH, initial fluoride concentration and Mg/Al molar ratio in CHT were found to be 6.0, 5mg/L and 2 respectively for the maximum percentage adsorption of 94.4%. The equilibrium isotherm showed that the uptake of fluoride ion by CHT was consistent with the Langmuir and Freundlich equations and that the Langmuir model gave a better fit to the experimental data than the Freundlich model. The maximum uptake capacity of CHT for fluoride ion by the Langmuir isotherm model was estimated to be 0.4762 mg/g. The influence of varying pH of solution, initial fluoride concentration and Mg/Al molar ratio in the structure of CHT on the kinetics of fluoride removal has also been explored. Kinetic models were used to fit the experimental data, and it was found that the pseudo-second-order kinetics model could be used to describe the uptake process satisfactorily. The present work demonstrates that calcined hydrotalcites may be promising adsorbents for effective removal of fluorine from water resources.

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## List of abbreviation

ANOVA	Analysis of variance
CHT	calcined hydrotalcite.
INEERI	Indian National Environmental Engineering Research Institute
LDH	layered double hydrotalcite
LSD	least significant difference
MDG	millennium development goal
NF	Nanofiltration
PRESS	predicted residual sum of squares
IR	Infrared
RO	Reverse Osmosis
R <sup>2</sup>	Correlation coefficient
RSM	Response surface methodology
USEPA	United States of America Environmental protection Authority
WHO	world health organization

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# 1. Introduction

## 1.1 back ground

Water is essential to sustain life, and a satisfactory (adequate, safe and accessible) supply must be available to all. Improving access to safe drinking-water can result in tangible benefits to health [1]. But nowadays, pure drinking water is available to very few people and others take more or less contaminated water. Throughout history, the quality of drinking water has been a factor in determining human welfare [2]. Deprived sections of the society consumed contaminated water and get sick. It is clear that water pollution should be a concern of every citizen. Water polluted by natural sources such as microorganisms, heavy metals and fluoride has caused great hardship for people forced to drinking. Contamination of drinking water by fluoride poses great risk to human health causing disease called Fluorosis [3].

Contamination of water by fluoride ion occurs naturally during the dissolution of fluoride containing rocks, and artificially from agricultural and industrial waste discharges [4-6]. The occurrence of high fluoride concentrations in ground water and the risk of fluorosis associated with using such water for human consumption is a problem faced by many countries, notably India, Sri Lanka, China, the Rift valley countries in east Africa including Ethiopia, and parts of South Africa [7].

Surface waters seldom contain fluoride beyond the level, whereas excess fluoride may be present in ground waters depending on the presence of fluoride rich minerals as well as hydro-geological conditions [4-6]

In the most extensive database on fluoride distribution in Ethiopian surface and ground water reported that 24.5% of the 1438 samples analyzed had concentration above the 1.5 mg/L optimal concentration recommended by World Health Organization(WHO) [8]. For countries in tropical regions, the recommended fluoride concentration is even lower (about 0.8 mg/L) because of the relatively higher water consumption.

Fluoride is often described as a ‘double-edged sword’ as inadequate ingestion is associated with dental caries, where as excessive intake leads to dental, skeletal and soft tissue fluorosis-

which has no cure. Considering the fact that fluorosis is an irreversible condition and has no cure, prevention is the only solution for this menace. Harmful effects of fluoride intake are primarily, but not exclusively, linked to high levels of fluoride in the drinking water [9].

At present, there are few treatment options that are used for controlling excessive levels of fluoride in drinking water. Based on the mechanism of fluoride removal, the methods can be categorized into chemical precipitation (by alum, lime, lime and alum and calcium chloride), adsorption (activated alumina, clay and fly ash), ion exchange (by synthetic resins and bone char) and membrane technologies (reverse osmosis and electro dialysis). The methods used by industrialized countries such reverse osmosis, electro-dialysis and ion exchange require more technical support for operation, and maintenance and the capital investment cost is very high. Amongst techniques for the removal of fluoride from ground water, adsorption has been reported to be the most effective.

As high-fluoride groundwater is often the only available and reliable source of water in low-precipitation fluorotic areas like Ethiopia, simple methods for low-cost defluoridation of drinking water via adsorption employing cheap and efficient adsorbents are urgently needed.

Of several types of adsorbents, Mg/Al mixed oxides derived from Mg/Al Layer Doubled Hydroxalicates (LDH), have been demonstrated to reconstruct their original layered structure after adsorption of various anions ( $\text{OH}^-$ ,  $\text{CO}_3^-$ ,  $\text{NO}_3^-$ , etc) in aqueous solutions and are good ion-exchangers/adsorbent for removal of toxic anions from contaminated water.

## 1.2.Statement of the problem

Currently, waterborne chemicals pose the greatest threat to the safety of water supplies, particularly of ground water in some parts of the world. Contamination of drinking water by fluoride is one that affects human health and wellbeing.

Excessive and undesirable level of fluoride in drinking water supplies is a major problem in the Rift Valley of Ethiopia. Since ground water forms a major source of drinking water in the rift valley area, both dental and skeletal fluorosis are important public health problems in this area, in addition to its social and economic problems.

In the Rift Valley Regions of Ethiopia, about 90 % of the water samples analyzed have fluoride concentrations  $\leq 7$  mg/L (Redda et al., 2006). It has been reported that people in the Rift Valley of Ethiopia are consuming water up to 33 mg /L of fluoride. The WHO has set 1.5 mg/L as the maximum permissible limit for fluoride in potable water. Therefore adequate measures for the reduction of the level are important. It is also expected that the fluoride concentration may increase mainly because of the excessive utilization of ground water as these area are characterized by water scarcity. In areas where alternative water sources are not available, physical or chemical treatment of water is the best option to control fluorosis. The methods of fluoride removal used by industrialized countries require more technical support for operation and maintenance than is possible in the rural areas of developing countries

The abundant technologies used for removing fluoride from water such as reverse osmosis, activated alumina, and synthetic resins are difficult to implement in Ethiopia due to their high cost, the need for skilled manpower for system operation and maintenance, and the challenges of ensuring a continuous supply chain for the required chemicals and materials.

Simple and low-cost technologies such as the Nalgonda technique and bone char have been tried in Ethiopia, but they have proven inefficient under the prevailing water quality conditions.

Fluoride in drinking water is one such straggling problem that needs a demonstrably successful technological solution to ensure drinking water quality that improves health, backed up by health and chemical data.

Nowadays, the water community cannot ignore demand for a robust solution for fluoride. Yet most of the ground water treatment methods cannot be applied in most developing countries, including Ethiopia, because the population is too poor to afford expenses for the development of the plant used for fluoride removal. Thus, it is required to implement appropriate adsorbent that are accessible to the rural community with technically simple, cost effective, and easily transferable technology.

### **1.3 Objective of the Study**

#### **1.3.1. General objective**

The general objective is to investigate the fluoride removal efficiency of newly synthesized calcined Mg/Al hydrotalcite type of clay from drinking water.

#### **1.3.2. Specific objectives**

The specific objectives of this study are:

- To prepare and characterize three different types of Mg/Al hydrotalcite derived mixed oxides with Mg/Al molar ratio of 1, 2 and 3.
- To investigate fluoride removal efficiency of the three prepared Mg/Al mixed oxides from aqueous solution by varying initial fluoride concentration and pH of solution.
- To find the optimal values of Mg/Al molar ratio, initial fluoride concentration and pH of solution to obtain higher fluoride removal and perform kinetic and adsorption model analysis.
- To study the regeneration of used adsorbent.

#### 1.4. Significance of the Study

Fluoride contamination of groundwater, both anthropogenic and natural, is a major problem worldwide and hence its removal attracted much attention to have clean aquatic systems. The advantages of the research are discussed below:

- Providing better technology for the removal of fluorides from ground water since mostly tested methods are difficult to implement in Ethiopia due to their high cost, the need for skilled manpower for system operation and maintenance, and the challenges of ensuring a continuous supply chain for the required chemicals and materials.
- Even though the research was motivated by challenges in rural villages of Ethiopia, the results of this work will also benefit those living in rural communities of other countries impacted by fluoride
- Gives hope for using low-cost material for removing excess fluoride from drinking and domestic water especially for the rural population in Ethiopia and other developing countries in order to combat dental fluorosis and skeletal fluorosis.
- The government of Ethiopia and NGOs can use this adsorbent and demonstrate through pilot projects for the achievement of MDG.
- The government of Ethiopia can use this adsorbent and demonstrate through pilot projects.
- The technology is adaptable to domestic use and applicability in batch as well as in continuous operation to suit needs simplicity of design, construction, operation and maintenance.
- The reusability of the media makes it eco- friendly having little wastage of water and least disposal problem and percentage of regeneration is considerably high.
- It provided fluoridated water of uniform acceptable quality for the public due to the highest removal capacity of Mg-Alhydrotalcite derived mixed oxides from ground water containing fluoride from 1.5 to 20 mg/L.
- Eliminates embarrassment and anxiety over the appearance of the society teeth due to suffering of dental fluorosis.
- It can be used as foundation in the research and scientific world for further improvement of the efficiency and regeneration of the material.

# 1. Literature Review

## 2.1 Human Health Effects of fluoride intake

Fluoride is one of the very few chemicals for which significant health effects have been correlated to exposure through drinking water. Approximately 75–90 per cent of ingested fluoride is absorbed in the human body [10]. Depending upon its concentration and total amount ingested, fluoride in drinking water can be beneficial or harmful, particularly to infants and young children.

The absorbed fluoride is distributed rapidly throughout the body where it is mainly retained in the skeleton and a small proportion is retained in teeth, soft tissues, and body fluid and accumulates in the kidneys. A low daily dose of fluoride is known to be responsible for inhibiting the formation of dental caries but excessive exposure to fluoride in drinking water, or in combination with fluoride from other sources can give rise to a number of adverse health effects [11].

The regular consumption of low levels of fluoride in drinking water  $< 0.5$  mg/L during childhood is linked with the occurrence of preventable dental caries in later years. The consumption of drinking water containing ‘optimal’ amounts of fluoride (0.5 - 1.5 mg/L) has beneficial effects on the teeth by hardening enamel and reducing the incidence of caries [14].

The increase in the concentration of fluoride ( $>1.5$  mg/L) leads to negative effects of fluorosis. When the fluoride concentration exceeds 1.5 mg/L, aesthetically objectionable dental fluorosis becomes manifest in most populations. Mottling of teeth is one of the earliest and most easily recognized symptoms. These effects are not shown if the teeth were already fully grown prior to the fluoride overexposure [11].

WHO (2004b) report shows excessive fluoride intake (3-6 mg/L) can lead to severe and permanent bone and joint deformations of skeletal fluorosis and the consumption of drinking water with even higher fluoride concentrations (10 mg/L) can lead to crippling fluorosis, which causes the hardening and calcifying of the bones.

Although exposure to 4-8 mg/L of fluoride in temperate climate has not been found to be associated with clinical signs or symptoms of skeletal fluorosis, prolonged exposure to 6 mg/L of fluoride in the tropics may result in osteosclerosis depending on the climatic conditions and

fluoride ingestion from other sources, appropriate fluoride level of 0.5-1 mg/L in drinking water is recommended.

The amount of fluoride increases in the bones up to the age of 55 years but children are the ones affected most and those affected remain crippled or deformed for the rest of their lives [13].

## **2.2. Fluorosis**

Fluorosis, developed in the population who depends on water with high concentrations of fluoride for their daily drinking usage, is one of the most frequently occurring endemic diseases. It can occur in three forms: Dental fluorosis, skeletal fluorosis, and non-skeletal fluorosis. Dental fluorosis results in hypo-mineralization of tooth enamel due to the continuous ingestion of excessive amount of F during tooth development. This results in a variety of pathological changes in the structure of teeth and if not prevented during childhood can hamper dental esthetics and psychological well-being. It is regarded as an unfortunate side effect to its caries protective benefits. Skeletal fluorosis affects the bones and major joints of the body. The bone gets hardened and less elastic, resulting in an increased frequency of fractures. Non-skeletal fluorosis affects invariably all the soft tissues, organs and systems of the body. Excessive F results disturbances in soft tissues due to chronic intoxication.

The problem of fluorosis has a definite relationship with the following factors [15]

- fluoride concentration in drinking water
- period of exposure
- climatic factors (temperature)
- fluoride exposure from other sources and
- nutritional status

### **2.2.1 Distribution of fluorosis in the world**

Elevated levels of fluoride in drinking water occur in a number of parts of the world and these often have significant adverse impacts on public health.

The latest information shows that fluorosis is endemic in at least 25 countries across the globe. Known fluoride belts on land include: one that stretches from Syria through Jordan, Egypt, Libya, Algeria, Sudan, Kenya and Tanzania, and another that stretches from Turkey

through Iraq, Iran, Afghanistan, India, northern Thailand and China. There are similar belts in the America and Japan. Fourteen countries in Africa, eight in Asia and the Middle East and six in the Americas face the problem of fluoride concentration above 1.5 mg-F/L in drinking water. Many of these countries are confronted with the problems of endemic dental and osteofluorosis [16].

The global prevalence of fluorosis is reported to be about 3.2%.The total number of people affected is not known, but a conservative estimate by UNICEF would number in the tens of millions. Wang Hongtao estimated that in the order of 80 million people worldwide suffer from fluorosis. The majority of these people live in tropical countries. The highest fluoride concentration ever found in natural water was 2800 mg/L, recorded in Lake Nakuru in the Rift valley in Kenya [17, 18].

### **2.2.2 Distribution of fluorosis in Ethiopia**

Fluorosis is assessed as a risk for a population of close to 8.5 Million in Ethiopia. The population at risk lives mainly in the Rift Valley spread over different regional states: Afar, Amhara, Oromia and SNNPR. Moreover, there is an influx of migrants into this potentially rich part of the country. In the absence of rivers in large part of the area, communities largely depend either on rain-water harvesting ponds or increasingly on groundwater from public boreholes for their drinking water supply [19, 20].

The fluoride level of drinking water collected from deep wells in large farms, villages and towns of the Ethiopian Rift Valley ranged from 1.5 mg/L to 36 mg/L. Dental fluorosis was found to be widespread among children, mainly in the age group of 10 to 14 years. Skeletal fluorosis invariably occurred in those that were consuming water with fluoride levels of more than 4 mg-F/L for over 10 years. The most common incapacitating neurological complication of crippling skeletal fluorosis was cervical radiculo-myelopathy [21].

### **2.2.3 Socio-Economic impacts of fluorosis**

Fluorosis has significant socio-economic impacts.Children with dental fluorosis can suffer significant embarrassment and anxiety over the appearance of their teeth. No matter how much they might brush and floss, the fluorosis stains do not go away.It is currently estimated that water fluoridation causes cosmetically objectionable fluorosis in 2 to 12% of the population.The cosmetic and psychological effects of fluorosis are significant.

Recent research, however, has found that fluorosis rates in fluoridated areas now range as high as 70 to 80%. Not only has the prevalence of fluorosis increased, but its severity has increased as well.

The aesthetic problems related to dental fluorosis and the psychological impact are hard to quantify yet should not be underestimated especially among young people. Moreover, persons who develop skeletal fluorosis suffer considerable hardship and have reduced productivity. Fluorosis often precludes the ability to work, driving suffering individuals and their families deeper into poverty [22].

### 2.3. Nature and distribution of fluoride in Ethiopia

Fluorine is the most electro-negative reactive element known, as result not found free in the environment. Fluoride is found at significant levels in a wide variety of minerals, including fluorospar  $\text{CaF}_2$ , cryolite  $\text{Na}_3\text{AlF}_6$ , and fluoroapatite  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$  [23]. The average crustal abundance is  $300 \text{ mg kg}^{-1}$  [24]. Fluoride is a natural constituent of the biosphere, and, consequently, of clay and soil. It is commonly associated with volcanic activity and fumarolic gases. Thermal waters, especially those of high pH, are also rich in fluoride [10]. Fluoride can also be released to the environment from anthropogenic sources through discharge of agricultural and industrial products such as glass, electronics, steel, aluminum, pesticide and fertilizer manufacture's [25].

The inherent fluoride content, however, varies greatly from one area to another. The East African Rift Valley which cuts through Ethiopia is geomorphologically still an active volcanic region. The volcanic rocks particularly in the young basalt contain high concentrations of fluoride and fluorapatite. Large fault systems in the Valley create conditions that allow very deep percolation of infiltrating surface water. The floor of the Rift Valley which is characterized by high hydrothermal activity accelerates the solubility of fluorite.

The volcanic base-rock in the African Rift system is predominantly alkaline, and rich in e.g. sodium and fluoride. The soil produced by the weathering of these rocks is similarly rich in fluoride. After precipitation, however, rainwater leaches fluoride from soils as well as from crystalline rocks. The surface waters of East Africa, therefore, usually have high fluoride concentrations. Furthermore, since the hydrochemistry of aquifers is strongly influenced by

the surrounding lithology, the fluoride content of ground water of Rift Valley is high, frequently to the extent that the waters are rendered unfit for human consumption [26, 27].

The water supplies in the Ethiopian Rift Valley come mainly from boreholes with depths from 10 to 100 meters; the majority is deep boreholes.

The Ethiopian Rift Valley ground water has very high fluoride levels, ranging from 0.4 to 36 mg/L. The water sources used in areas with the highest population densities have fluoride contents of 3.5 to 13.0 mg/L. Studies from other countries and our own experience in Ethiopia have shown that these levels cause dental fluorosis in children and over a prolonged period skeletal and crippling fluorosis.

The guideline value for drinking water specified by the Ministry of Water Resources in Ethiopia indicates that the fluoride concentration should not exceed 3 mg/L.

In the Ethiopian Rift Valley dental mottling has been recognized in areas with fluoride concentrations in water as low as 2 mg/L. Higher levels, above 4 mg/L cause severe disfiguring dental fluorosis with enamel hypoplasia [28]. The fluoride level of ground water from different sample sites in the rift valley regions of Ethiopia are given below [78]:

**Table.2.1. Fluoride Content of Water samples in Various Areas of the Ethiopian Rift Valley.**

Samples sites	Fluoride Concentration (mg/L)	Source of water	Years in service
Dubti (village)	1.2	Borehole	9
Logiya (town)	1.0	Borehole	10
Mille (town)	0.4	Borehole	10
Gewane (town)	0.7-2.5	Borehole	16
Amibara (farm)	2.4-3.0	Borehole	5
MelkaWarer (farm)	3.5	Borehole	9
Melkasedi (farm)	1.5-4.3	Borehole	13
Awash (station)	1.4-1.6	Treated river	20

Meterhara (estate)	2.5-6.2	Borehole	20
Abadir (farm)	4.0	Borehole	12
Wolenchiti (town)	2.5	Borehole	15
Nazareth (town)	0.8 - 3.3	Borehole	20
Wonji-Shoe (estate)	2.5-14.0	Borehole	30
Koka (town)	26.0	Borehole	20
AlemTena (town)	9.0	Borehole	17
Sami berta (village)	9.0	Borehole	23
Meki (town)	0.7-1.0	Borehole	6
Zeway (town)	1.0 1.6	Borehole	10

#### 2.4 .WHO and Ethiopian guidelines limit on fluoride

The World Health Organization had set guidelines limits on fluoride. The guidelines, with 1.5 mg/L as the upper limit of safe level are based on an average per capita daily water consumption of 2 liters. This 1.5 mg /L fluoride guideline value set was subsequently re-evaluated and revised by the world health organization [29]. The 1.5 mg /L guideline value of WHO is not a fixed value but is intended to be adapted to take account of local conditions such as diet, water consumption, etc.

The guideline value for drinking water specified by the Ministry of Water Resources in Ethiopia indicates that the fluoride concentration should not exceed 3 mg/ L.

However, it is abundantly clear that the daily consumption of water in hot tropical environments is much higher than the WHO proposes average and can be as high as 10 L/day. In this regions, exposure risk increases due to high consumption of water. Brouwer reported the development of dental fluorosis from consumption of water with fluoride concentration as low as 0.8 mg/L and crippling fluorosis above 7.0 mg/L [30].

