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# Production and characterization of Kaolinite Clay and process optimization for deflouridation of ground water in Afar Region

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BAHIR DAR UNIVERSITY

BAHIR DAR INSTITUTE OF TECHNOLOGY

SCHOOL OF RESEARCH AND POSTGRADUATE STUDIES

FACULTY OF CHEMICAL AND FOOD ENGINEERING

Production and characterization of Kaolin Clay and process optimization  
for defluoridation of ground water in Ar Region

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Bahir Dar, Ethiopia

November 15, 2017

Production and characterization of Kaolinite Clay and process optimization for  
defluoridation of ground water in Ar Region

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A Thesis submitted to the school of Research and Graduate Studies Bahir Dar  
Institute of Technology, Bahir Dar University in partial fulfillment of the requirements  
for the Degree of Master of Science in Process Engineering in the Faculty of Chemical  
and Food Engineering

Supervised by Dr. Alemayehu Kiflu

Bahir Dar, Ethiopia

November, 2017

## DECLARATION

I, the under signed, declare that the thesis comprises my own work. In compliance with internationally accepted practices, I have dually acknowledged and refereed all materials used in this work. I understand that non-adherence to the principles of academic honesty and integrity, misrepresentation/ fabrication of any idea/data/fact/source will constitute sufficient ground for disciplinary action by the university and can also evoke penal action from the sources which have not been properly cited or acknowledged.

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This thesis has been submitted for examination with my approval as a university advisor.

Advisor Name: \_\_\_\_\_

Advisor Signature \_\_\_\_\_



## A B S T R A C T

In many parts of the world, fluoride in drinking water is responsible for notable public health issues. The presence of a small amount of fluoride in drinking water is beneficial to human health but a high amount ( $> 1.5 \text{ mg/L}$ ) has adverse health effects. Kaolinite clay has been found to remove fluoride by adsorption process. Its composition is  $\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_8$  with  $\text{SiO}_2$ : 46.54 wt.%,  $\text{Al}_2\text{O}_3$ : 39.5 wt.% and  $\text{H}_2\text{O}$ : 13.96 wt.%. The present study is aimed to prepare new adsorbent kaolinite clay that can serve as a valuable defluorinating agent. Characterization of the produced adsorbent was done by Fourier transform infrared spectroscopy (FTIR), BET and XRD. BET analysis reveals surface area and porosity of synthesized adsorbent and the result indicates the smaller particle size has larger surface area and pore volume. The XRD shows the morphology of the adsorbent and result indicates the crystalline structure of the adsorbent. The investigation of fluoride removal was attempted using raw and activated clay. The clay was activated with concentrated  $\text{H}_2\text{SO}_4$  and the effects of various experimental parameters including temperature, pH, particle size, contact time and dose of the adsorbents were investigated using a batch adsorption technique. Experiments were carried out by batch adsorption at temperature of 25, 40, 50, 60 and  $70^\circ\text{C}$  and the removal efficiencies of these materials with respect to time (30 - 150 min), pH (2 - 8), adsorbent dose (0.5 - 2.5 g/L) and particle size (ranges from 0.075 to 0.30 mm) were studied. Results showed that adsorption equilibrium is attained at 60 min by keeping the other parameters constant for both adsorbents used and the extent of fluoride removal increased with decrease in particle size of the adsorbent and increased with increase in contact time and amount of adsorbent used. In all parameters, activated clay was better than raw kaolinite clay in removing fluoride. In this thesis the paramount value of fluoride removal by both adsorbents was obtained at pH 4; temperature  $50^\circ\text{C}$ , particle size of 0.075 mm and 1.5 gram of adsorbent dosage according to experiments. Adsorption data were modeled using the Freundlich and Langmuir adsorption isotherms and best adsorption fits were obtained with Langmuir adsorption isotherms for both adsorbents. The experimental data produced a straight line fit with a relatively good correlation coefficient ( $R^2$ ) indicating the acceptability of the model for the studied activated and raw kaolinite clay defluorination system.