## 2.5. Fluorosiscontrolling approaches

There are some remedial measures to combat fluorosis in areas where fluoride concentration is beyond the permissible level. These are:-

- The first and most important option is finding alternative sources such as searching a safe water source in the vicinity by drilling a new well. It may be possible to get safe water by drilling a new well and/or drawing the water from different depths.
- Transporting water from a distant source. This is an important option in endemic fluorosis areas, but initial cost will be high.
- Blending high fluoride with low fluoride water.
- Dual water sources. If there are sources with both high and low fluoride levels, the source having low fluoride levels can be strictly limited to drinking and cooking and the water source with high fluoride can then be used for other purposes.
- Provision of bottled water for growing children, this is not economically feasible in poor developing countries.
- Rainwater harvesting. Household-roof rainwater harvesting and container storage can provide potable water for families, but it is seasonal. In areas where alternative sources are not available treatment of contaminated water is the most reasonable approach [31].

## 2.6. Defluoridation Techniques

Defluoridation was the conventional and widely tested method for supplying safe water to the fluorosis affected communities. Defluoridation is defined as, the downward adjustment of level of fluoride in drinking water to the optimal level.

In drinking water with high concentration of fluoride, defluoridation of water at the point of use or source has to be experienced in order to eliminate any negative effects. Various techniques and materials have been used throughout the world to carry out water defluoridation [32].

These can be broadly divided into three categories based on mechanism of fluoride removal: precipitation, membrane and adsorption methods.

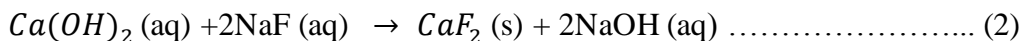
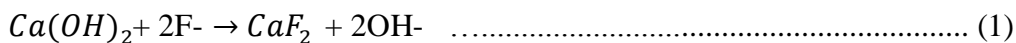
### 2.6.1. Precipitation method

Precipitation method involves the addition of chemicals (coagulants and coagulant aids) to the water and the subsequent precipitation of a sparingly soluble fluoride salt as insoluble fluorapatite. Fluoride is removed either by precipitation, co-precipitation, or adsorption onto the formed precipitate. Fluoride removal by chemical precipitation using Aluminium salts (eg. Alum), Poly Aluminium Chloride, Poly AluminiumHydroxysulphate, Brushite, iron, lime and magnesium compounds, and calcium phosphate were investigated by several researchers. Treatment with lime and magnesium makes the water unsuitable for drinking because of the high pH after treatment [33].

The use of alum and lime has been extensively studied for defluoridation of drinking water, and it is popularly known as the Nalgonda technique by the Indian National Environmental Engineering Research Institute (INEERI) to be used at both the community or household levels [34]. It involves addition of aluminium sulfate ( $Al_2(SO_4)_3 \cdot 18H_2O$ ), lime and bleaching powder followed by rapid mixing, flocculation, sedimentation and filtration. The dose of alum increases with increase in the fluoride and alkalinity levels in the raw water. During this flocculation process many kinds of micro-particles and negatively charged ions including fluoride are partially removed by electrostatic attachment to the floc. Its use is most popular in India; and it has also been applied in Ethiopia on household and community level [35]. According to Muller report, Nalgondadefluoridation units can reduce fluoride concentrations from ~10 mg/L to ~2.5 mg/L, but none of the evaluated plants in East Africa meet the WHO international guideline value of 1.5 mg/L [36,37].

The technique has been operated in a number of villages in India as fill and draw type and hand-pump attached plants (Meenakshi and Maheshwari, 2006).

Chemical precipitation technique involves addition of aluminum salts along with lime to the F rich water followed by flocculation and sedimentation or filtration. In the first step, lime reacts with F impurities such as NaF, HF, etc. to form insoluble calcium fluoride.



Essentially, in the second step, aluminum sulfate or aluminum chloride or both together, is added. Aluminum salt acts as a coagulant and is often being used for viable and effective fluoride removal from water. The basicity present in water with alum yields an aluminum salt,  $[\text{Al}(\text{OH})_3]$ , which is insoluble. It has been reported that the pH of the contaminated water increases up to 12; however, the best F removal is achieved between the pH ranges of 6-7 (Aoudj et al., 2012). The dose of alum is typically around 20 fold the lime required.

The merits of this technology is its use both at domestic and community levels, possible manual operation, cost-effectiveness and flexibility in design considerations depending on the concentration of fluoride in the area [33].

Despite the Nalgonda Technique being utilized in many cases and places, it has not yet been demonstrated to be the method of choice. The primary barriers to its application in rural and remote communities are:-

- the requirement of continual correct chemical dosing and close monitoring to ensure effective fluoride removal
- system effectiveness is influenced by the raw water quality
- potential to increase the TDS of the treated water
- continuously produces a sludge that requires appropriate disposal, and
- An increase in the concentration of aluminum ion from deviation of pH 7 and on the amount of suspended aluminum hydroxide flocs.

### **2.6.2 Membrane Method**

Membrane filtration technology has been utilized for many years in small volume treatment of pure and ultra-pure water for many industries and is increasingly being utilized for the treatment of drinking water.

In membrane filtration, the water containing high concentration of pollutants is passed through a semi permeable membrane. The membrane discards atoms on the criteria of size and electric charge. The pollutants are removed from the water and collected at retentate side; whereas, clean water is recovered through permeate.

Defluoridation based on membrane methods is used in developed countries for drinking water treatment. It includes reverse osmosis, nanofiltration, electrodialysis and electrocoagulation [37].

## **Reverse Osmosis and Nanofiltration**

Reverse Osmosis (RO) membranes first became commercially available in the 1960s for treating seawater/brackish water and today are the most common type of membrane processes used in potable water treatment in the US [11]. Nanofiltration (NF) is another newer type of membrane filtration with growing interest and popularity. Both processes are capable of removing a large spectrum of contaminants from water, including turbidity, pathogens, salts, hardness, heavy metals and natural and synthetic organics, although NF membranes exhibit lower removal capabilities and operate at lower pressures than RO membranes [36]. RO is a well-established technique for the removal of fluoride from water. Its fluoride removal efficiency can reach up to 95-98% and the USEPA recommends RO as one of two options for the 'Best Available Technologies' for the removal of fluoride. Both RO and NF are superior to other traditional treatments because they do not require additional chemicals and frequent maintenance. Even though RO and NF processes are highly effective for fluoride removal, the systems require high treatment technology capital costs, high energy consumption is not selective for fluoride ion removal and specifically trained operators. RO systems may also cause significant water losses, typically 10-35%, which can have further implications on aquifer stores and water conservation measures. Membrane fouling by colloidal material and certain dissolved salts can affect the treatment performance [39-41].

Nanofiltration (NF) is a relatively new process in contrast to RO, ultrafiltration (UF) and microfiltration (MF), and it is emerging as a practically functional technology in treating industrial wastewaters. Nanofiltration is characterized by attributes between reverse osmosis (RO) and ultrafiltration (UF). Regardless of the similarity in operation with RO, NF is operated at a comparatively lower pressure yielding identical permeate flux even at lesser pressure. NF removes less than 60% of the monovalent ions as opposed to 90% by RO membranes. RO can completely demineralize water with very low or practically no selectivity for monovalent ions but it suffers from high operating pressure, low permeate flux and high energy requirements (Alarcon-Herrera et al, 2013). In particular, fractional defluoridation can be attained by altering the operating variables of the NF process; while simultaneously keeping the required F content in the water.

## **Defluoridation by electro dialysis**

Electrodialysis is another emerging technique for removing ionic compounds from aqueous media using ion exchange membranes in which the applied electric field acts as a driving force and is responsible for separation of contaminants. The application of electric current between two electrodes results in passage of cations to the cathode and anions to the anode through the negatively charged cation exchange membrane and positively charged anion exchange membrane, respectively. The end result is the increased and decreased concentration of cations and anions in alternate partitions. The global trend is shifting towards electro dialysis as an alternate technique for defluoridation primarily because of its simplicity and ability to overcome the shortcomings of the chemical processes.

The basic principle of the process is the adsorption of fluoride with freshly precipitated aluminum hydroxide, which is generated by the anodic dissolution of aluminum or its alloys in an electro chemical cell [42].

The fluoride ion concentration could be brought down by 96% (0.8 mg/L), which is below the prescribed limit by WHO. Sahli et al. (2007) also suggested that electro dialysis gives better performance for the removal of Cl and F from brackish water. The combination of adsorption and electro dialysis appears to be a cost-effective and better method to remove F ions from brackish groundwater. The most predominant advantages offered by membrane processes are: very high removal capacity (up to 98%), one step purification and disinfection, and no chemical usage. However, it is not entirely appropriate as it removes all ions from the water. A remineralization process is required after the treatment as some minerals are essential and must be present in potable water. Moreover, it is costly due to high initial membrane cost and operating cost. Also, disposal of concentrated fluoride sludge which is produced at retentate side can be a major problem.

### **2.6.3 Ion exchange method**

Many reports have highlighted the efficacy of ion exchange with other techniques (Onyango et al., 2005, 2006). Usually, ion exchange technique removes fluoride by adsorption rather than exchanging ions. The fundamental reason is that the fluoride concentration is comparably lower than other ions present in water. Cation exchange resins are more selective for F

removal than anion exchange resins (Meenakshi and Viswanathan, 2007). However, the defluoridation capacity and selectivity for fluoride is dependent on the type of resin. The loading of metal ions influences the fluoride removal drastically, owing to variations in their properties (Luo and Inoue, 2004). Thus, it is difficult to maximize the defluoridation capacity (DC) of ion exchange resins while simultaneously enhancing the fluoride selectivity.

This method uses charged anion resins to seize fluoride ions in the water. Synthetic chemicals, namely, anion and cation exchange resins have been used for fluoride removal. Some of these are Polyanion (NCL), Tul-sionA - 27, Deacedite FF (IP), Amberlite IRA 400, Lewatit MIH - 59, and Amberlite XE – 75. The fluoride exchange capacity of these resins depends upon the ratio of fluoride to total anions in water [43].

#### 2.6.4 Adsorption Method

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term adsorption encompasses both processes, while desorption is the reverse process. Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favorable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption.

- Physisorption or physical adsorption is a type of adsorption in which the adsorbate adheres to the surface only through Van der Waals (weak intermolecular) interactions, which are also responsible for the non-ideal behavior of real gases.
- Chemisorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to the Van der Waals forces which cause physisorption.

A common mechanism by which the adsorption of fluoride ions occurs onto solid particles can be given by the following three steps:

1. Mass transfer of fluoride ions to the external surface of the adsorbent
2. Fluoride ion adsorption onto external particle surface,
3. Intra-particle diffusion of fluoride ions from the exterior surface and possible exchange with elements on the pore surface inside particles.

During recent years adsorption is gaining wide attention for fluoride uptake even in developing countries. This technique functions on the adsorption of fluoride ions onto the surface of an active agent. Adsorption methods can be implemented for the removal of fluoride due to physical, chemical, or ion exchange interactions with the adsorbents [44].

Amongst other methods, adsorption is a conventional technique which is widely used for defluoridation of water because it is economical, robust, environmentally benign and efficient. Adsorption techniques are easy to use and a lot of adsorbents have been investigated. A wide range of materials has been tried and studied for fluoride uptake as adsorbent, such as activated alumina, activated carbon, cement paste, aluminum hydroxides, aluminum oxide hydroxide, bone char, various types of clays and red mud etc [10]. Researchers have also worked on defluoridation using wastes of industrial and biotic origins.

However, these promising adsorbents are not still commercially available. In the case of commercial options available in the worldwide market, the activated alumina and the bone char are the most used and effective adsorbents for fluoride removal from water. But now they have proven inefficient under the prevailing water quality conditions.

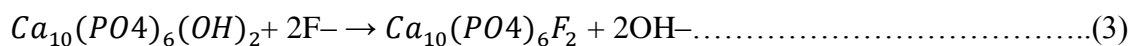
All in all, the choice of the adsorbent seems to be reliant on factors such as the ability to absorb from dilute solutions, pH, removal duration, adsorbent stability, regeneration, and adsorption capacity in the presence of competing ions, and the economics (Mohapatra et al., 2009).

Some of the most frequently encountered adsorbents used for fluoride up take from water are reviewed below.

#### ***2.6.4.1. Bone Char***

Bone char is commonly used in developing countries for defluoridation of drinking water. The principal active component of bone char is  $Ca_3(PO_4)_2$ , 57 - 80 %,  $CaCO_3$  6 - 10 % and

activated carbon 7 - 10 % [10]. Raw BC, prepared from animal skeletons by calcination at 300 - 600 °C, and the temperature used optimize its properties as a defluoridating agent. Therefore, BC prepared by heating to 550 °C in low oxygen atmosphere provides good quality adsorbent. The fluoride removal mechanism of BC is believed to be due to its chemical composition, mainly as hydroxyapatite. The removal process is considered to be ion exchange between fluoride in the solution and carbonate of the apatite comprising bone char [10]. The bone char media has the capability of producing water with a residual fluoride concentration of less than 0.1 mg L-1 from an initial fluoride of 12.0 mg L-1 .The principal reaction is hydroxyl-fluoride exchange of apatite:



The advantage of defluoridation method by BC is; locally available, low cost, simple and easy to build large scale community plant. Disadvantages of this technique are; the bone char harbors bacteria and hence unhygienic. It may give taste without a regular fluoride analysis, nothing indicates when the material is exhausted and the fluoride uptake is ceased. It is a technique sensitive procedure, since the efficiency of bone char as an adsorbent for fluoride is a function of the charring procedure which should be done cautiously. Moreover, the use of bone-char may invite cultural and religious objections. At a domestic level, BC defluoridation appears to be suited to Thailand and Africa, but so far there is no experience in wide scale implementation [45].

#### 2.6.4.2. Clay

The term clay is often used in a non-specific description of either a soil consisting of a range of small particles or very fine-grained earthy substances comprising a combination of minerals, inorganic amorphous material and organic matter or a specific clay mineral [46].

Clay is a sedimentary material composed mainly of fine particles of hydrous aluminum silicates and other minerals and impurities [10]. Both clay powder and fired clay are capable of sorption of fluoride as well as other pollutants from water. The first comprehensive study of fluoride adsorption onto minerals and soils was published in 1967.

According to different studies on the defluoridation capacity of clay and usability of the method, they reach on different conclusions. However, in general they found that the adsorption capacity of clays was low [11]. Thus, Zevenbergen conclude that based on the

study the capacity of the ando soil of Kenya was 5.5 mg/g while GirmaMoges [47] found that the capacity of ground and fired clay pot of Ethiopia was not more than 0.2 mg/g. Bardsen and Bjorvatn (1997) also studied the sorption capacity of clay calcined at 600 °C and found that, 0.07 mg/g.

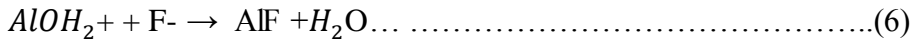
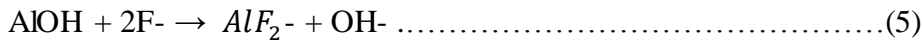
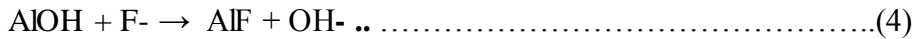
Moges studied the defluoridation of water using fired clay chips in Ethiopia[47]. Their findings indicated that defluoridation efficiency is affected by factors such as dose of the medium, the pH of the solution, the contact time and initial fluoride content. A packed column of the ground clay pot chip was also tested for defluoridation. The column defluoridates 6 L of tap water containing 10 mg L<sup>-1</sup> fluoride to below 1.5 mg L<sup>-1</sup>.

Thus the benefits of defluoridation by clay are: abundant in nature, locally available and relatively low cost. But, the major drawbacks are low capacity and it may also retained toxic heavy metals and wide range of other pollutants in its strata [48].

#### **2.6.4.3. Activated Alumina**

Activated alumina is a granular form of aluminum oxide ( $Al_2O_3$ ) with very high internal surface area, typically in the range of 200-300 m<sup>2</sup> g<sup>-1</sup>. This high surface area allows the material a very large number of sites where adsorption can occur. It has been widely used for removal of fluoride from drinking water. It is prepared by low temperature dehydration (300 oC - 600 oC) of aluminum hydroxides (Haoet *al.*, 1986). The crystal structure of alumina contains cation lattice discontinuities giving rise to localized positive charge, and makes alumina to attract various anionic species. Fluoride removal capacities of AA mainly depend on pH. The narrow pH range of 5.5 to 7 is best for efficient removal of fluoride [25]. Higher removal at lower pH values due to reduction of negative charges at the surface of AA. The removal of fluoride from water by adsorption on locally produced hydrated alumina has been also demonstrated by BeneberuShimelis [49]. The result indicated that F<sup>-</sup> adsorption is affected by factors such as initial F<sup>-</sup> concentration, thermal pretreatment, dose of adsorbent, contact time and the pH of the solution. It was found that the treated adsorbent has a highest fluoride adsorption capacity than the untreated adsorbent, at 1hr contact time and 1.6 g/L dose with minimum removal capacity 23.75 mg/g. The mechanism of fluoride removal is most probably by ligand exchange reaction at the surface of activated alumina. Thus fluoride

binding to a positively charged or neutral activated alumina can be represented by the following reactions.



Most studies in the laboratory are performed with single component system, i.e. considering fluoride ion only. But in reality water resources to be treated constitute other components such as chloride, nitrate, sulfate, bicarbonate and others. These components could have an effect on fluoride removal efficiency. The adsorption sites on the activated alumina are also attractive to a number of anions other than fluoride. Some studies showed that the presence of other coexisting ions in water have an effect on fluoride removal efficacy of activated alumina.

The studies show that chloride and sulfate ions have very little effect on the fluoride removal capacity of activated alumina but bicarbonates have a profound effect on fluoride removal efficiency of activated alumina [50].

Activated alumina happens to be one of the most popular and widely used solid adsorbents for the defluoridation of potable water and many reports are available on large-scale installations (Chauhan et al., 2007). Alumina is popular amongst other adsorbents because it maintains its structural stability without shrinkage, swelling or disintegration in water (Serbezov et al., 2011). Granules of activated alumina having a very high surface area of ~200-300 m<sup>2</sup>/g possess a substantial number of active sites to facilitate adsorption.

The disadvantages with activated alumina are; Adsorption of fluoride is possible only at specific pH range, needing pre-and post- pH adjustment of water. Frequent activation of Alumina is needed, which make the technique expensive. Regeneration generates concentrated fluoride solution, causing disposal problems. Adsorption efficiency of the activated alumina diminishes with increasing number of usage-regeneration cycle [21].

In Ethiopia a method based on adsorption by activated alumina has been practiced in Wonji-Shoa and Methara sugar estates since 1962. Despite the fact that activated alumina is the most effective and widely used material, all plants at the sugar factories are not functional at present mainly due to high cost of imported activated alumina [51].

#### *2.6.4.4. Aluminum Oxide Hydroxides*

Aluminum oxide hydroxide (AlOOH) exists in many structural forms, boehmite is one of its structural form. It is the major constituent of many bauxite minerals. It can also be synthesized in the laboratory, for instance, by neutralizing inorganic or organic aluminum salts in basic media. It has ion exchange ability, and its hydroxyl group has selective adsorptivity for anions of interest. The removal of phosphate from water by adsorption onto AlOOH has been investigated by Tanada [52]. Rate of adsorption phosphate ion on AlOOH was faster than other adsorbents. The result indicated that the amount of phosphate adsorbed onto AlOOH is influenced by pH, dose of adsorbent, contact time and other competing adsorbate, and conclude that aluminum oxide hydroxide could be used for the removal of phosphate from water. Therefore, a similar pattern of fluoride adsorption onto AlOOH would be expected.

Recently, aluminum oxide hydroxide has shown good adsorption capacity both in batch and packed bed continuous systems on laboratory scale as compared to activated alumina [40, 49]. Conversely, at present nanotechnology has developed quickly in various fields over the past decade and nanometric material has attracted much attention for its special properties, and has been growing interest in the application of nano particles as sorbents for fluoride. Thus compared with the traditional micron-sized materials used for separation processes, nano-sized carriers possess a good performance due to the high surface-area to volume ratio and the absence of internal diffusion resistance [45]. Furthermore, the surface properties, electronic structure, coordination, etc., are modified when the material dimensions reach nano scale. Thus, the nano adsorbents with higher specific surface area have superior adsorption capacity. Most atoms on the surface of the nano particles are unsaturated and can easily bind with other atoms. Sundaram studied the defluoridation efficiency of nano-scale hydroxyapatite and showed promising results. Though the removal of fluoride using nano alumina had been reported earlier and few reports also describing the potential of nanometer-scale aluminum oxide hydroxide (nano-AlOOH) to remove fluoride from aqueous solutions are available. Therefore, in this study nano-AlOOH was synthesized in the laboratory scale and used as an adsorbent to remove fluoride from aqueous solutions and investigated the effect of different parameters, such as contact time, dose, initial adsorbate concentration, thermal treatment, pH etc [53,54].

#### 2.6.4.5 Bio- adsorbent

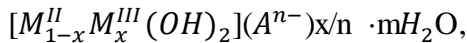
Jamode studied the removal of fluoride by fresh leaves obtained from khair (*Acacia catechu*), pepal (*Ficus religiosa*) and neem (*Azadirachta indica*) trees [40]. The result showed that low-cost bio-adsorbent could be efficiently used for the removal of fluoride ions over a wide range of initial fluoride ion concentrations and the removal efficiencies decrease with high initial fluoride concentration. There is no need to regenerate the adsorbent because they are locally abundant and cheap to acquire.

The seeds extract of Moringa is also used as coagulant for drinking water clarification. It is known to be bioadsorbent for the removal of turbidity, chemical contaminants and microorganisms from water [55].

#### 2.6.4.6. Hydrotalcites

Hydrotalcite, first discovered in Sweden around 1842, is a hydroxycarbonate of magnesium and aluminum and it occurs in nature in forms of foliated and contorted plates and/or fibrous masses. They are formed in nature by the weathering of basalts or from precipitation in saline water sources.

Hydrotalcites (HT) are synthetic or natural layered materials made of positively charged two-dimensional sheets of mixed hydroxides with water and exchangeable charge-compensating anions. Their most general formula can be written as follows:



where  $M^{II}$  is divalent cation like  $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ , etc.,  $M^{III}$  trivalent cations like  $Al^{3+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$ , etc.,  $A^{n-}$  interlayer anion and  $x$  is defined as the  $M^{III}/(M^{II}+M^{III})$  ratio. Brucite is the crystallographic structure from which hydrotalcites are derived. In brucite ( $Mg(OH)_2$ ),  $Mg^{2+}$  ions are six fold coordinate to  $OH^-$  to form octahedra that share edges with their neighbors to constitute infinite two-dimensional sheets. Anionic clays crystallize in a layer-type lattice as a consequence of the presence of relatively small, twofold positively charged ions in proximity with polarisable  $OH^-$  ions. These sheets are stacked on top of each other and held together by weak interactions through hydrogen atoms. In brucite-type layers, the divalent cations can be substituted by trivalent cations with similar radius thus creating an excess of positive charges. The interlayer space between each brucite sheets is filled with water and anions that compensate the positively charged layers [56, 57].

This region is highly disordered and the amount of water is a function of the temperature, of the water vapour pressure and of the nature of the anions present. In the mineral hydrotalcite the bivalent metal is  $Mg^{2+}$  and the trivalent metal is  $Al^{3+}$ . The excess of positive charges on the hydroxide layers arises from the partial substitution of  $Mg^{2+}$  by  $Al^{3+}$  and can be compensated by carbonate anions, which is the preferred anion found in natural HTs. The most popular hydrotalcite is the stoichiometric double magnesium–aluminium hydroxide the formula of which is  $Mg_6Al_2(OH)_{16}(CO_3) \cdot 4 H_2O$ . The degree of partial substitution of  $Mg^{2+}$  by  $Al^{3+}$  noted as  $x$  in the general formula can vary in the range 0.1–0.5 or 0.2–0.5, giving rise to the family of Mg–Al hydrotalcites.

Hydrotalcite is a layered double hydroxide of general formula  $Mg_6Al_2(OH)_{16}(CO_3) \cdot 4 H_2O$ , whose name is derived from its resemblance with talc and its high water content. Layered double hydroxides (LDH) comprise an unusual class of layered materials with positively charged layers and charge balancing anions located in the interlayer region. The layers of the structure may stack in different ways, to produce a 3-layer rhombohedral structure (3R Polytype), or a 2-layer hexagonal structure (2H polytype) which was formerly known under the name manasseite. The two polytypes are often intergrown. The carbonate anions that lie between the structural layers are weakly bound, so hydrotalcite has anion exchange capabilities. Hydrotalcite suspension contains the active ingredient hydrotalcite (aluminium magnesium carbonate hydroxide hydrate).

hydrotalcites” (HT), that is, the solids that have a structure closely related to that of the mineral hydrotalcite, that is, rhombohedral  $Mg_6Al_2(OH)_{16}(CO_3) \cdot 4 H_2O$ , enter the family of anionic clays. Hydrotalcites have three important characteristics that make them interesting for various applications. First, HTs have a good anion-exchange capacity and are therefore used as ion-exchangers, adsorbents or sensors. Secondly, most of them, depending on the composition, behave as solid bases; that is, why they were widely studied and successfully used as basic catalysts for several reactions such as self condensation, cross-aldol condensation of aldehydes and ketones, Knoevenagel condensation, Claisen–Schmidt condensation, Michael addition, transesterification, and alkylation.

Thirdly, hydrotalcite can be prepared with several reducible bivalent (Ni, Cu, Co) and trivalent (Fe, Cr) cations in the structure together with the classical ones (Mg, Zn, Al) serving

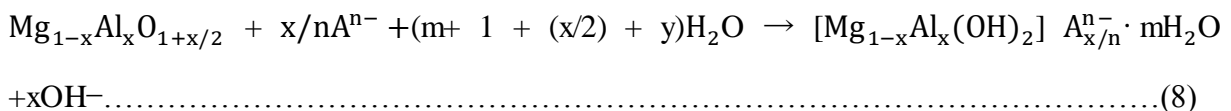
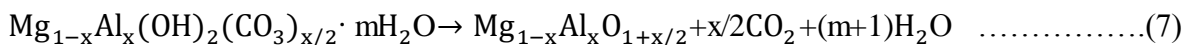
as precursors for the preparation of different mixed oxides active for oxidation and hydrogenation/dehydrogenation reactions.

The LDHs materials have received increasing attention because of their many applications as precursors to magnetic materials, catalysts, and anion exchangers. Due to the large surface areas (20–120 m<sup>2</sup>/g) and high anion-exchange capacities (3.0–4.8 meq/g), HT have been studied as a new emerging class of potential adsorbents for removing toxic anionic species from aqueous systems. The selective binding of anions by HTs is affected to a considerable extent by the properties of the anions [58-64].

As there is no overall charge, hydrotalcites are quite stable. Many types of hydrotalcites can be formed from different combinations of divalent and trivalent cations, and different interlayer anions. The anion may be divalent, such as carbonate, sulphate and phosphate, or it may be monovalent, such as fluoride, chloride or nitrate. Hydrotalcites generally prefer to have a divalent anion in their structure. Studies have been done on the preference of hydrotalcites to anions, and a divalent anion will usually out-compete the monovalent anion. These studies also demonstrated that hydrotalcites have a strong preference to the carbonate anion.

The interesting properties of hydrotalcites arise when they are calcined; this process removes the interlayer water, interlayer anions, and the hydroxyls. The resulting material is an atomic mixture of metal oxides which are characterized by a high specific surface area and homogeneous dispersion of the metal cations. The mixed metal oxides can take up anions from aqueous solution, resulting in a concomitant reconstruction of the original layered structure, the so-called “memory effect. The structure is directly related to the arrangement of the metals in the hydrotalcite and could not be achieved by mechanical means.

Calcinedhydrotalcites have been demonstrated to reconstruct their original layered structure after adsorption of various anions and are good ion exchangers/adsorbents for removal of toxic anions from contaminated water [70], as expressed by the following two equations:



The exact calcination temperature will vary depending on the type of hydrotalcite used, but is usually between 573-773K. The calcination effectively destroys the hydrotalcite structure. The calcined hydrotalcite is able to reform the original structure when it is exposed to water and anions. Water will be absorbed to reform the hydroxyl layers; anions and water will be absorbed into the interlayer. The anions that will be absorbed do not necessarily need to be the anion that was in the original hydrotalcite, any available anion will be absorbed. The ability to remove anions is what makes the 'memory effect' of hydrotalcites so useful. They can be used as potential ion exchangers/adsorbents for the removal of toxic anions from waste waters.

Researchers have reported the use of HT and their calcined products as adsorbents for both organic and inorganic contaminants present in natural waters.

Hydrotalcite-like compounds and their calcined product remove diverse anionic pollutants from waters by two mechanisms: anionic exchange for Hydrotalcite and reconstruction for Hydrotalcite, and both can be affected by structural characteristics of these adsorbents such as degree of layer substitution, interlayer anion and crystallinity.

In general, the most interesting properties of the oxides obtained by calcination are the following:

- 1, High surface area
- 2, Basic properties
- 3, Formation of homogeneous mixtures of oxides with very small crystal size, stable to thermal treatments, which by reduction form small and thermally stable metal crystallites.
- 4, "Memory effect", which allows the reconstruction under mild conditions, of the original hydrotalcite structure when contacting the product of the thermal treatment with water solutions containing various anions [65-69].

Among the different adsorbents, calcined layered double hydroxides (LDHs) are promising pollutant removers due to their high layer charge densities. Adsorption by calcined hydrotalcite is much higher, because the adsorption occurs probably by both surface adsorption and reconstruction mechanism.

These materials are currently garnering attention not only for their potential uses as adsorbents but also as catalyst supports, catalysts, and polymer additives, as well as for their applications in the ceramic industry.

Natural hydrotalcites found in small quantities and are found intermeshed with spinel and other material due to the existence of non equilibrium conditions during the formation of the deposits. Other minerals such as penninite and muscovite as well as heavy metals are also found in natural hydrotalcite deposits that results in decrease adsorption capacity of natural HT compared to the synthesized HT. There are as yet known techniques for separating these materials and purifying the natural hydrotalcite.

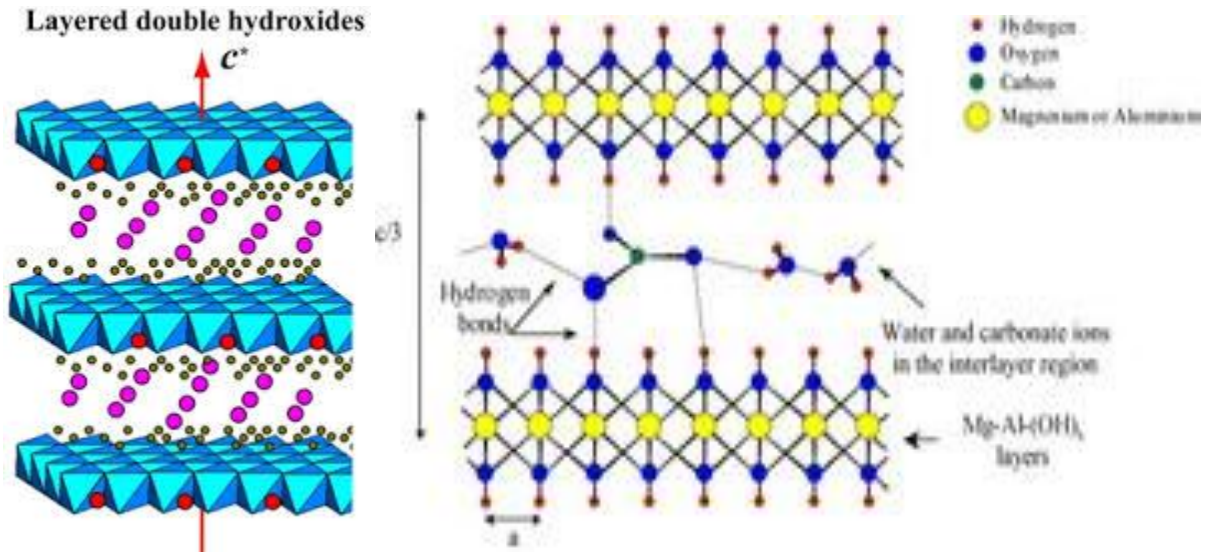


Fig.2.1. Structure of Mg-Al hydrotalcites

## 2.7. Mechanism of removal of fluoride ions by calcined hydrotalcite and recycled hydrotalcite

The regeneration of hydrotalcite is due to the ability of calcined hydrotalcite to incorporate anions into its structure by means of the so called memory effect. Hydrotalcite containing carbonate as the interlayer anion decomposes into magnesium and aluminium oxides when heated 450°C. The calcined product or mixed oxide obtained by calcination  $Mg_{1-x}Al_xO_{1+x/2}$  can be rehydrated, recovering the pristine structure and incorporate anions, such as fluoride, to rebuild the initial layered structure or to balance the positive charged layers according to the above equation.

OH<sup>-</sup> is produced during rehydration of CHT. As a result, controlling the PH of the solution is important in order to maintain a driving force for removal of fluoride ion by CHT. Experience in this area has shown that the hydrotalcite reconstruction by rehydration process plays an

important role in the removal of anionic species from water. The CHT after removal of fluoride can be regenerated using 0.1 M NaOH and 0.1 M HCl solution followed by calcinations at 450°C

## 3. Materials and Methods

### 3.1. Material and Equipments

#### 3.1.1 Chemicals and reagents

A calcined hydrotalcite sample, grey in color, less than 250  $\mu\text{m}$  particle size was used as adsorbent. The adsorbent was used directly for the experiments without any treatment. The chemicals used for the study were Analytical grade  $\text{Mg}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  and  $\text{NaOH}$ , for adsorbent preparation,  $\text{NaF}$  for preparation of the water samples, Hydrochloric acid and Sodium hydroxide for pH adjustment. All experiments used distilled water.

#### 3.1.2. Instruments

- Stuart SBS40 shaking water bath: was used to agitate the CLDH / aqueous fluoride solution.
- pH meter combined with a glass electrode: to measure the pH of the solution.
- Furnace
- Filter paper (Advantec, 45 $\mu$ ): to filter the content of the flasks.
- Analytical balance: to weigh the samples.
- Spectrophotometer model DR 3900: to measure the fluoride content of the solution.
- Infrared spectrophotometer model 500: to characterize CHT.

### 3.2. Preparation of hydrotalcite derived Mg/Al mixed oxide

In the co-precipitation, three solutions with Mg/Al molar ratios of 1.0, 2.0 and 3.0 were prepared by mixing appropriate amounts of hydrated magnesium nitrate  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and hydrated aluminum nitrate  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ .

Accordingly preparation by co-precipitation used two burette that contained nitrate solutions (molar ratio Mg/Al =1, 2 and 3) and 1 M  $\text{NaOH}$ . A solution of sodium hydroxide was slowly mixed to a mixture of solution of hydrated magnesium nitrate  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and hydrated aluminum nitrate  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  from the burettes in to a 1L glass flask, under magnetic stirring. The mixing step was carried out for 1 h, at room temperature, under stirring. The pH of the solution was recorded with a pH meter equipped with an electrode (pH = 10). Variation of pH during preparation was about  $\pm 0.05$ . After the co-precipitation was made,

aging of gel this was done in a round-bottomed flask while stirring for 24 hours. The hydrotalcite powders were recuperated by centrifugation and washed several times with de mineralized water until  $\text{pH} = 7$ . Filtering was performed using a Buchner funnel connected to a vacuum pump. Drying was carried out in an oven at a temperature of  $110\text{ }^{\circ}\text{C}$  for 24 hours under air atmosphere. Then, the dried samples were crushed to convert it into fine powder using attrition mill and sieved and retained at geometrical mean size  $\mu\text{m}$  between  $200\text{ }\mu\text{m}$  -  $250\text{ }\mu\text{m}$  for use in the experiments as adsorbent.

The synthesized samples were denoted HT-A (with the A values from 1, 2 and 3). A part of the samples were calcined in a furnace at  $450\text{ }^{\circ}\text{C}$  for 24 hours, in order to be transformed into magnesium-aluminum mixed oxide type (denoted hereafter as CHT-A with  $A = 1, 2$  and 3). Heat treatment at  $450\text{ }^{\circ}\text{C}$  evolves carbonates and water in the layered structure so that its layered structure collapsed.



Fig.3.1. Prepared calcined hydrotalcites A. CHT-1 B. CHT-2 C. CHT-3

### 3.3. Characterization of prepared Mg/Al hydrotalcite by infrared (IR) spectrophotometer

Fresh and used calcinedhydrotalcite-like compounds with different Mg/Al ratio were characterized for surface group identification employing Buck Scientific Model 500 Infrared Spectrophotometer .

#### **Procedurefor IR sample preparation and measuring**

1. The concentration of the calcinedhydrotalcite in KBr was in the range of 0.2% to 1%. 2mg of CHT and 300 to 400 mg of KBr was grounded together using mortar to get a homogeneous fine powdered mixture.
2. Two stainless steel disks were taken out of the desiccators. A piece of the precut cardboard (in the tin can next to the oven) was placed on top of one disk and filled the cutout hole with the finely ground mixture.
3. The second stainless steel disk was put on top and transfers the sandwich onto the pistil in the hydraulic press. With a pumping movement, the hydraulic pump handle moved downward. The pistil was started to move upward until it reached the top of the pump chamber.
4. Then, the pump handle was moved upwards and pumped until the pressure reached 20,000 prf and left for a few seconds and with the small lever on the left side, the pressure was released.
5. The disks was removed and pulled apart.
6. The film was removed, which was homogenous and transparent in appearance.
7. The sample was inserted into the IR sample holder and attached with scotch tape.
8. The spectrum was run.

### 3.4. Fluoride adsorption experiment

A 1000 mg/L sodium fluoride stock solution was prepared by using deionized water. Standards at a required concentration range were prepared by diluting an appropriate amount of stock solution with deionized water.

Fluoride adsorption experiments were carried out in batch at room temperature maintaining volume of solution, pH, mass of adsorbent, and shaking speed constant. First, an appropriate amount of CHT adsorbent (0.05gm) was dispersed into an Erlenmeyer-flask containing 50ml of an appropriate concentration of fluoride solution. Then the mixture was mixed continuously from 30min to 3 1/2hrs using Stuart SBS40 shaker.

10 ml of aqueous samples were extracted, at selected time intervals, up to a maximum of 30 min to 3 1/2hr and separated by filtration. Finally, after completion of adsorption experiment, the supernatant were recovered by filtration to determine the residual fluoride concentration by spectrophotometer. Moreover the solids remaining at the end of the experiment were recovered, dried and stored for future characterization.

### **Fluoride analysis technique**

The standard SPADNS method was used for analysis of fluoride in the water using DR/ 3900 Spectrophotometer. Using SPADNS reagent solution steps for fluoride determination by DR/ 3900 Spectrophotometer are:

1. The program number for fluoride was stored by pressing 190 and the display showed dial nm to 580.
2. The wave length dial was rotated until the small display showed 580nm. When the correct wavelength was dialed in, the display quickly show: zero samples then: \_ mg/L F<sup>-</sup>.
3. The 10 ml cell was inserted into the cell compartment.
4. 10 ml of the sample fluoride solution was measured in to a dry 10ml sample cell.
5. 10 ml of deionized water was measured in to a dry sample cell(blank)
6. 2.0 ml of SPADNS reagent was mixed in to each cell
7. Then a one minute reaction period was begin after pressing SHIFT TIMER
8. When the timer beeped, the display showed \_ mg/L F<sup>-</sup>.