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## LIST OF ABBREVIATION S

WHO	World Health Organization
PS	particle size
RC	Raw clay
AC	Activated clay
BET	Brunauer Emmett Teller
FTIR	Fourier Transform Infrared
XRD	X-ray diffraction
GBH	Granular acid treated bentonite
EBCT	Empty contact time

# 1. INTRODUCTION

## 1.1 Background

The supply of clean water is scarce and always contaminated by several pollutants. Fluorine is one of such contaminants that contaminate water all over the world. The primary sources of fluoride in the ground water are fragile rocks that contain fluoride, for example, fluorite, fluorapatite, and cryolite and hydroxyl apatite. The industrial effluents from aluminum, phosphate, semiconductor, glass and ceramic industries, uranium, electroplating, toothpaste manufacturing units and coal plant adds fluoride to the ground water. The other sources of fluoride intake for human beings are water, air, food, cosmetic and medicine. The relationship between fluoride and fluorosis was first noted in the early part of the 20<sup>th</sup> century when it was observed that residents of certain areas of U.S.A. developed brown stains on their teeth. In 1930s it was observed that the prevalence and severity of this type of mottled enamel was directly related to the amount of fluoride ingested [2]. Excessive fluoride exposure may cause irreversible demineralization of bone and tooth tissues, a condition known as fluorosis. With prolonged exposure to higher fluoride concentrations, dental fluorosis progresses to skeletal fluorosis.

Fluoride ion exists in natural water and it is an essential micronutrient in preventing dental caries and facilitating the mineralization of hard tissues, if taken at a recommended range of concentration. Higher level of fluoride in groundwater is a worldwide problem, which includes various countries from Africa and Asia as well as USA. Notably India, Sri Lanka, China, East African Rift Valley countries such as Ethiopia, Kenya, Somali and Djibouti, Turkey, and parts of South Africa [1]. The permissible limit of fluoride is 1.5 mg/L set by the World Health Organization (WHO). The fluoride found above 1.5 mg/L in ground water causes severe health problems like dental fluorosis, skeletal fluorosis, and non-skeletal fluorosis. Apart from fluorosis, excess fluoride in water causes diseases like cancer, damage kidney, liver-nervous systems, thyroids, respiratory problems, Alzheimer, reduce pregnancy. The fluorosis was pervasive among the 200 million people groups from more than 30 nations over the globe [3].

Dental fluorosis, which is characterized by discolored, blackened, mottled or chalky white teeth, is clear indication of exposure to fluoride during childhood when the teeth were developing. These effects are not apparent if the teeth were already fully grown prior to fluoride overexposure;

therefore, the fact that an adult may show no signs of dental fluorosis does not necessarily mean that his or her fluoride intake is within the safety limit [4].

Chronic intake of excessive fluoride can lead to the severe and permanent joint deformations termed as skeletal fluorosis. Early symptoms include sporadic pain and stiffness of joints: headache, stomach ache and muscle weakness can also be warning signs. The next stage is osteosclerosis (hardening, calcifying of the bones) finally the spine, major joints, muscles and nervous system are damaged. Both dental and skeletal, fluorosis is irreversible and no treatment exists, the only remedy is prevention by keeping fluoride intake within safe limit [5].

Hence, it is necessary to reduce the fluoride concentrations to permissible levels and for which promising investigations are being put all over the world.

Ethiopia is among the most affected nations in Africa by the fluoride problem. Fluoride concentration, as high as 33 mg/L Hawasa, Zway Adama Metahara and southern Afar, has been reported in drinking water sources in Ethiopia. Excess fluoride in drinking water is prevalent in all of the Rift Valley regions of the country [3]. According to the Ministry of Water and Energy of Ethiopia, rural drinking water supply in the Rift Valley region is, to a large extent, dependent on groundwater. Hence, it becomes necessary to reduce the fluoride concentration within permissible limit of 1.5 mg/L according to the Ethiopian Standard for drinking water. However, the Ministry of Water Resources on the basis of economic, practical and technical considerations proposed guideline for drinking water quality of fluoride at 3.0 mg/L [7]. The limit varies among countries and the age of people exposed. World Health Organization (WHO) has set a limit between 0.5 and 1.5 mg/L [8]. After many years of use of drinking water from drilled wells in the Rift Valley, Ethiopia, dental and skeletal fluorosis has become a serious medical problem [9].