The final fluoride concentration, the percentage removal of fluoride and the adsorption loading of CHT were determined and calculated. Equilibrium studies were conducted in a 500ml flask by mixing 50ml of fluoride solution with 0.05g CHT.

The defluoridation capacity ( $q_e$ ) on the adsorbent and efficiency (% adsorption) from the residual fluoride concentration was calculated from the difference between the initial concentration  $C_o$  and the residual concentration  $C_t$  in solution as follows:

$$\text{Adsorption capacity } (q_e) = \frac{(C_o - C_t)}{m} V \dots\dots\dots(1)$$

$$\% \text{ Fluoride adsorption} = \frac{C_o - C_t}{C_o} * 100 \dots\dots\dots(2)$$

where m and V are respectively the mass of adsorbent and the volume of the solution.



Fig3.2. Adsorption experiment sample preparation and fluoride determination using spectrophotometer

### 3.6. Effect of operating parameters

Three calcined hydrotalcite samples namely, CHT-1, CHT-2 and CHT-3 that exhibited better adsorption capacity were investigated to study the effect of different operating parameters such as Mg/Al molar ratio on CHT, initial fluoride concentration and pH of the solution on the fluoride adsorption potentials of three CHT.

#### Effect of Mg/Al molar ratio on fluoride adsorption efficiency

Three calcined hydrotalcite samples namely, CHT-1, CHT-2 and CHT-3 that exhibited better adsorption capacity were studied in order to investigate the effect of different operating parameters on the fluoride adsorption potentials of three CHT.

### **Effect of pH on fluoride adsorption efficiency**

Generally pH is considered to be an important parameter which controls the adsorption at water-adsorbent interfaces. The effect of pH was studied by varying pH of the fluoride solution using either NaOH or HCl at a range of 6 to 8.0. The pH level was selected in accordance to the pH of drinking water accepted by WHO and USEPA ranging from 7-8.5 and 6.5-8.5 respectively. The two real fluorinated ground water sample taken from Hawassa also shows a pH of 7.24 and 7.55. The adsorption was done by adding 0.05 g of the calcined hydrotalcite to 50 mL of different concentrations of fluoride solution ranging from 5 to 15 mg/L contained in plastic bottles. The bottles were placed in a thermostatic shaker. The samples were then filtered and the residual fluoride concentration was measured in DR3900 spectrophotometer.

### **Effect of initial fluoride concentration on fluoride adsorption efficiency**

Even though the maximum concentration of fluoride in ground water of rift valleys of Ethiopia reaches 36mg/L, as shown in Table 2.1 most of the ground water was found to have a concentration of 5 to 15mg/L. Therefore the initial concentration effect on fluoride adsorption was studied at different initial fluoride concentrations (5, 10, 15 mg/L) by keeping other parameters constant.

## **3.7. Adsorption kinetics and Isotherm Analysis**

### **3.7.1. Adsorption kinetics Analysis**

Best performing calcined hydrotalcite type and optimal studied variables (pH and initial fluoride concentration) will be selected in order to study the kinetics of adsorption experiment based on reaction kinetics of pseudo-first order and of pseudo-second order.

The effect of shaking time on the adsorption kinetics of fluoride ion was studied by selecting the optimal variables (pH and initial concentration) obtained during previous experiment for calcined hydrotalcites with Mg/Al molar ratio of 2. The adsorbent dose was 0.05 gm/L. The pseudo-first order and pseudo-second order adsorption models were used to study the adsorption kinetics of present experimental data.

The pseudo-first-order and pseudo-second-order kinetic models can be expressed as follows:

$$\text{Log } (q_e - q_t) = \text{log } q_e - (K_1/2.303)t \dots\dots\dots(3)$$

$$t/q_t = 1/(K_2 q_e^2) + (1/q_e)t \dots\dots\dots(4)$$

where  $q_e$  and  $q_t$  are the adsorption amount of fluoride at equilibrium and at any time (mg  $g^{-1}$ ), respectively,  $K_1$  ( $min^{-1}$ ) is the equilibrium rate constant of pseudo-first-order and  $K_2$  ( $g(mgmin)^{-1}$ ) represents the pseudo-second-order rate constant of the kinetic model.

### 3.7.2. Adsorption Isotherm Analysis

Over the years, a wide variety of equilibrium isotherm models (Langmuir, Freundlich, Brunauer–Emmett–Teller, Redlich–Peterson, Dubinin–Radushkevich, Temkin, Toth, Koble–Corrigan, Sips, Khan, Hill, Flory–Huggins and Radke–Prausnitz isotherm), have been formulated.

The mathematical correlation, which constitutes an important role towards the modeling analysis, operational design and applicable practice of the adsorption systems, is usually depicted by graphically expressing the solid-phase against its residual concentration.

Two of the more common mathematical formulations used in establishing adsorption isotherms are the two parameter isotherms Langmuir and Freundlich equations.

#### A. Langmuir isotherm model

Langmuir isotherm has been used to quantify and contrast the performance of different adsorbents. The Langmuir equation applicable to adsorption is described as:

$$C_e / q_e = 1 / Q_o * b + C_e / Q_o \dots\dots\dots (5)$$

where  $C_e$  = the equilibrium concentration of the adsorbate (mg/liter) in solution.

$q_e$  = the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g).

$Q_o$  and  $b$  = Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. When  $C_e / q_e$  is plotted versus  $C_e$ , the slope is equal to  $1 / Q_o$  and the intercept is equal to  $1 / Q_o b$ .

#### B. Freundlich isotherm model

Freundlich isotherm is the relationship describing the non-ideal and reversible adsorption, not restricted to the formation of monolayer. The Freundlich equation applicable to adsorption is described as:

$$\text{Log } q_e = \text{log } K_f + 1/n \text{ log } C_e \dots\dots\dots (6)$$

where  $C_e$  = the equilibrium concentration of the adsorbate (mg/liter) in solution.

$q_e$  = the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g).

$K_f$  and  $n$  = constants incorporating all factors affecting the adsorption such as adsorption capacity and intensity, respectively. Values of  $K_f$  and  $n$  may be calculated by plotting  $\log(q_e)$  versus  $\log(C_e)$ . The slope is equal to  $1/n$  and the intercept is equal to  $\log(K_f)$ . Both of these are “two-parameter” equations. That is, other than the variables  $q_e$  and  $C_e$ , there appear only two parameters in the equations. The two parameters are evaluated by “fitting” the data to the equations. In almost every case, one of these two equations fits the data quite well. Thus, there is no need for more elaborate isotherm equations, particularly those involving three or more parameters. The isotherm studies are carried on by varying the initial concentration of the fluoride solution. In groundwater, the fluoride concentration remains constant, so it seems more representative of natural waters to run isotherm studies on dose-variation of adsorbents instead of studies on fluoride concentration variation [78]

### 3.8. Statistical Data Analysis

A total of 27 batch adsorption experiments (three times replicated) on CHT were carried out by varying initial pH of solution (6, 7, and 8), CHT's Mg/Al molar ratio (1, 2, and 3) and initial concentration of fluoride (5, 10 and 15mg/L) in order to determine the optimum adsorption conditions. The data was analyzed and modeled using Version 6.0.8 design expert. The software used to develop the mathematical model that will describe the effect of main and interaction factors on the response. Factorial design is used to test the effect of each factor. In full factorial experiment, all possible combination of factor levels was tested. And it was determined the effects of individual factors and assessed the effect of change of variables at a time.

Table.3.1. coded and uncoded variables and their values

Parameters	Coded and uncoded Values		
	-1	0	+1
Mg/Al Molar ratio	1	2	3
Fluoride Concentration(mg/L)	5	10	15
pH	6	7	8

Three different levels for each experiment in coded form were -1, 0 and +1. Further, it was assumed that three functions exist between the response and the input factors.

Regression analysis and analysis of variance was carried out for fitting the model to the experimental data and to examine the statistical significance of the model. This method of experiment design helps to differentiate the significance of the main and the interaction factors. Three dimensional response models were generated. The response surface plots were generated for different variables, while holding the values of third variable constant (at the central value) such response surface plots gives accurate geometrical representation and provide useful information about the behavioral system with experimental design. The model obtained was used to interpret the effect of various variables on the response i.e. final fluoride concentration and percent adsorption. The optimization process was aimed at finding the levels of three independent variables (pH, initial concentration of fluoride and Mg/Al molar ratio) which would give possible minimum value of final fluoride concentration and higher percent adsorption. Each analysis assay was done three times from the same sample to determine reproducibility [77].

### 3.9. Regeneration of hydrotalcites after the adsorption of fluoride ions

The loaded CHT-2 after removal of fluoride was regenerated. The desorption study can give a clear idea about the mechanism of adsorption along with the stability of the adsorbent for further use. Desorption studies were carried out by using the fluoride adsorbed CHT-2 adsorbent. First the fluoride-adsorbed CHT-2 is generated after adsorbing 5 mg/L fluoride solution on 0.05 mg/L CHT-2 at pH 6.0. After the equilibration, the residue was filtered and the filtrate was measured for fluoride content. 0.1 M sodium hydroxide solution was selected

as the desorption reagent since its effectiveness has been proven by many previous studies (Zhang et al., 2005, Xiaomei et al., 2007). Desorption experiments were conducted by taking 4.72 mg/g fluoride loaded CHT-2 in bottles and the solutions at different pH 2-13 were selected as the desorption reagents by addition of 0.1 M NaOH. The samples were agitated for 3 hours in a water bath shaker at room temperature. Then the suspensions were filtered and the adsorbent is neutralized by adding 0.1 M HCl solution followed by calcinations at 450 °C.

One experiment was done to check the reusability of calcined hydrotalcites after regeneration, desorption of fluoride and calcinations at the specified temperature. The adsorption experiment was performed by using the regenerated CHT at optimal condition that was obtained from the experimental design at a pH of 6.0, initial concentration of 5 mg/L and Mg/Al molar ratio of 2.0.

## 4. Result and Discussion

### 4.1. Characterization of the calcined hydrotalcite samples

The structure of as-synthesized hydrotalcite samples was confirmed by infrared Spectrophotometer methods.

#### 1. Infrared of uncalcined hydrotalcite

The IR spectrum of the uncalcined hydrotalcite samples presented in Fig. 4.1 for different hydrotalcites of different Mg/Al molar ratio in which subset 1, 2 and 3 represents hydrotalcite with Mg/Al molar ratio 1, 2 and 3 has an intense broadband between 1700 and 600  $cm^{-1}$ .

Besides that, this broadband may also represent characteristics stretching vibration of the  $Mg^{2+}$ --OH<sup>-</sup> bond. Additionally, the band at around 1632  $cm^{-1}$  may be assigned to the adsorbed interlayer water since this is the bending vibration for  $\delta$  HOH. Meanwhile, the absorption band at 1383  $cm^{-1}$  is attributed to the  $CO_3^{2-}$  absorption and the impurities of  $NO_3^-$  which is probably due to the synthesis solution. Finally, the broadband at around 663  $cm^{-1}$  is a superposition characteristic band of boehmite and hydrotalcite in this frequency interval. Sharp peaks at around 1400 and 1600  $cm^{-1}$  correspond to symmetric and asymmetric stretching absorption of C-O and C=O in  $CO_3^{2-}$ , and broad peaks below 1000  $cm^{-1}$  corresponding to Mg-OH or Al-OH stretching absorption.

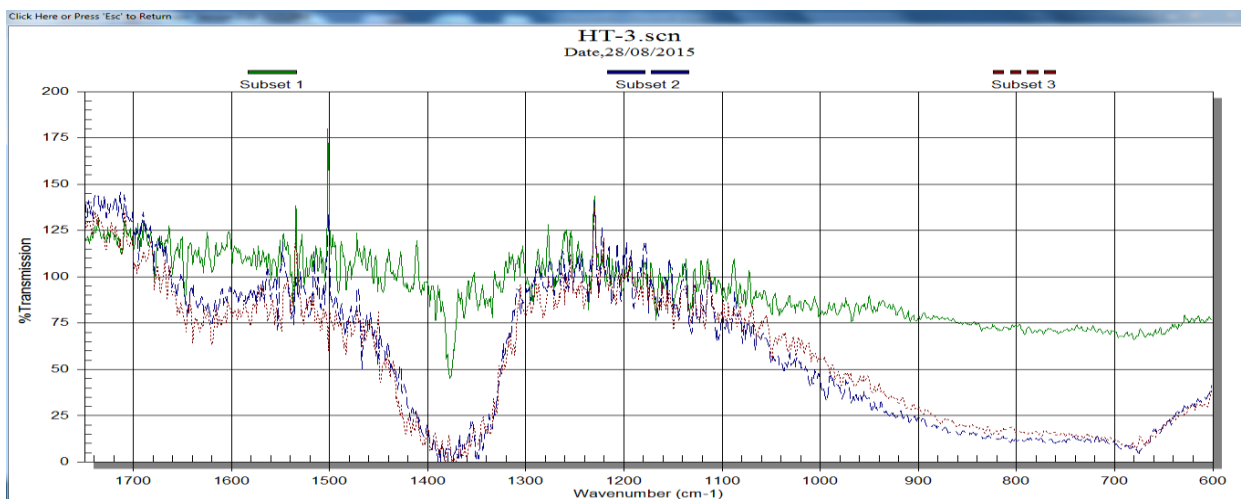


Fig 4.1. IR spectra of Mg-Al hydrotalcites with Mg/Al molar ratio of 1, 2 and 3 respectively

## 2. Infrared of calcined hydrotalcite

Upon calcination, there is a decrease in the intensity of water and carbonate characteristic peaks for Mg-Al hydrotalcite as shown in Fig. 4.2. This is due to the removal of water and  $CO_2$  vapours during calcination at low temperature (Parida and Das, 2000). Besides that, it can be seen for Mg-Al hydrotalcite that the broadband at  $663\text{ cm}^{-1}$  has disappeared confirming the disappearance of the hydrotalcite structure. However, the bands for  $NO_3^-$  is still present in the calcined samples as temperatures higher than  $450^\circ\text{C}$  are required to remove the interlayer nitrates (Kustrowski et al., 2005). The IR spectra of calcined Mg-Al hydrotalcites showed that some weak bands exist in the  $700\text{--}600\text{ cm}^{-1}$  wavenumber range which means that the hydrotalcite structure is still preserved.

IR confirms the removal of water and  $CO_3^{2-}$  by definite reduction in the absorption peaks around  $1400\text{ cm}^{-1}$ , and  $1600\text{ cm}^{-1}$  however its structure was easily reconstructed by rehydration or even by simple exposure to air, since it has high adsorption ability for water.

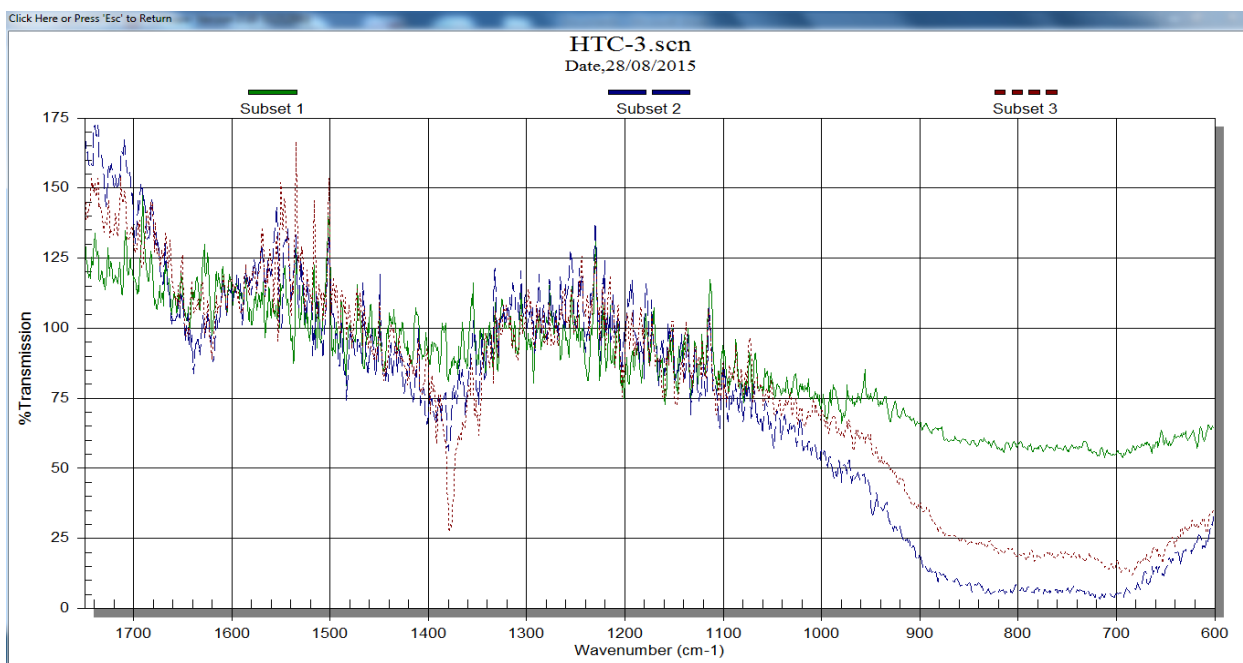


Fig 4.2. IR spectra of calcined Mg-Al hydrotalcites with Mg/Al molar ratio of 1, 2 and 3 respectively.

### 3. Infrared of fluoride loaded calcined hydrotalcite

IR spectra on Fig 4.3 show that the band is observed at  $1355\text{ cm}^{-1}$  in the spectrum of Mg-Al hydrotalcite of the sample with Mg/Al molar ratio of 1, 2 and 3 given by subset 1, 2 and 3 respectively in the picture. This band is assigned to the vibrational absorption of interlayer  $\text{CO}_3^{2-}$ , as reported previously. After calcinations and adsorption of fluoride, this band shifts to higher frequency ( $1385\text{ cm}^{-1}$ ). This could indicate surface adsorption of carbonate anions, which is a property of calcined LDHs. The band between  $400$  and  $800\text{ cm}^{-1}$  is attributed to superposition of the characteristic vibrations of magnesium and aluminum oxides. It can be concluded that the interlayer anion in hydrotalcite after uptake of fluoride by CHT is mainly fluoride. Besides that, it was also evident from the IR spectrum that calcination caused the removal of water and  $\text{CO}_2$  gas.

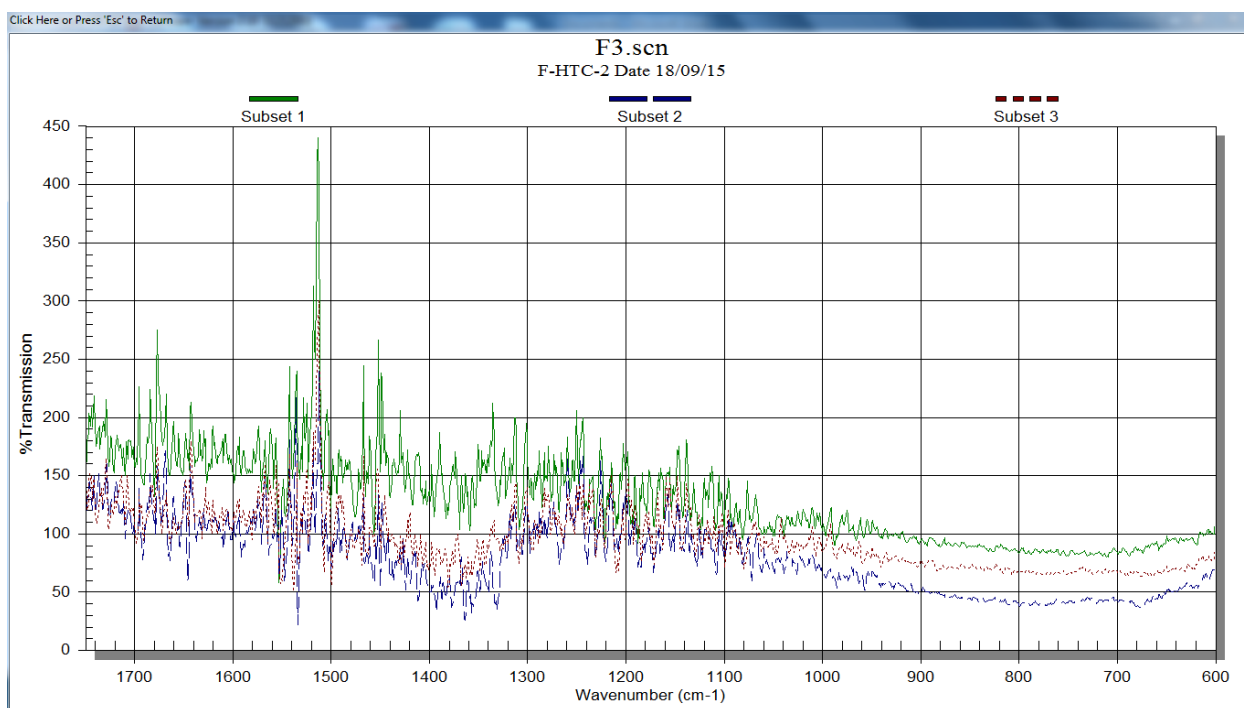


Fig 4.3. IR spectra of fluoride loaded calcined Mg-Al hydrotalcites with Mg/Al molar ratio of 1, 2 and 3 respectively.

## 4.2. Effects of parameters on fluoride adsorption by calcined hydrotalcite

In this part the results obtained from the adsorption experiments were presented in Annex-1 Table 1.2. The effect of different parameters on the adsorption of fluoride was discussed. Based on the analysis of variance, the percentage adsorption was significantly affected by various interactions between the process variables. This result demonstrated the advantage of using design of experiments in capturing the interaction between variables that affects the percentage adsorption. The effect could be due to the independent variable alone or due to their interaction. The individual and interaction influence of operational variables on adsorption of fluoride was explained below:

### 4.2.1. Effect of initial concentration of fluoride on percent adsorption of fluoride

Figure 4.4 A-C shows the effect of initial concentration of fluoride in the range of 5.0 mg/L to 15.0 mg/L on percent adsorption of fluoride by (0.05 g) CHT-1, CHT-2 and CHT-3 adsorbent at different pH and it can be observed that initial concentration of fluoride had a significant effect on fluoride adsorption. The effect of different initial concentrations of fluoride for CHT of different Mg/Al molar ratios is discussed below:

#### 4.2.1.1. Effect of initial concentration of fluoride on percentage adsorption of fluoride at a pH of 6.0

Figure 4.4.A. shows the effect of initial concentration of fluoride on percent adsorption of fluoride at a pH of 6.0 for 0.05g of each of CHT-1, CHT-2 and CHT-3. As shown in Figure 4.1.A. for 5mg/L initial fluoride concentration the % adsorption of CHT-2 is much greater than % adsorption of CHT-1 and CHT-3 whereas the % adsorption of CHT-3 is greater than that of CHT-1 at an initial fluoride concentration of 5mg/L. The % adsorption of CHT-2 was greater than 90% at an initial fluoride concentration of 5mg/L. There was a decrease in fluoride adsorption by CHT-2 when the equilibrium solution initial concentration was greater than 5 mg/L.

Similarly the % adsorption of CHT-2 at an initial fluoride concentration of 10mg/L was greater than CHT-1 and CHT-3 but CHT-1 and CHT-3 have almost the same % adsorption of fluoride. At an initial fluoride concentration of 15 mg/L the % adsorption of CHT-1 and CHT-3 were approximately equal. At this initial concentration of fluoride the % adsorption of CHT-

2 was lower than both CHT-1 and CHT-3. The results on Figure 4.4.A shows that percentage adsorption increased from 82.2% to 94.4 % by decreasing initial fluoride concentration from 15 to 5 mg/L at pH 6.0 for CHT with Mg/Al molar ratio 2. It can be seen that the percentage removal of fluoride increases with decreasing initial fluoride concentration during adsorption of fluoride by CHT-2.

This result was verified by result of adsorption isotherm that showed the best fit was found to be Langmuir isotherm which is characterized by monolayer. Therefore there exist only vacant site on adsorbent for fluoride adsorption. There is no interaction between the adsorbed fluoride ions resulted a multilayer adsorption. The minimum residual concentration of fluoride obtained is 0.28 mg/L with an initial of 5 mg/L by CHT-2 adsorbent at pH of 6, which reaches the standard for drinking water quality.

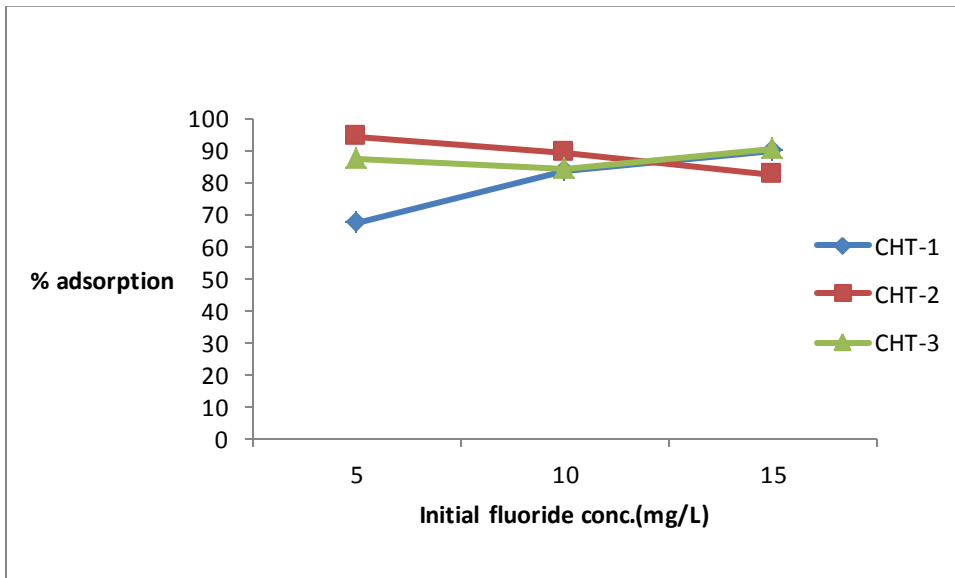


Fig.4.4.A. Effect of initial concentration of fluoride on the percentage adsorption capacity for CHT-1, CHT-2 and CHT-3 at a pH of 6.0 and amount of adsorbent 0.05gm

#### ***4.2.1.2. Effect of initial concentration of fluoride on percentage adsorption of fluoride at a pH of 7.0***

Figure.4.4.B shows the effect of initial fluoride concentration on percentage adsorption of 0.05mg/L of CHT-1, CHT-2 and CHT-3 at a pH of 7.0. It is clearly seen in the Figure 4.4.B that the % adsorption of CHT-2 is higher than that of CHT-1 and CHT-3 at initial fluoride concentration of 5, 10 and 15mg/L. Nearly the % adsorption of CHT-2 was 90% for initial

fluoride concentration of 5, 10 and 15 mg/L. At an initial fluoride concentration of 5mg/L CHT-1 had greater % adsorption than CHT-3 but for an initial fluoride concentration of 10mg/L this observation is reversed. But when the initial fluoride concentration increased to 15mg/L their % adsorption became equal.

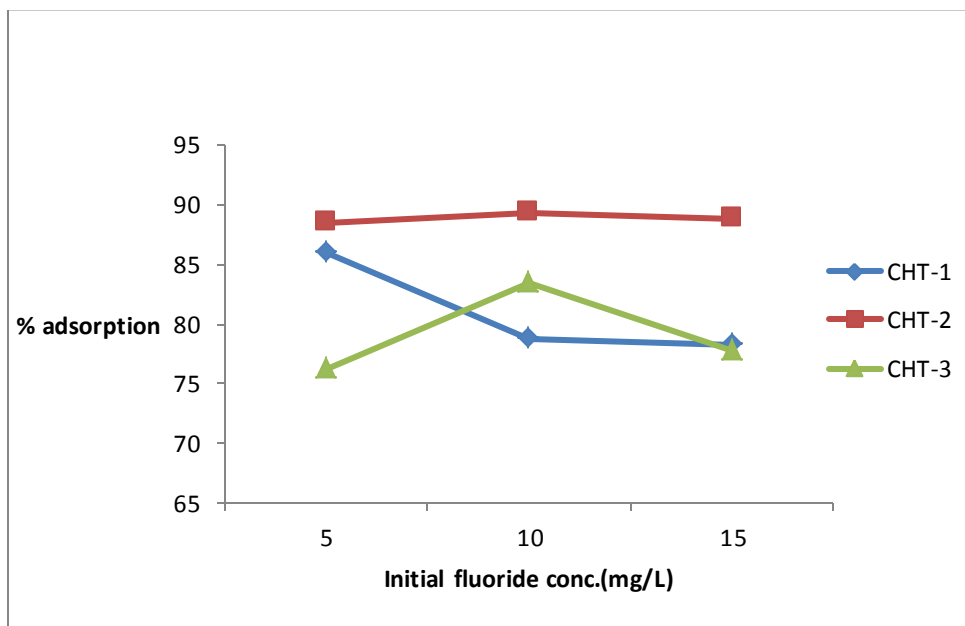


Fig.4.4.B. Effect of initial concentration of fluoride on the percentage adsorption capacity for CHT-1, CHT-2 and CHT-3 at pH of 7.0 and amount of adsorbent 0.05gm

#### *4.2.1.3. Effect of initial concentration of fluoride on percentage adsorption of fluoride at a pH of 8.0*

Figure 4.4.C shows the effect of initial concentrations of fluoride on % adsorption of CHT-1, CHT-2 and CHT-3 with different Mg/Al molar ratios at a pH of 8.0. The percentage adsorption of CHT-1 was greater than both CHT-2 and CHT-3 at initial fluoride concentration of 5mg/L but their adsorption efficiency gets closer as the initial fluoride concentration increases.

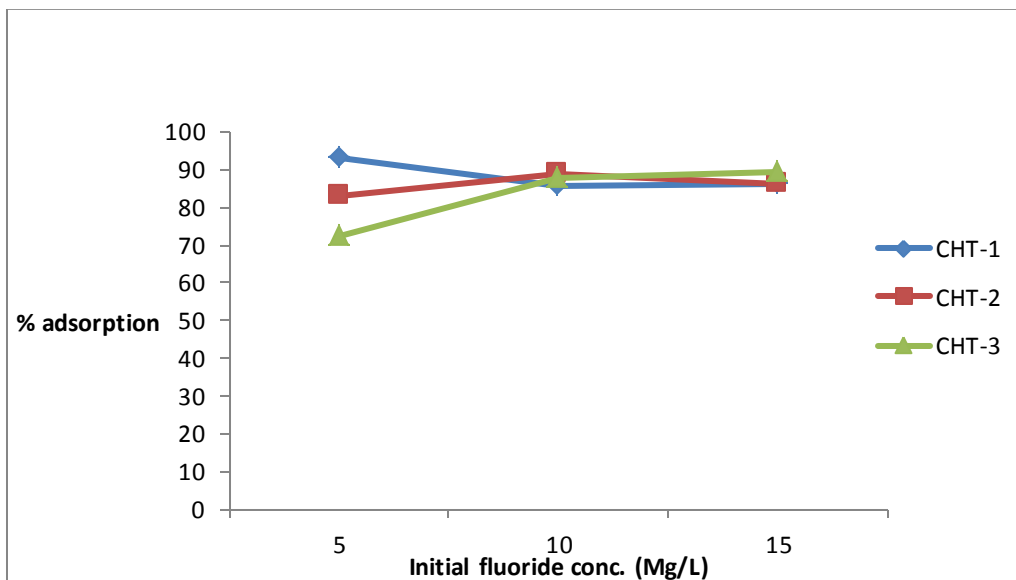


Fig.4.4.C. Effect of initial concentration of fluoride on the percentage adsorption for CHT-1, CHT-2 and CHT-3 at pH of 8.0 and amount of adsorbent 0.05gm.

#### 4.2.2. Effect of pH of a solution on percentage adsorption of fluoride

Generally, the pH is an important variable, which controls the percentage adsorption at water adsorption interfaces as shown in Figures 4.5.A-C.

Figures 4.5.A-C show the effect of pH in the range of 6.0 to 8.0 on percentage adsorption of fluoride by CHT-1, CHT-2 and CHT-3 at different initial fluoride concentration and it can be observed that pH values had a significant effect on fluoride adsorption. The effect of pH on adsorption of fluoride for CHT of different Mg/Al molar ratios at constant initial fluoride concentration is discussed below:

##### 4.2.2.1. Effect of pH on percentage adsorption of fluoride at an initial fluoride concentration of 5mg/L

As Figure 4.5.A shows a higher % adsorption was observed for CHT-2 at a pH of 6.0. At this pH the efficiencies of CHT-1 and CHT-3 are lower but comparably CHT-3 has greater % adsorption than CHT-2. There was a decrease in fluoride adsorption by CHT-2 when the equilibrium solution pH was greater than 6.0.

The % adsorption of CHT-1 was lower than 70% at a pH of 6.0. At a pH of 7.0 the % adsorption of CHT-2 and CHT-3 were approximately equal and is greater than 90%. The efficiency of CHT-1 was greater than CHT-2 and CHT-3 at a pH of 8.0. CHT-2 had greater % adsorption than CHT-3 at a pH of 8.0. It is evident that the removal was 88.4% and 94.4% for CHT-2 adsorbent at pH of 7 and 6 respectively.

It was observed that the fluoride uptake capacity of CHT-2 decreased with the increase of initial pH. The percentage adsorption was inversely related to the pH i.e. smaller pH gives high percentage adsorption while larger pH results a lower percentage adsorption of fluoride by CHT-2.

It is obvious that fluoride ions are removed much faster at lower pH than at high pH. This result can be attributed to the increase in the concentration of competing anions  $\text{OH}^-$ , at higher pH. The CHT-2 cannot be used when the pH is lower than 5.0, however, because the layered material may be partly dissolved, leading to a decrease in adsorption loading.

In the present study fluoride adsorption on the surface is coupled with a release of  $\text{OH}^-$  ions, and favored at low pH values, decrease of adsorption with increase of pH ( $>4$ ) may be because of stronger competition of hydroxide ions on adsorbent surface.

The fluoride adsorption on CHT surface is partly thought to be because of anion exchange at acidic pH and by Van der Waals forces at alkaline pH ranges.

The fluoride adsorption efficiency of CHT-2 was maximum at a pH of 6 in this study, this result is also verified by the statistical output from optimization of process parameters using Design expert. These results indicate that the adsorbent exhibits a commendable removal capacity at lower range of pH.

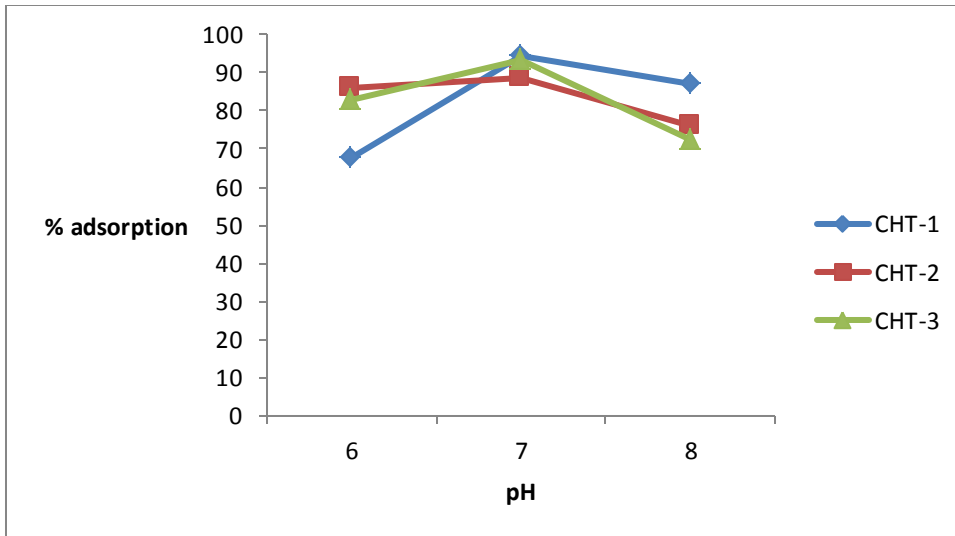


Fig.4.5. A. Effect of pH on the percentage adsorption of fluoride by CHT-1, CHT-2 and CHT-3 at an initial fluoride concentration of 5 mg/L and 0.05gm adsorbent.

**4.2.2.2. Effect of pH on percentage adsorption of fluoride at an initial fluoride concentration of 10mg/L**

As shown below in Fig 4.5.B the percentage adsorption of CHT-2 was around 90 % for all pH values and remains almost constant. In general CHT-2 had higher efficiency than CHT-1 and CHT-3 in pH values of 6, 7 and 8. CHT-3 had greater % adsorption than CHT-1 at a pH of 7 and 8. At a pH 7 their % adsorption was less than 85% but at a pH of 8 they attain more than 85% adsorption capacity

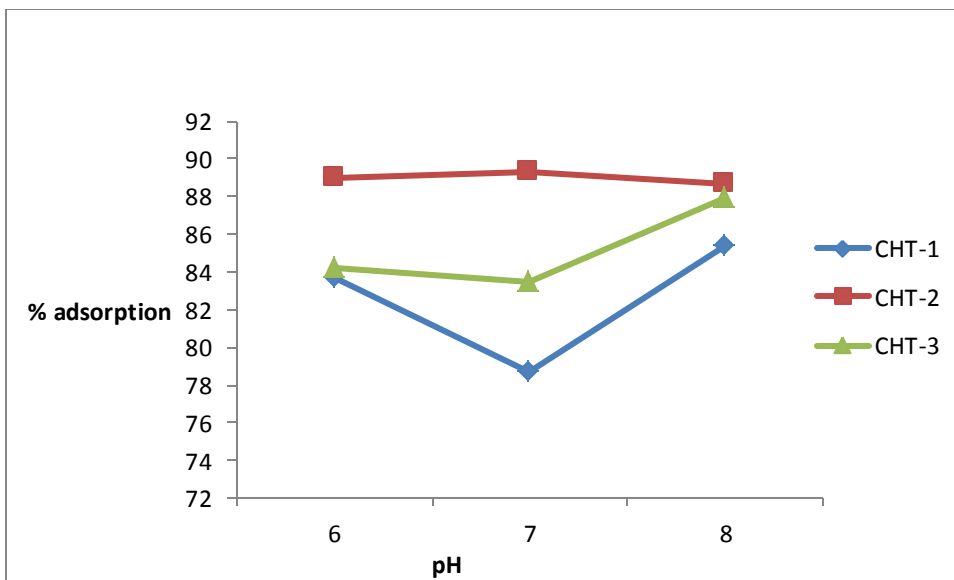


Fig.4.5.B.Effect of pH on the percentage adsorption of fluoride by CHT-1, CHT-2 and CHT-3 at an initial fluoride concentration of 10 mg/L and 0.05gm adsorbent.

**4.2.2.3. Effect of pH on percentage adsorption of fluoride at an initial fluoride concentration of 15mg/L**

The percentage adsorptions of CHT-1 and CHT-3 were greater than CHT-2 at a pH of 6.0 as shown in Fig 4.5.C. Their efficiency was greater than 85% but CHT-2 had lower than this value at a pH of 6.0. Unlike the result observed at pH 6.0, CHT-2 had higher % adsorption around 90% at a pH of 7.0. At a pH of 8.0 CHT-2 and CHT-3 had the same adsorption capacities but CHT-1 has lower % adsorption. When the pH of the solution increased from 7 to 8, % adsorption of CHT-2 remains the same.