The effect of fluoride on human health by the prolonged use of drinking water with fluoride is presented in Table 1.

Table 1.1 Health effects on prolonged use of fluoridated drinking water [9]

Fluoride ion concentration,(mg/lit)	Health outcome
<0.5	Dental caries
0.5-1.5	Optimum dental health
1.5-4.0	Dental fluorosis
4.0-10	Dental and skeletal fluorosis
>10.0	Crippling fluorosis

For communities in developing countries like the Rift Valley regions of Ethiopia where the groundwater is fluoride rich and provision of alternative water supply is difficult, treatment of contaminated water is the only option to provide safe drinking water. Available techniques for the removal of fluoride belong to the following major categories: chemical precipitation, membrane processes, adsorption by activated alumina, ion exchange and Nalgonda technique [16]. It is widely recognized that adsorption is an ideal and appropriate technique compared to other techniques, for small community water source defluoridation.

Table 1. Comparison of fluoride removal technologies [16]

Technology	Advantages	Disadvantages
Coagulation/precipitation: calcium hydroxide/aluminum hydroxide	High efficiency; commercially available chemical	Expensive, efficiency depends on pH and presence of ions in water, adjustment and readjustment of pH is required, elevated residual aluminum concentration, formation of sludge with high amount of toxic aluminum fluoride complex and high amount of retained water (sludge dewatering is required prior disposal)
Membrane filtration: reverse osmosis/nanofiltration	High efficiency; remove other contaminants	High capital high running and maintenance costs toxic wastewater produced
Electrochemical treatments: dialysis, electro-dialysis, electro-coagulation	High efficiency; high selectivity	High cost during installation and maintenance



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Ion-exchange Strong basic anion-exchange resin with quaternary ammonium functional groups	High efficiency	Expensive, vulnerable to interfering ions (sulfate, phosphate, chloride, bicarbonate etc.), replacement of media after multiple regenerations, used media present toxic solid waste, regeneration creates toxic liquid waste, efficiency highly pH-dependent
Adsorptive materials activated alumina activated carbons other natural and synthetic adsorbents	Greater accessibility, low cost simple operation, availability of wide range of adsorbents	High efficiency often demand adjustment and readjustment pH, some common water ions can interfere fluoride adsorption

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In recent years, the use of low cost adsorbents has been investigated to remove fluoride from water. Such materials include activated carbon, natural zeolite, hydroxyl apatite, calcite, fluor spar and quartz, fly ash, silica gel, bone char [11], spent catalyst, red mud and bentonite [12]. Studies in Ethiopia as well as other developing countries indicated the possibility of using low cost adsorbents such as bone char, clay soils, diatomaceous earth, lateritic soils and other related materials [13].

In this thesis an innovative technique has been presented for defluoridation of drinking water employing activated kaolinite clay. Clay is an earthy sedimentary material composed mainly of fine particles of hydrous aluminium silicates and other minerals and impurities. Clay is fine, plastic when moist, retains its shape when dried and sinters hard when fired. These properties utilized in manufacture of pottery, brick and tile. Both clay powder and fired clay are capable of adsorption of fluoride as well as other pollutants from water. The ability of clay to clarify turbid water is well known. This property is believed to have been known and utilized at domestic level in ancient Egypt. In the present work the study of defluoridation of water by adsorption method using acid treated kaolinite clay and raw kaolinite clay has been done. The effects of contact time and temperature on the defluoridation property of acid activated clay have been experimentally studied.

## 1.2 Health impacts of fluoride

About 95% of fluoride in the body is deposited in hard tissues and it continues to be deposited in calcified structure even after other bone constituents (Ca, P, Mg, carbonate and citrate) have reached steady state. Due to such deposition, bone deformation causes irreversible damages. The other problems associated with health impact of fluoride are generally overlooked because of the notion prevailing that fluoride only affects bones and teeth. Other problems arising due to the excessive intake of fluoride are fiber degeneration, low hemoglobin levels, deformities in red blood cell, excessive thirst, headache, skin rashes, osteoporosis, neurological manifestation, depression, gastro intestinal problems, urinary tract malfunctioning, nausea, tingling sensation in fingers and toes, repeated abortions, male sterility, etc. In Afar region the fluoride concentration reaches up to 120 mg/L and this prolonged exposure of excessive fluoride causes dental and skeletal fluorosis in the region.