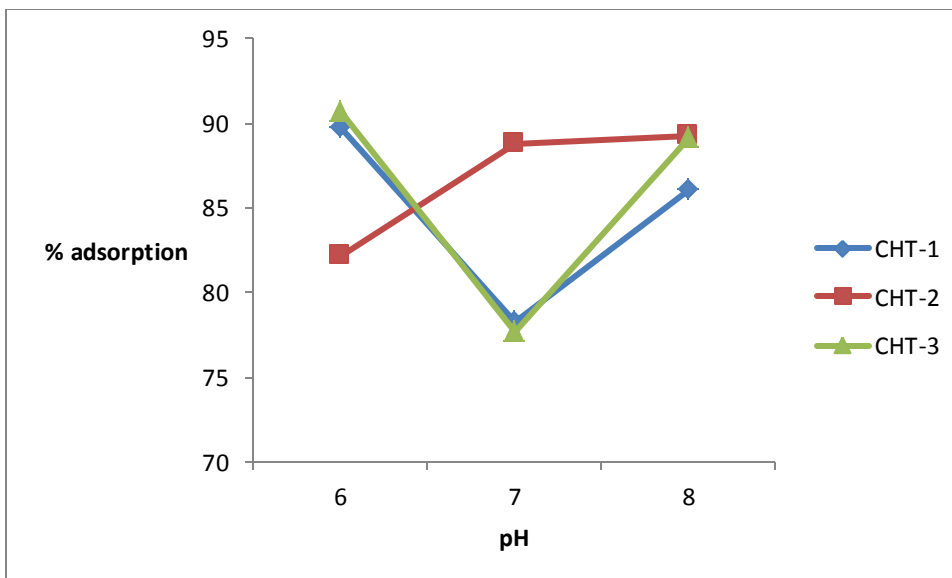


Fig.4.5.C.Effect of pH on the percentage adsorption of fluoride by CHT-1, CHT-2 and CHT-3 at an initial fluoride concentration of 15 mg/L and 0.05gm adsorbent.

#### 4.3. Interaction effect of initial concentration of fluoride, pH and Mg/Al molar ratio on adsorption of fluoride

The interaction effect of initial fluoride concentration and pH on adsorption of fluoride by CHT-2 was found to be the most important factor affecting adsorption potential according to the statistical result from analysis of variance as this parameter gives a significant effect.

The adsorption capacity of CHT at different values of the variables was shown in three dimensional response contour plots(Fig 4.6) and 3D surface (annex-3 Fig 3.1). The plot corresponds to the different number of combination of the two selected variables. It indicates the mutual interaction of all components with respect to their variables. Based on fluoride values the interactions of two of the variables were found to be highly significant for the adsorption capacity.

It is shown in all interaction graphs that an increment in pH and initial concentration of F<sup>-</sup> decreases the removal efficiency or percent adsorption. But as clearly shown in the 3D plot as their value decrease the percent adsorption increases significantly. Percentage adsorption between 86.1 and 86.6 % was achieved when either pH or initial concentration of F<sup>-</sup> increase and the other decrease. However the interaction effect of Mg/Al molar ratio in calcinedhydrotalcite varies with respect to other interactive variables.

These systems have an increasing trend for decreasing both initial concentration of fluoride and pH in a given interactive effect. This could be due to the fact that the positive coefficient for the linear parameter (combined effect of both initial fluoride concentration and pH) played the main role when they are at lower level and it increases the percent adsorption. While at higher level, the individual effects of initial fluoride concentration and the pH showed more significant negative effect, leading to the decrease of the percentage adsorption. This was consistent with the physical explanation.

Figure 4.6.illustrates the combined effect of pH and initial fluoride concentration on percentage adsorption holding the third variable constant.The third variable is held at zero level. Contour plots were drawn to show the relationship between dependent and independent variables of the developed model.

The responses corresponding to the contour plots of 2FI predicted model indicated that, for low pH, percentage adsorption reduces with decrease in initial fluoride concentration.

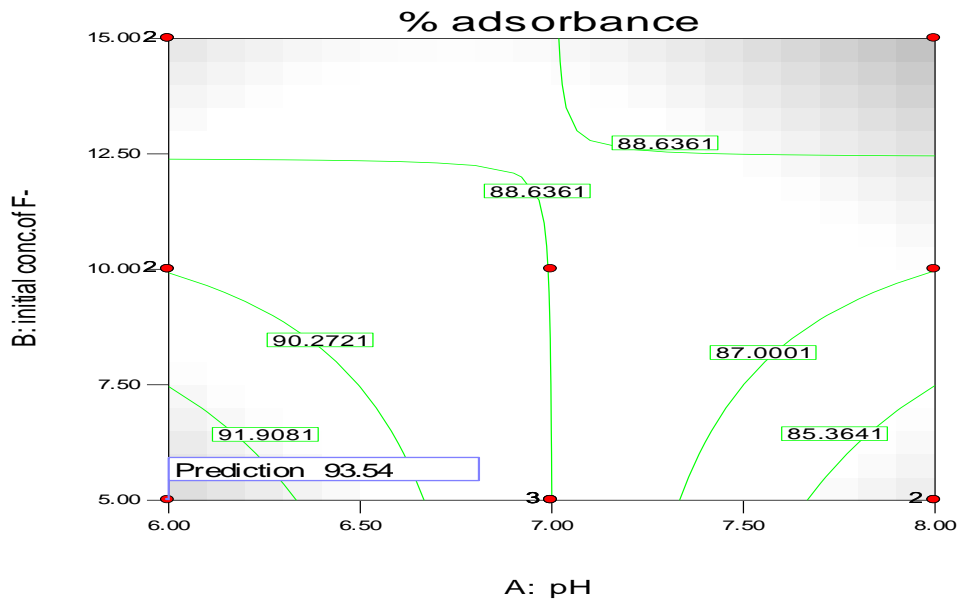


Fig.4.6. contour plot showing interactive effect of initial conc. of F<sup>-</sup> and Mg/Al molar ratio on final concentration of fluoride

#### 4.4. Adsorption kinetics

Kinetic studies were carried out to see the effect of initial fluoride concentration on the fluoride removal rate. The effect of time factor was studied up to 210 min at different initial fluoride concentration (5-15 mg/L).

It has also been observed that the removal of fluoride is very rapid in the first 30 min and then reaches a maximum. For the adsorbent dose of 0.05 g/L, the amount of fluoride ion adsorbed at each concentration increased rapidly in the beginning and slowly at the end. The equilibrium was reached within 180-210 min.

The fluoride adsorption on CHT was found to be very fast, almost 90.2% of the total adsorption was completed within 60 minutes and the equilibrium was attained within 3 h at all the studied concentrations. The change in the rate of removal might be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient is high. After 3 h, the fluoride uptake rate by adsorbent had been decreased due to the decrease in number of adsorbent sites. This removal percentage is remarkably higher than the systems reported earlier by using different types of clays [61]. Adsorption by calcined hydrotalcite is much higher, because the adsorption occurs probably by both surface adsorption and reconstruction mechanism. The nature of surface adsorption might be due to the high surface area of the small particles leads high affinity towards adsorption of fluoride.

In order to elucidate the adsorption kinetic process, the data of Table 4.1 were fitted using the two most widely used models (i.e. pseudo-first-order rate and pseudo-second-order rate models).

The parameters of the kinetic models and the linear regression coefficients ( $R^2$ ) were obtained and shown in Table 4.2. Obviously, the kinetic data were fitted better to second order and the  $q_e$  values calculated from the pseudo-second-order rate model, are very consistent with the experimental  $q_e$  values indicating that the experimental kinetic data for fluoride adsorption by calcined hydrotalcite works well with this model.

Table .4.1. Kinetic data

Adsorbent dose(gm)	pH	t(min)	Initial fluoride conc. (mg/L)	$C_e$ (mg/L)	$q_t$ (mg/g)	$q_e$ (mg/g)	$q_e - q_t$ (mg/g)	$\log(q_e - q_t)$	$t/q_t$
0.05	6	30	5	0.55	4.45	4.69	0.24	-0.61979	6.741573
0.05	6	60	5	0.49	4.51	4.69	0.18	-0.74473	13.30377
0.05	6	90	5	0.44	4.56	4.69	0.13	-0.88606	19.73684
0.05	6	120	5	0.39	4.61	4.69	0.08	-1.09691	26.03037
0.05	6	150	5	0.34	4.66	4.69	0.03	-1.52288	32.18884
0.05	6	180	5	0.31	4.69	4.69	0	-	38.37953
0.05	6	210	5	0.31	4.69	4.69	0	-	44.77612

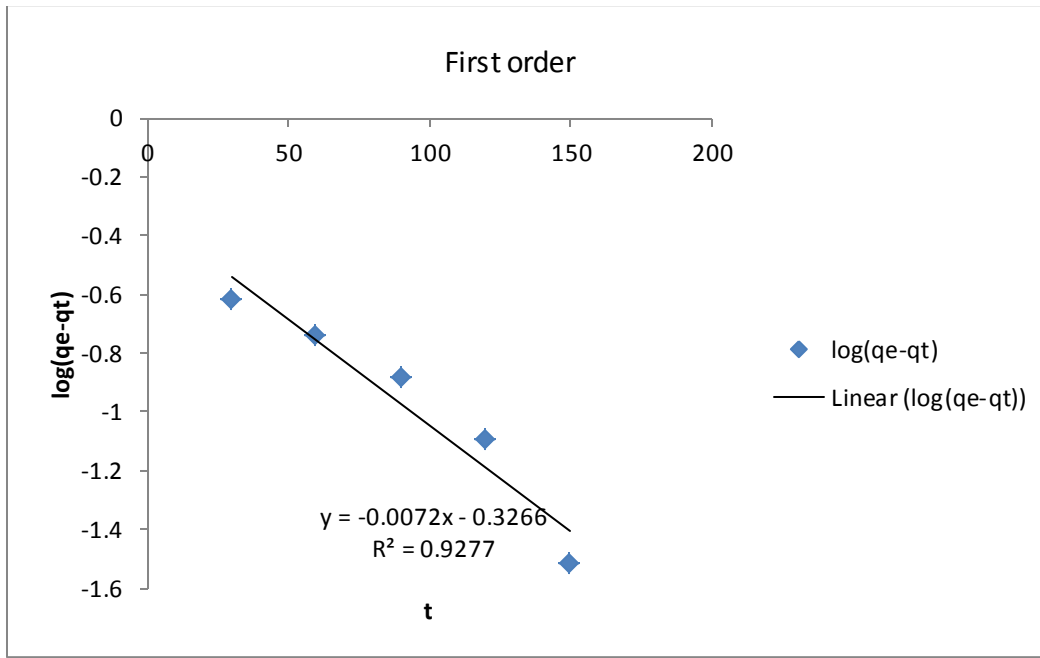


Fig.4.7. Pseudo first order kinetic plot for fluoride adsorption

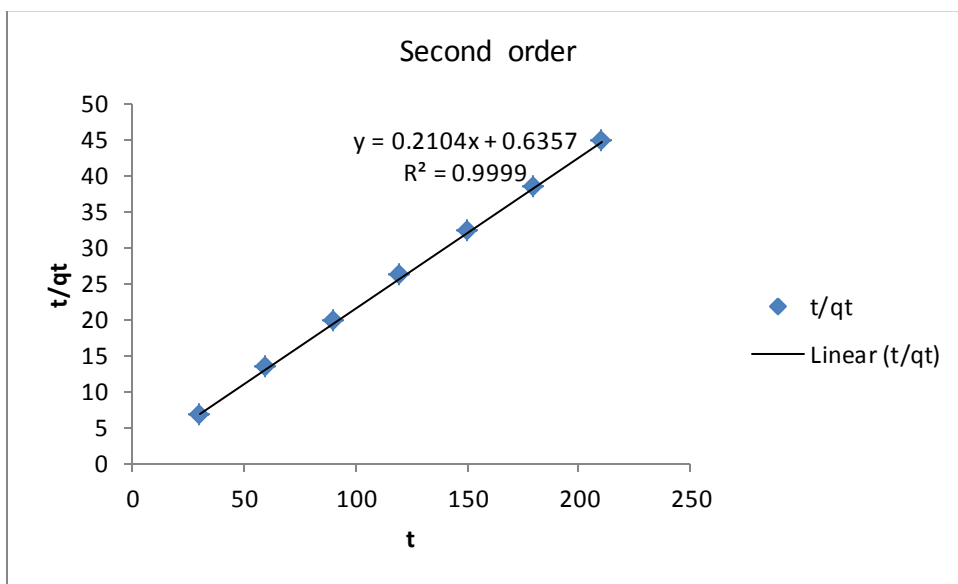


Fig.4.8. Pseudo second order kinetic plot for fluoride adsorption

Table 4.2: Parameters for Pseudo-first order and Pseudo-second order kinetic model

Order	parameter		
	Equation	$R^2$	$q_e$
First order kinetics	$Y = -0.007x - 0.326$	0.927	0.472
Second order kinetics	$Y = 0.210x + 0.635$	0.999	4.76

#### 4.5. Adsorption isotherm

The experimental data obtained for different initial fluoride concentrations (5 to 15 mg/L with an interval of 5) at constant temperature and pH were plotted in a linearized form of Langmuir and Freundlich adsorption isotherms. Equilibrium studies were carried out to determine the optimum conditions for maximum fluoride removal by CHT.

Experimental data were fitted to Langmuir and Freundlich isotherms. The maximum adsorption capacity for fluoride ions onto CHT was 4.184 mg g<sup>-1</sup>.

$Q_o$  is adsorption capacity for Langmuir isotherm and 'b' is an energy term which varies as a function of surface coverage strictly due to variations in the heat of adsorption. The

Freundlich constant, 'n' indicates the degree of favorability of adsorption and  $K_f$  is the isotherm constant.

Figure 4.9 and 4.10 shows that the Langmuir isotherm is a better model than the Freundlich isotherm on the basis of correlation coefficients ( $R^2=0.98$  for Langmuir,  $R^2= 0.978$  for Freundlich). The best fit Freundlich parameters are  $K_f = 1.71$ ,  $n = 25.64$ . The n value in the range of 0.1 -1 indicates a favorable adsorption process. The best fit Langmuir parameters are  $Q= 4.184$  mg/g,  $b= 29.85$ L/mg.

The removal of fluoride by different adsorbents has been studied in recent years and some of these reports provide Q values. Although these values were obtained under different range of conditions, they can be useful in criterion of the adsorbent capacity. The Q value obtained in these study is greater than those of reported for alum sludge (3.94mg/g), activated alumina (3.34 mg/g), flyash (4.02 mg/g) and coal (2.44 mg/g).

The adsorption data of fluoride on fitted to both Langmuir and Freundlich isotherm models as shown in Fig. 4.9 and 4.10. The calculated isotherm parameters along with correlation coefficients are given in Table 4.4. The magnitude of the Langmuir constant 'b' has small value which indicates a low heat of adsorption. The 'n' value indicates the bond strength between adsorbate and adsorbent and heterogeneous nature of the surface.

Table 4.3: Adsorption isotherm data

Adsorbent dose(gm)	pH	Time	Initial fluoride conc. (mg/L)	$C_e$ (mg/L)	$q_e$ (mg/g)	$C_e/q_e$	$1/C_e$	$\log C_e$	$\log q_e$
0.025	6	90	5	0.78	4.37	0.17849	1.282051	-0.10791	0.228833
0.05	6	90	5	0.61	4.46	0.136771	1.639344	-0.21467	0.224215
0.1	6	90	5	0.46	4.51	0.101996	2.173913	-0.33724	0.221729
0.125	6	90	5	0.42	4.58	0.091703	2.380952	-0.37675	0.218341
0.15	6	90	5	0.39	4.61	0.084599	2.564103	-0.40894	0.21692
0.175	6	90	5	0.35	4.65	0.075269	2.857143	-0.45593	0.215054
0.2	6	90	5	0.34	4.66	0.072961	2.941176	-0.46852	0.214592

Table 4.4: Parameters for Langmuir and Freundlich adsorption isotherm model

Order	parameter			
	Equation	$R^2$	$Q_o$	
Freundlich	$Y = 0.039x + 0.233$	0.978	-	$n = 25.64, K_f = 1.71$
Langmuir	$Y = 0.239x - 0.008$	0.98	4.184	$b = -29.85$

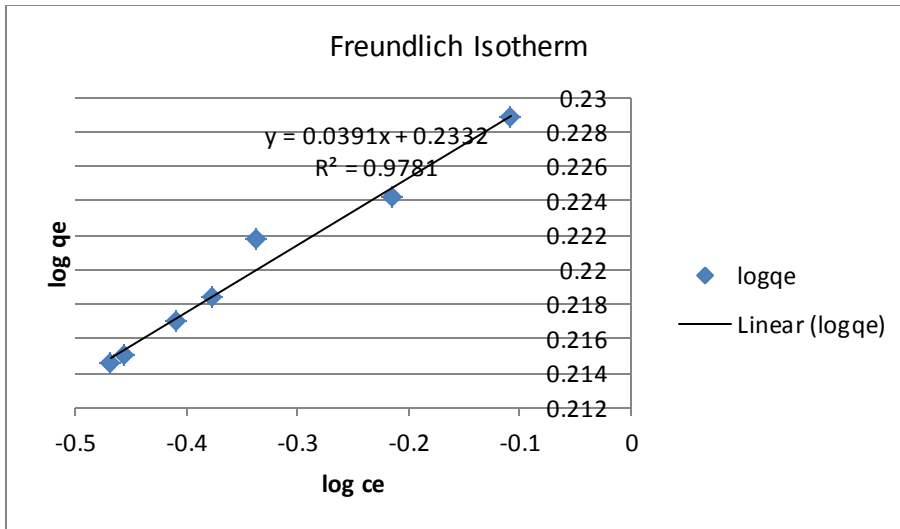


Fig.4.9. plot of Freundlich isotherm

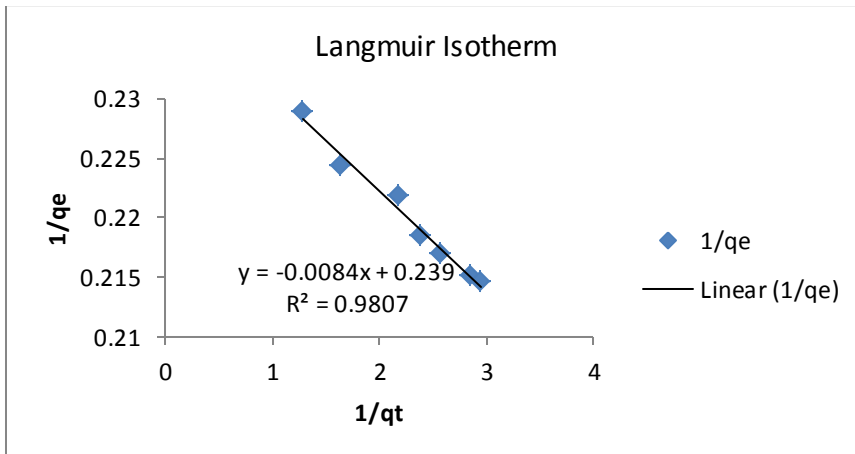


Fig.4.10. plot of Langmuir isotherm

#### 4.6. Analysis of variance (ANOVA) and development of regression model equation for CHT-2

Response surface 3-Level factorial design was used to develop a correlation between the adsorption process variables and the final fluoride concentration. It is a useful statistical method in which interaction between factors as well as 2FI effects are taken in to account and quantified in addition to the examination of each factor at two levels. According to the sequential model sum of squares, the models were selected based on the highest order polynomials for which the additional terms were significant and the models were not aliased.

For percentage adsorption of CHT in fluorinated aqueous solution, the mean and the 2FI models were suggested by the software. 2FI model was selected in this case due to the higher order polynomial and insignificant lack-of-fit shown in table 4.5 and 4.6.