## 1.3 Factors affecting fluorosis

The severity of fluorosis is influenced by concentration of fluoride in water and period of its usage. Nutritional status and physical strain also play vital role in deciding total effects of fluoride pollution. For example, increases the body retention capacity of fluoride. Environmental factors include annual mean temperature, humidity, rainfall, duration of exposure, etc. Besides, other factors such as pH in terms of alkalinity, age, fresh fruits and vitamin C reduces fluoride toxicity. Defluoridation of drinking water is the only pragmatic approach to solve the fluoride pollution problem as the use of alternate water sources and improvement of nutritional status of population at risk have their own limitations and are expensive affairs.

## 1.4 Problem Statement

Availability of safe water for consumption is the one of the most important gifts to mankind. But, unfortunately, the increase in concentration of contaminants such as fluoride above the permissible limit in groundwater resources over the years has become a serious concern in many countries. Ethiopia is among the most affected nations by the fluoride problem where excess fluoride in drinking water is prevalent in all of the Rift Valley regions of the country. Afar is one part of the rift valley region in Ethiopia. Ethiopian Ministry of Water Resources proposed guideline standard for drinking water quality of fluoride at 3.0 mg/L but fluoride concentration at this level causes dental fluorosis. In Afar region the fluoride concentration reaches up to 120 mg/L and this prolonged exposure of excess fluoride causes dental and skeletal fluorosis in the region. Hence, it becomes necessary to reduce the

fluoride concentration within permissible limit of 1.5 mg/L according to the WHO Standard for drinking water. Although, there are different conventional methods for fluoride removal, most of the methods have high operational and maintenance cost, low fluoride removal capacities, generation of large volumes of sludge and complicated procedures involved in the treatment. Therefore, the viable option is to look for low cost processes that can be using local expertise and based on locally available and cost effective fluoride adsorbent. Thus the locally available kaolinite clay adsorbent can be applied for removal of excess fluorides to the allowable limit of fluoride in drinking water supplies in Afar region.

## 1.5 Objectives

### General objective

The general objective is to produce economically effective and locally available kaolinite clay adsorbent for defluoridation of ground water in Afar region.

### Specific objectives

- Preparation and characterization of kaolinite clay adsorbent.
- To investigate the effect of process parameters (temperature, particle size, time and adsorbent dosage) on percent removal of fluoride.
- To determine the optimum operating conditions for the defluoridation process.
- To analyze adsorption isotherms of kaolinite clay adsorbents on fluoride removal and select best value so that easy to apply for supply of non fluoride water.

## 2. LITERATURE REVIEW

### 2.1 Distribution of Fluorosis

The latest information shows that fluorosis is endemic in at least 25 countries across the globe. The total number of people affected is not known, but a conservative estimate would number in the tens of millions. In 1993, 15 of India's 32 states were identified as endemic for fluorosis [15]. In Mexico, 5 million people (about 6% of the population) are affected by fluoride in groundwater. Fluorosis is prevalent in some parts of central and western China and caused not only by groundwater but also by breathing airborne fluoride released from the burning of fluoride coal. Worldwide, such instances of industrial fluorosis are on the rise [6].

Ethiopia is one of the 25 countries where the population suffers from the consumption of fluoride rich drinking water [17]. People in several areas of the Ethiopian Rift Valley are consuming water with up to 33 mg/l of fluoride. So it is required to implement appropriate water treatment procedures using local resources that are accessible to the rural community with technically simple, cost effective, and easily transferable technology. In this study we investigate the possibilities of utilizing kaolinite clay as a low cost defluoridation adsorbent.

Both dental and skeletal fluorosis is prevalent in the rift valley region of Ethiopia including afar region because of high fluoride waters that originate from springs and lakes [18]. An extensive study was done among 1,456 individuals in 14 communities in the central Rift Valley and reported dental fluorosis prevalence was between 69% and 98% (mean 84%) in the groups sampled. Slight, no significantly higher rates were found in young males (82.5%) as compared to young females (81%), in the age group-10 years. In a similar study from the Ethiopian Rift Valley, showed prevalence of dental fluorosis in permanent anterior teeth, ranging from 34% to 75% in 8 year-old children residing in various villages of the Wonji-Shoa Sugar area and 77% among adults (20-25 years old) [18].

#### 2.1.1 The origin and distribution of fluoride in Ethiopia

Concentrations of fluoride greater than the WHO guideline value of 1.5 mg/l have been found in ground waters from several parts of Ethiopia, but are recognized to be high in the Rift valley zone [19]. Concentrations often greater than 10 mg/l are found in waters from the Rift valley. Moderately high (unacceptable) concentrations have also been found in ground waters from volcanic rocks in the highlands. Concentrations in groundwater from the ancient basement rocks are typically (e.g. Mekele area) [19].

Unusually low fluoride concentrations have been reported in groundwater from wells and springs in the Rift Valley town of Arba Minch and the nearby escarpments in southern Ethiopia. This is apparently due to inputs of low-fluoride runoff from the highlands or from nearby rivers or lakes [18]. The problematic fluoride concentrations were derived from hot springs (high temperature) and by weathering of the volcanic bedrocks (presence of alkalinity ( $\text{HCO}_3^-$ )) [20]. Fluoride concentrations above 5.0 mg/l in the Rift Valley were found mostly in hot springs (100% of all sources), lakes (78%), shallow wells (54%) and boreholes (35%) and the low concentrations (below 1.5 mg/l) in springs and rivers [21].

Figure 2.1 Fluoride distributions within the rift valley of Ethiopia [23]

## 2.2 Guidelines and standards

In 1984, WHO conducted an extensive review and found that there were insufficient data to conclude that fluoride produces cancer or birth defects. In addition, WHO noted that mottling of teeth (i.e. dental fluorosis) is sometimes associated with fluoride levels in drinking water above  $1.5 \text{ mg L}^{-1}$  and crippling skeletal fluorosis can ensue when fluoride levels exceed  $10 \text{ mg L}^{-1}$ . A guideline value of  $1.5 \text{ mg L}^{-1}$  was therefore recommended by WHO as a level at which dental fluorosis should be minimal (WHO, 1984)

The  $1.5 \text{ mg L}^{-1}$  fluoride guideline value that was set in 1984 was subsequently evaluated by WHO and it was concluded that there was no evidence to suggest that it should be revised (WHO, 1996, 2004). The  $1.5 \text{ mg L}^{-1}$  guideline value of WHO is not a fixed value but is intended to be adapted to take account of local conditions (e.g. diet, water consumption [21]). However, the Ethiopian Ministry of Water Resources on the basis of economic, practical and technical considerations proposed guideline for standard drinking water quality of fluoride at  $3.0 \text{ mg/L}$  [24]

## 2.3 Commercial Defluoridation Methods

The process of removal of fluoride is generally termed defluoridation. Numerous commercial methods have been described employing various materials for fluoride removal since 1930 [23]. Bower and Hatches studied the defluoridation of water by minerals and soils by the release of  $\text{OH}^-$  ions. The equilibrium information fitted well with the Langmuir isotherm model. The adsorption of fluoride at an equilibrium concentration of  $16 \text{ mg/l}$  for various soils and minerals were alkaline soils ( $59$  to  $120 \text{ mg/g}$ ); acid Aiken soil ( $1060 \text{ mg/g}$ ); gibbsite and kaolinite ( $190$  to  $295 \text{ mg/g}$ ); dehydrated halloysite ( $1400 \text{ mg/g}$ ); hydrated (expanded) halloysite ( $1777 \text{ mg/g}$ ) and  $\text{Al}(\text{OH})_3$  ( $32600 \text{ mg/g}$ ). Goethite, bentonite and vermiculite adsorbed only traces of fluoride [24].