Table 4.5. Sequential Model Sum of Squares

Source	Sum of squares	DF	Mean square	F-value	Prob> F	
mean	1.012E+005	1	1.012E+005			Suggested
Linear	24.83	2	12.41	1.05	0.3844	
2FI	61.86	1	61.86	9.95	0.0116	Suggested
quadratic	0.85	2	0.43	0.054	0.9477	
cubic	5.19	2	2.60	0.26	0.7807	Aliased
residual	49.90	5	9.98			
total	1.014E+005	13	7797.00			

Table 4.6. Lack of Fit Tests

Source	Sum of squares	DF	Mean square	F-value	Prob> F	
Linear	67.91	5	13.58	1.36	0.3717	
2FI	6.04	4	1.51	0.15	0.9543	Suggested
quadratic	5.19	2	2.60	0.26	0.7807	
cubic	0.000	0				Aliased
Pure error	49.90	5	9.98			

The design matrix in actual terms and the experimental results of fluoride adsorption by CHT are given in annex Table 1.3.

The multiple regression coefficients were obtained by employing a least square technique to predict 2FI model for the adsorption of fluoride. Hence, the best fitting model was determined. The quality of the model developed was evaluated based on the correlation coefficient value. The various  $R^2$  for the equation model are given in Table 4.7. A relatively high  $R^2$  value indicates that there was good agreement between the experimental and model predicted values. The smaller the standard deviation, the better the model, as it gives predicted values closer to the actual value of the response. This indicates that the predicted value for the response is more accurate and closer to the actual value. This implies that the 2FI regression model can be used to explain the fluoride adsorption.

**Table.4.7. Comparison of different R- Squared values**

Std. Dev.	2.49	R-Squared	0.6078
Mean	88.24	Adj R-Squared	0.4771
C.V.	2.83	Pred R-Squared	-0.2180
PRESS	173.72	Adeq Precision	7.098

The value of  $R^2$  (R- squared) and Adj R-squared were found to be 0.6721 and 0.5379 respectively. A negative "Pred R-Squared" implies that the overall mean is a better predictor of the response than the current model. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 7.098 indicates an adequate signal. This model can be used to navigate the design space.

The application of response surface methodology (RSM) based on the estimates of the parameters indicated an empirical relationship between the response and input variables. A 2FI model equation was fitted to the experimental data of each independent variable.

The 2FI model describing the effects of process variables on percentage adsorption in terms of actual variables is given by:

$\% \text{ adsorbance} = +146.15556 - 8.21483 * \text{pH} - 4.63266 * \text{initial conc. of F}^- + 0.66136 * \text{pH} * \text{initial conc. of F}^-$

The positive signs in the model terms indicate a synergistic effect; where as a negative sign indicated an antagonistic effect. The negative linear terms indicated that the percentage adsorption increase with decrease in pH and initial concentration of fluoride. The presence of positive interaction terms between pH and initial concentration of fluoride indicated that increasing their levels increases the percentage adsorption.

The adequacy of the models was further justified through ANOVA. The ANOVA for 2FI model for adsorption capacity is listed in Table 4.8. The significant terms in the models were identified by analysis of variance (ANOVA) for the one response. From the table, the model F-value of 4.65 implies that the model was significant and also the values of Prob>F less than 0.5 indicate that the model terms were significant. Significance was judged by determining the probability level that the F-statistic calculated from the data was less than 5%. The interaction (AB) effect was more significant model term whereas the individual process variables effect, pH (A) and initial fluoride concentration (B) were insignificant to the response within the design point under consideration.

We think about removing non significant model terms or factors from a model but in this case removing individual factors A and B will result in a model that is not hierarchical. The hierarchy principle indicates that if a model contains a high-order term, it should contain all the lower-order terms that compose it. Hierarchy promotes a type of internal consistency in a model, and many statistical model builders rigorously follow the principle (Douglas, 2001). Therefore, in order to minimize error, all of the coefficients were considered in the design.

One way of ANOVA was used for comparison of means. Mean separation was performed by LSD (least significant difference) for multiple comparisons of means. The analysis was carried out to investigate the effect of operating conditions on the percentage adsorption of calcined hydrotalcite. ANOVA indicated that almost all of the individual effects of the parameters were insignificant, the interaction of the factors was considered during model fitting and the individual effect was rather analyzed graphically. To visualize the combined effects of two of the factors on the response, contour plots were generated for two of the

factors while keeping the other one factor at its middle value using Design-Expert version 6.0.8.

The low lack of fit from the ANOVA analysis indicated that the model does indeed represent the actual relationships of reaction parameters, which are well within the selected ranges.

Table 4.8. ANOVA table of CHT-2 for Response Surface 2FI Model

Source	Sum of Squares	DF	Mean Square	F - Value	Prob > F	Source
Model	86.69	3	28.90	4.65	0.0316	significant
A	<i>21.31</i>	<i>1</i>	<i>21.31</i>	<i>3.43</i>	<i>0.0971</i>	
B	<i>1.897E-003</i>	<i>1</i>	<i>1.897E-003</i>	<i>3.052E-004</i>	<i>0.9864</i>	
AB	<i>61.86</i>	<i>1</i>	<i>61.86</i>	<i>9.95</i>	<i>0.0116</i>	significant
Residual	55.94	9	6.22			
<i>Lack of Fit</i>	<i>6.04</i>	<i>4</i>	<i>1.51</i>	<i>0.15</i>	<i>0.9543</i>	<i>not significant</i>
<i>Pure Error</i>	<i>49.90</i>	<i>5</i>	<i>9.98</i>			
Cor Total	142.63	12				

The graph of the predicted values obtained using the developed correlation versus actual values is shown in Fig. 4.11. The plot contains a line of unit slope (i.e. the line of perfect fit) with points corresponding to zero error between predicted values and actual. This plot therefore justifies the performance of the correlation. Thus, the regression model equation granted a very accurate description of the experimental data, in which almost all the points are very close to the line of perfect fit. This result indicates that it was successful in creating the correlation between the process variables to the percentage adsorption.

DESIGN-EXPERT Plot  
% adsorbance

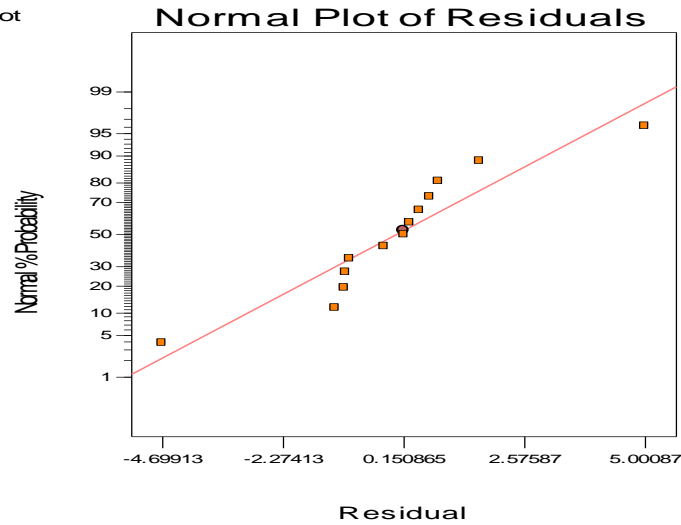


Fig 4.11. Normal probability plot of the studentized residuals to check for normality of residuals.

### Optimization of fluoride adsorption condition by CHT-2 using response surface methodology

By means of optimization function in design expert soft ware 6.0.8, it was predicated that at the following operating condition; 5 gm/L of initial fluoride concentration, pH of 6.0 and Mg/Al molar ratio of 2 in CHT, a maximum percent adsorption 93.5441% was obtained. In order to verify this prediction, experiments were conducted at this optimal condition and the results were comparable with the prediction. It was found that the experimental value of 94.4% of percentage adsorption agreed well with the predicted value.

Using design expert soft ware of numerical optimization tool, the optimized solutions for maximum adsorption is shown in table 4.9 below:

Table.4.9. optimization solutions for CHT-2

Number	pH	Initial conc.of F-	% adsorbance	Desirability	
1	6	5	<u>93.5441</u>	<u>0.930</u>	selected
2	8	15	90.3103	0.665	

### Optimization of fluoride adsorption condition by CHT-1 and CHT-3 adsorbents using response surface methodology

The result of optimization solution for the adsorption of fluoride from aqueous solution by CHT-1 and CHT-3 shows in the table below. As shown from the table CHT-1 is efficient at a pH of 6 and initial concentration of F<sup>-</sup> 15mg/L resulting percentage adsorption of 90.4%. CHT-3 shows a percentage adsorption of 89.63 % at a pH of 6 and initial fluoride concentration of 15mg/L. But both materials are not affected by both individual and interaction effects. As a result CHT-2 shows highest affinity towards adsorption capacity due to modification of particles and high surface area of the small particles.

Table.4.10. optimization solutions for CHT-1 and CHT-3

Type CHT	pH	Initial conc.of F <sup>-</sup>	% adsorbance		Effect of parameters (individual and interaction effect)
CHT-1	6	15	90.4	selected	Insignificant
CHT-3	8	15	89.63	selected	Insignificant

#### 4.7. Analysis of variance (ANOVA) for CHT-1 and CHT-2

The table 4.10below shows that, the "Model F-value" of 2.23 implies the model is not significant relative to the noise.

There is a 15.40 % chance that a "Model F-value" this large could occur due to noise. Values of "Prob> F" less than 0.0500 indicate model terms are significant.

In this case interaction effect of initial fluoride concentration and pH is a significant model term. Values greater than 0.1000 for pH and initial fluoride concentration indicates the model terms are not significant.

Table 4.11. ANOVA table for CHT-1 with Mg/Al molar ratio of 1.

Source	Sum of Squares	DF	Mean Square	F -Value	Prob > F	Source
Model	224.53	3	74.84	2.23	0.1540	<i>not significant</i>
A	10.20	1	10.20	0.30	0.5947	
B	30.44	1	30.44	0.91	0.3657	
AB	184.72	1	184.72	5.51	0.0436	
Residual	301.98	9	33.55			
Lack of Fit	260.03	5	52.01	4.96	0.0730	<i>not significant</i>
Pure Error	41.94	4	10.49			
Cor Total	526.51	12				

In Table 4.11 the "Model F-value" of 2.00 implies the model is not significant relative to the noise. There is a 18.57 % chance that a "Model F-value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case there are no significant model terms .

In conclusion the ANOVA table shown above(table 4.8, 4.10 and 4.11) for the three CHTs i.e CHT-2, CHT-1 and CHT-3 shows as the individual variables in the three types of CHT and interactions in CHT-3 have no significant effect to the response variable for adsorption of fluoride by this Mg/Al hydrotalcite derived mixed oxides. This confirms robustness and the effective applicability of the material at any different levels of the parameters(pH and initial fluoride concentration). So it can be used as adsorbent for the treatment of under ground waterhaving different pH and initial fluoride concentration regardless of their source. But the

optimal operating condition for the treatment of fluorinated underground water above the WHO and Ethiopian standard level of fluoride was given in section 4.6.

Table 4.12. ANOVA table for CHT-3 with Mg/Al molar ratio of 3.

Source	Sum of Squares	DF	Mean Square	F -Value	Prob > F	Source
Model	124.36	2	62.18	2.00	0.1857	<i>not significant</i>
A	45.84	1	45.84	1.48	0.2523	
B	49.59	1	49.59	1.60	0.2351	
Residual	310.61	10	31.06			
Lack of Fit	157.78	6	26.30	0.69	0.6754	<i>not significant</i>
Pure Error	152.82	4	38.21			
Cor Total	434.97	12				

#### 4.8. Regeneration of fluoride loaded hydrotalcite

Desorption of fluoride from fluoride adsorbed CHT surface at different pH are presented in Fig 4.12. from the experimental result data given in annex 1 Table 1.5. Evidently desorption efficiency of the solution varied with its pH value. Initially there was no release of fluoride up to pH 6, there after it started showing fluoride desorption. It was observed that at pH 12.5 around 87.2% desorption efficiency was achieved. Further rise of solution pH did not show much improvement in desorption efficiency. The removal rate of F<sup>-</sup> by the regenerated CHT-2 is reduced by 7.6%.

In general at optimal condition obtained from the experimental design at a pH of 6.0, initial concentration of 5 mg/L and with Mg/Al molar ratio of 2.0 the adsorption experiment by first recycled CHT gave a final concentration of 0.64 mg/L.

The result showed a decrease in its effectiveness due to decrease in the surface area of the desorbed CHT due to chemical treatment for recycling by caustic soda and hydrochloric acid. It can be concluded from the above observation that the adsorption of fluoride is a reversible process, thereby facilitating the recyclability of the material for further use.

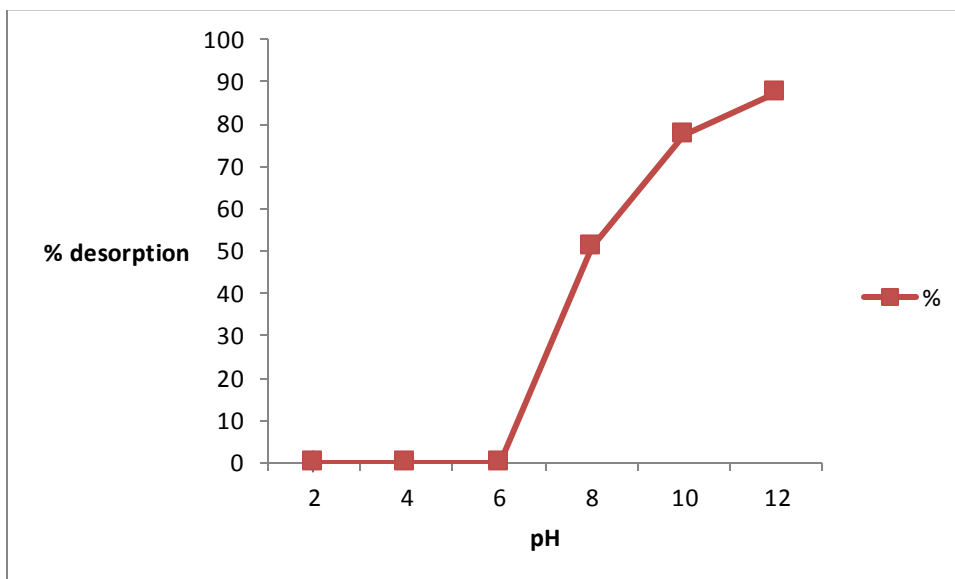


Fig.4.12. Desorption of fluoride from CHT-2 adsorbent at different pH.

## 5. Conclusion and Recommendations

### 5.1 Conclusion

The IR analysis gave IR spectrum which showed the characteristics of hydrotalcites. Besides that, it was also evident from the IR spectrum that calcination caused the removal of water and  $CO_2$  gas.

The efficiency of a calcined Mg-Alhydrotalcite as adsorbent to remove fluoride from aqueous solution has been studied. From the present study, it can be seen that the CHT can be used effectively for the removal of fluoride from aqueous solutions. The quantity eliminated was found to depend on the molar ratio of Mg/Al in CHT, the initial concentration of fluoride and pH of the solution. The interaction of pH and initial fluoride concentration significantly affect the adsorption of fluoride by CHT.

The CHT with an Mg/Al ratio of 2 has a marked ability to absorb anions. It was found that fluoride ions are removed much faster at low pH than at high pH. It was also found that the maximum removal of fluoride from aqueous solutions occurs at pH 6 in 3 h with an initial concentration of 5 mg/L, and that the retention of fluoride ions by the CHT-2 material was 94.4%. The residual fluoride was found to be 0.28 mg /L with an initial concentration of 5 mg/L, which meets WHO and national standard for drinking water quality. In general the optimum condition obtained from design expert for adsorption of fluoride by CHT is a pH of 6, initial concentration 5 mg/L and Mg/Al molar ratio of 2.00 result in a 93.5441 percent adsorption. It was found that the experimental value of 94.4% of percentage adsorption agreed well with the predicted value by performing experiments at this optimal condition. Equilibrium results could be fitted by the Langmuir isotherm and Freundlich isotherm, and the former is a better model. The adsorption is best described by Langmuir type isotherm for all adsorbent due to the surface in homogeneity. The kinetic data were fitted better to second order kinetics and the  $q_e$  values (4.76) calculated from the pseudo-second-order rate model, are very consistent with the experimental  $q_e$  values (4.72) indicating that the experimental kinetic data for fluoride adsorption by calcined samples works well with this model. It was

also observed that at pH of 12.5 around 87.2% desorption efficiency of fluoride from loaded CHT-2 was achieved verifying its highest capacity of reusability. The result indicates that CHT is a favorable adsorbent for removal of fluoride.

## 5.2. Recommendations

Further research should be done to improve the regeneration capacity of CHT adsorbent to be used in multiple defluoridation cycles. Detailed characterization of the adsorbent should be performed in order to provide a better understanding of the adsorption mechanism of fluoride on to the adsorbent.

An investigation on further optimization of the continuous process in terms of calcinations temperature, adsorbent particle size and the presence of competitor ions have to be performed. The future work for this project will include modification of the synthesis steps with the addition of metals (e.g. Li or Ni) into the adsorbent.

An investigation of the physical, chemical and biological characteristics of treated water must be carried out in order to reduce the health effect on the people who uses it. Research on the adsorption performance of the adsorbent in continuous operation and optimizing the column experimental parameters have to be performed. The efficiency and capacity of the adsorbent with real fluoride contaminated water samples should be assessed. Detailed feasibility study on the economical, social and technical aspects should be studied.

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## Annex 1. Summarized tables for the data generated during experimentation

Table 1.1. Design matrix experiment

No of run	PH	Initial conc.of F-( mg/ L)	Mg/Al molar ratio in CHT
1	6	5	1
2	6	5	2
3	6	5	3
4	6	10	1
5	6	10	2
6	6	10	3
7	6	15	1
8	6	15	2
9	6	15	3
10	7	5	1
11	7	5	2
12	7	5	3
13	7	10	1
14	7	10	2
15	7	10	3
16	7	15	1
17	7	15	2
18	7	15	3
19	8	5	1
20	8	5	2
21	8	5	3
22	8	10	1
23	8	10	2
24	8	10	3
25	8	15	1
26	8	15	2
27	8	15	3
28	6	10	2
29	7	5	2
30	8	5	2
31	6	15	2
32	8	10	2

Table1.2. Experimental result for the adsorption of Fluoride from aqueous solution

No	Final concentration of F- (mg/L)			Mean $\pm$ SD (mg/L)	% adsorption	Adsorption capacity (mg/g)
	Trial-1	Trial-2	Trial-3			
1	1.82	1.42	1.66	1.63 $\pm$ 0.201329	67.4	3.73
2	1.42	1.26	1.44	1.37 $\pm$ 0.098658	72.6	3.63
3	0.43	0.55	0.93	0.64 $\pm$ 0.261024	87.2	4.36
4	1.88	1.95	1.07	1.63 $\pm$ 0.489115	83.7	8.37
5	0.92	1.12	1.27	1.1 $\pm$ 0.175594	89	8.9
6	1.21	1.66	1.87	1.58 $\pm$ 0.337194	84.2	8.42
7	1.43	1.29	1.94	1.55 $\pm$ 0.342101	89.7	13.45
8	1.75	1.1	1.36	1.4 $\pm$ 0.327159	90.7	13.6
9	1.9	2.75	3.35	2.67 $\pm$ 0.728583	82.2	12.33
10	0.51	0.96	0.64	0.7 $\pm$ 0.231589	86	4.3
11	1.51	1.31	0.76	1.19 $\pm$ 0.388373	76.2	3.81
12	0.79	0.62	0.32	0.58 $\pm$ 0.237978	88.4	4.42
13	0.7	0.98	1.53	1.07 $\pm$ 0.422256	89.3	8.93
14	1.59	1.84	2.95	2.13 $\pm$ 0.723901	78.7	7.87
15	1.62	1.48	1.84	1.65 $\pm$ 0.181475	83.5	8.35
16	1.49	1.67	1.89	1.68 $\pm$ 0.200333	88.8	13.32
17	3.15	2.11	4.55	3.27 $\pm$ 1.224418	78.2	11.73
18	3.2	2.06	4.8	3.35 $\pm$ 1.37642	77.7	11.65
19	0.5	0.87	1.21	0.86 $\pm$ 0.355106	82.8	4.14
20	0.08	0.32	0.43	0.28 $\pm$ 0.178979	94.4	4.72
21	0.57	0.12	0.33	0.34 $\pm$ 0.225167	93.2	4.66
22	1.63	1.42	1.33	1.46 $\pm$ 0.153948	85.4	8.54
23	1.46	1.14	0.8	1.13 $\pm$ 0.330051	88.7	8.87
24	1.34	1.22	1.07	1.21 $\pm$ 0.135277	87.9	8.79
25	1.75	1.92	2.6	2.09 $\pm$ 0.449778	86.1	12.91
26	1.75	1.66	1.39	1.6 $\pm$ 0.18735	89.3	13.4
27	1.85	1.71	1.32	1.63 $\pm$ 0.274651	89.1	13.37
28	1.16	0.87	0.89	0.95 $\pm$ 0.161967	90.5	9.05
29	0.83	0.56	0.61	0.62 $\pm$ 0.143643	87.6	4.38
30	0.51	0.92	0.75	0.79 $\pm$ 0.205994	84.2	4.21
31	1.20	1.09	1.32	1.21 $\pm$ 0.115036	91.9	13.79
32	1.2	1.4	1.0	1.2 $\pm$ 0.2	88	8.9

Table 1. 3. Data for experimental design for adsorption by CHT-2

	Std	Run	Block	pH	Initial conc.of Fluoride	Response, percentage adsorption
	11	1	Block 1	7.00	5.00	87.6
	3	2	Block 1	6.00	15.00	82.2
	6	3	Block 1	7.00	5.00	88.8
	12	4	Block 1	8.00	5.00	84.2
	2	5	Block 1	7.00	15.00	89
	8	6	Block 1	6.00	10.00	88.7
	4	7	Block 1	8.00	10.00	88.4
	10	8	Block 1	6.00	10.00	90.5
	5	9	Block 1	7.00	10.00	89.3
	9	10	Block 1	8.00	15.00	89.3
	13	11	Block 1	6.00	15.00	91.9
	1	12	Block 1	6.00	5.00	94.4
	7	13	Block 1	8.00	5.00	82.8

Table 1.4. Desorption experiment result

pH of desorbing solution	Final conc. Of Fluoride desorbed	Percentage desorption
2	0	0
4	0	0
6	0	0
8	2.4	50.9
10	3.65	77.4
12	4.12	87.2

Table 1.5.physical characteristic of calcinedhydrotalcite

Constituents	CHT
Inorganic material	hydrotalcite
Particle size(nm)	251
Density(g/cm <sup>3</sup> )	0.72
BET surface area(m <sup>2</sup> /g )	30.53
pH	10.2
Micro pore volume(ml/g)	0.04-0.07
Total pore volume(ml/g)	0.2-0.42

## Annex 2. Characterization results of CLDH using infrared spectrophotometer

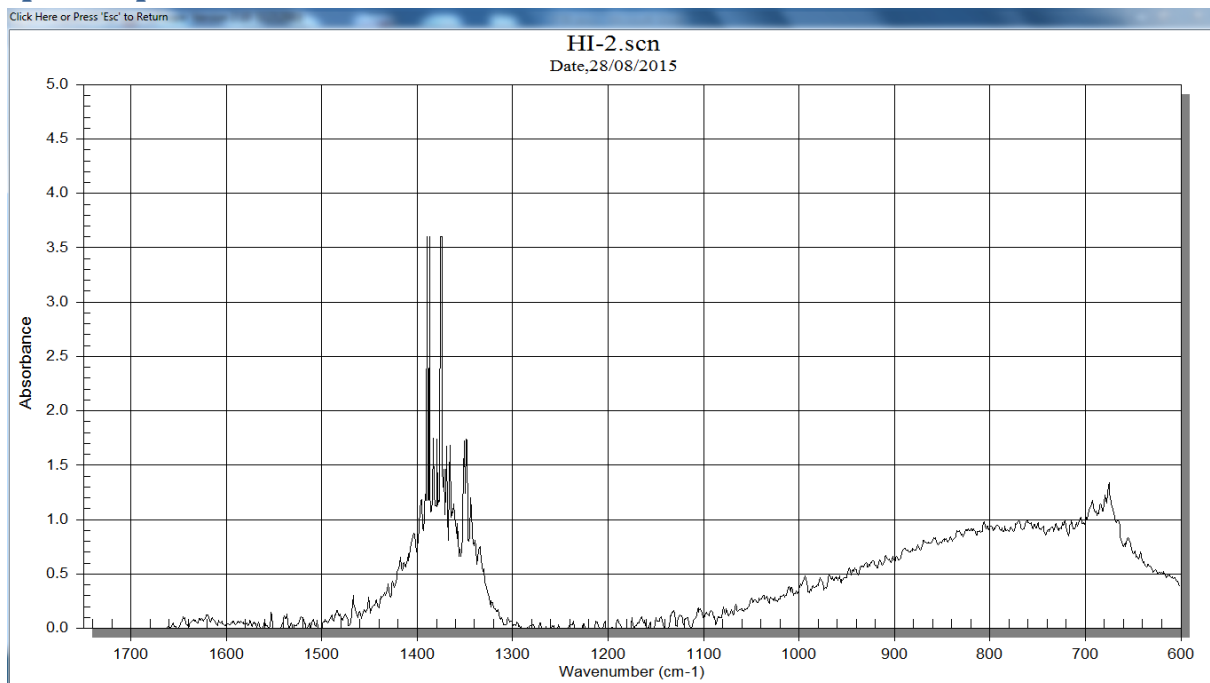


Fig.A.2.1.IR spectra of Mg-Al hydrotalcites with Mg/Al molar ratio of 2.

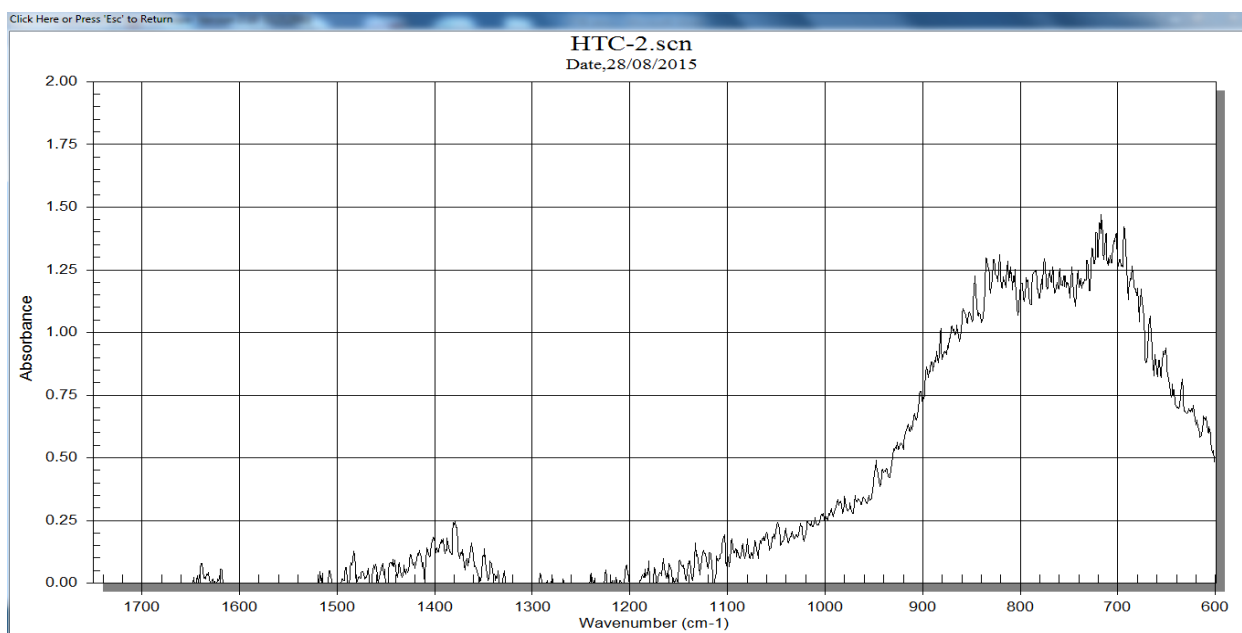


Fig.A.2.2.IR spectra of calcined Mg-Al hydrotalcites with Mg/Al molar ratio of 2.

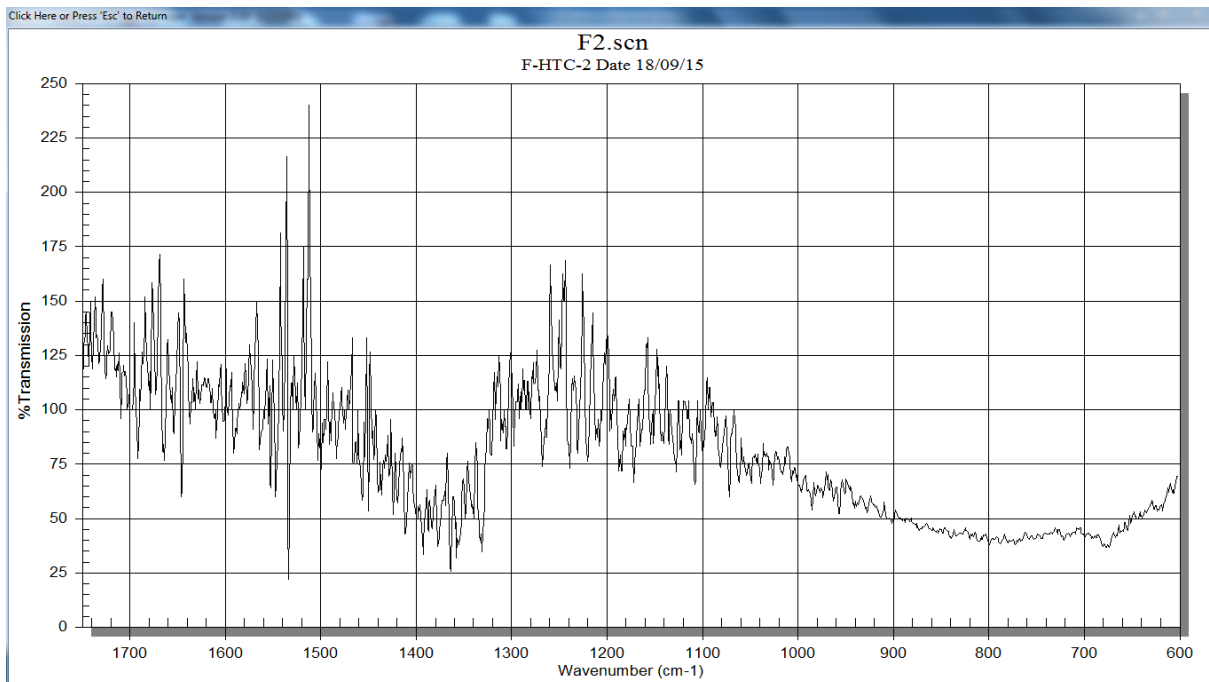


Fig.A. 2.3. IR spectra of fluoride loaded calcined Mg-Al hydrotalcites with Mg/Al molar ratio of 2.

### Annex 3. Design expert 6.0.8 result for the analysis of the experiments

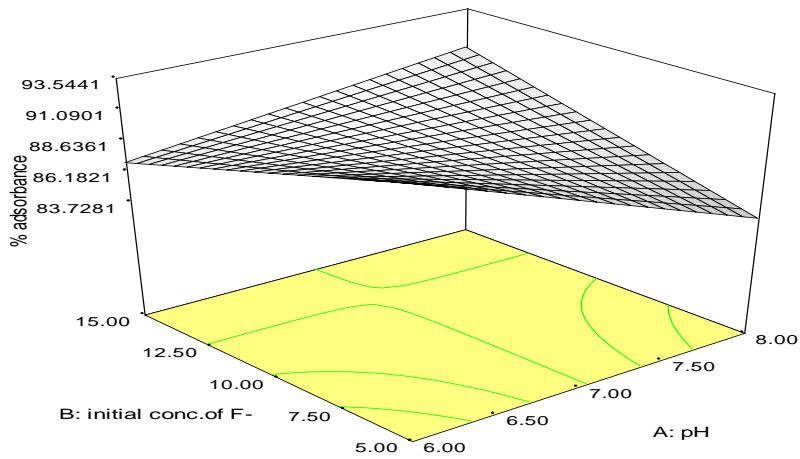


Fig .A.3.1. 3D surface plot showing interactive effect of pH, initial conc. of fluoride on percent absorbance

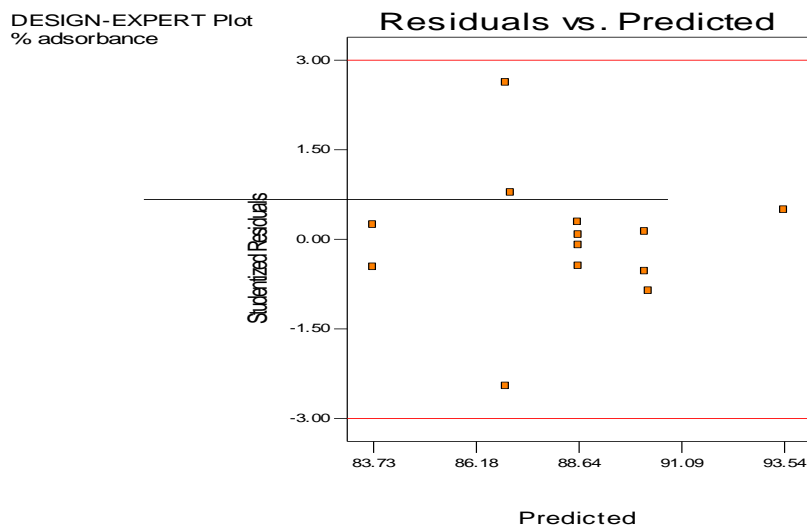


Fig .A.3.2. Residuals versus predicted values to check for constant error.

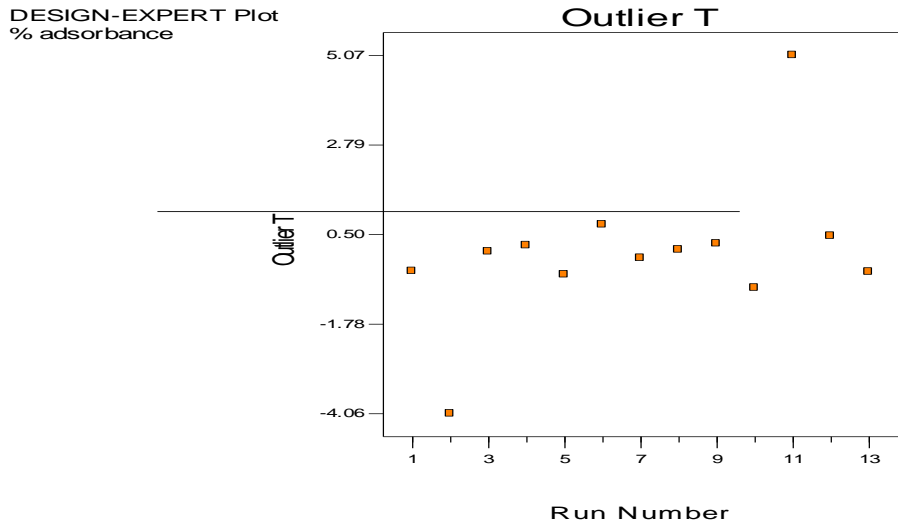


Fig.A. 3.3.Outlier t versus run order to look for outliers, i.e., influential values.

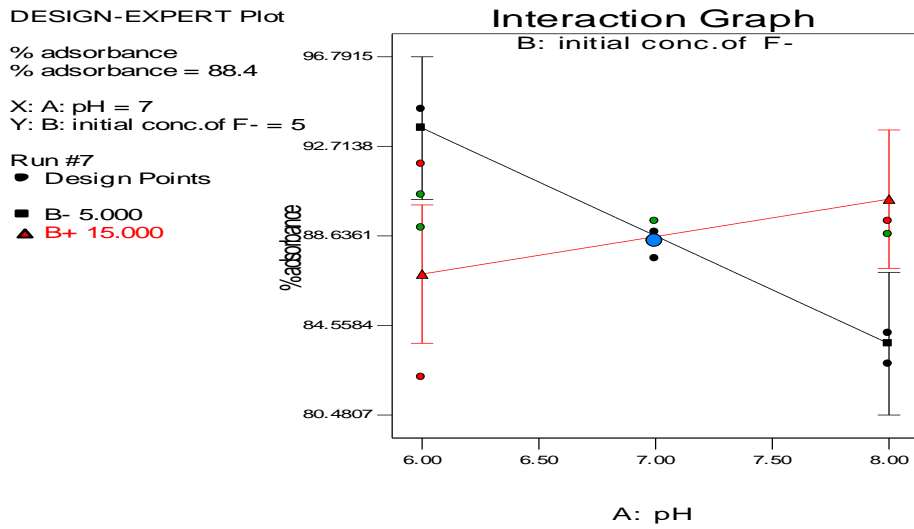


Fig.A.3.4.Interaction effect of initial concentration of fluoride and pH.

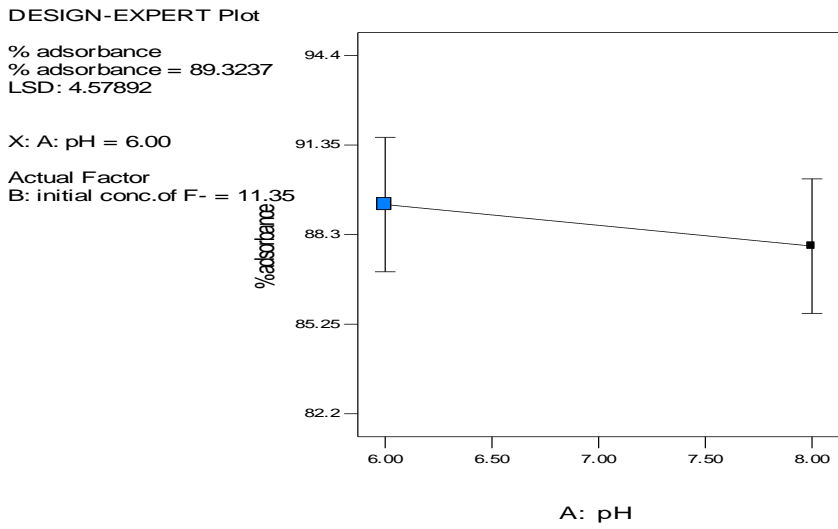


Fig .A.3.5.Effect of pH on percentage adsorbance.

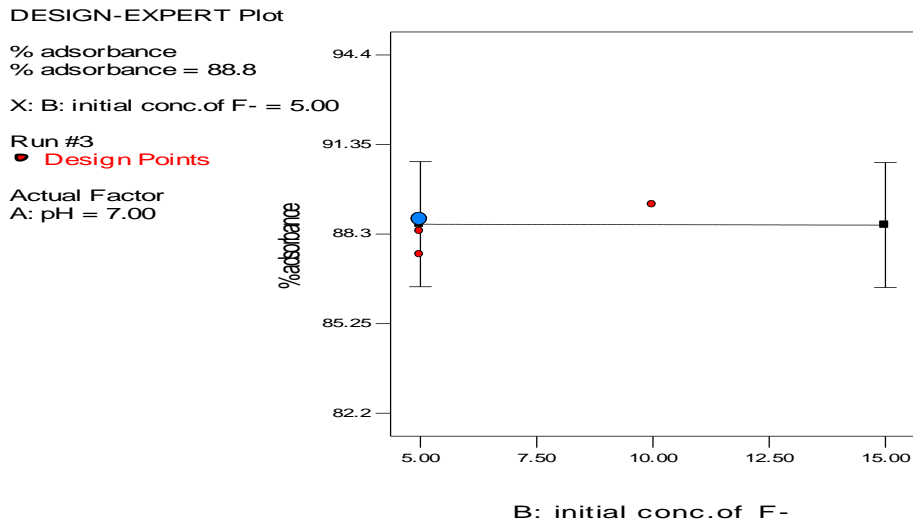


Fig .A.3.6. Effect of initial concentration of fluoride on percentage adsorption