Omuetti and Jones used Illinois soils for the removal of fluoride from water. It was reported that at low concentration of fluoride both Langmuir and Freundlich isotherm models described adsorption on soils. The optimum pH range for the maximum fluoride removal was between  $5.5$  and  $6.5$ . The presence of amorphous aluminium oxyhydroxides was responsible for the removal of fluoride [25].

Chaturvedi et al. used china clay for fluoride removal from water. The optimal condition suitable for defluoridation consists of low fluoride concentration, high temperature and acidic pH. The maximum fluoride adsorption was mainly occurred due to the presence of alumina in china clay [26].

Hauge et al. studied the defluoridation of drinking water using pottery. The clay fired at  $600^\circ\text{C}$  temperature was found most effective for removal of fluoride [27].

Bjorvatn and Bardsen studied the defluoridation capacity of calcined red soil (laterite) at 570°C mainly consists of silicon, aluminium and iron from water. The defluoridation capacity of red soil from Balang in Adamoua province, North Cameroon was more as compared to that of Ngaoundere. The fluoride removal was high initially in few hours and reached steady state within 48 hours [28].

Moges et al. used fire clay chip obtained from a region in Ethiopia for removal of fluoride from water. The defluoridation capacity of 200 mg/kg and 76 mg/kg was obtained by the adsorbent dose of 30 and 240g respectively. A packed column with same ground clay pot treated 6 liters of tap water containing 10 ppm fluoride to below 1.5 ppm, whereas 20 liters of 10 ppm water showed removal efficiency of 25 mg/Kg at saturation point [29].

Karthikeyan et al. used montmorillonite clay for removal of fluoride from water at neutral pH. Adsorption increased with time and reached an optimum level at 50 min. The particle size of 75 micron gave the maximum fluoride removal of 82%. The optimum pH for maximum fluoride removal was 2.0. The adsorption results were best fitted with Langmuir isotherm than Freundlich isotherm model. The Langmuir adsorption capacity was ranging from 1.485 to 1.910 mg/g at temperature range of 30 to 60°C. The thermodynamic study revealed that the adsorption reaction was spontaneous and endothermic. The adsorption process followed particle diffusion model [30].

Meenakshiet al. used raw kaolinite (RK) and micronized kaolinite (MK) clay by mechanochemical activation for defluoridation of water. The optimum pH for maximum removal of fluoride was observed to be 3.0 and defluoridation capacity of RK and MK was 0.120 mg/g and 0.134 mg/g respectively. The equilibrium was reached within 30 minutes for both materials. The experimental data of MK fitted well with Langmuir isotherm than Freundlich isotherm model. The Langmuir adsorption capacity of MK at 303K, 313K and 323K temperature was 0.609, 0.714 and 0.782 mg/g respectively. The adsorption process by MK followed the pseudo order besides intraparticle diffusion models. The adsorption reaction of MK was endothermic and spontaneous process [31].

Maiti et al. used acid treated raw laterite for defluoridation of water. The optimum pH for maximum fluoride removal was 5.0. The presence of bicarbonate and phosphate ions highly affected fluoride removal capacity. The experimental data comfortable well with Langmuir and Freundlich isotherm models. The maximum Langmuir adsorption capacity of adsorbent was found to be 36.3, 37.9 and 39.10 mg/g at 288, 305 and 315K temperature. Desorption of 96% was achieved at pH 12.0 [32].

Ma et al. used granular acid-treated bentonite (GHB) in batch and column mode for defluoridation of water. The optimum pH was 4.95 and the equilibrium of adsorption was reached within 40 min. The kinetic data followed the pseudo-second order equation. The experimental data fitted well with Freundlich isotherm than Langmuir isotherm model and adsorption capacity of adsorbent was 0.094 mg/g. In column study, the breakthrough capacity and exhaustion capacity increased with the decrease in flow rate and the escalation of initial fluoride concentration. The height of the mass transfer zone increased and the empty bed contact time (EBCT) reduced with the rise of flow rate. The height of the mass transfer zone increased with the rise of initial fluoride concentration. The experimental results were well fitted with Thomas model. Exhausted GHB was renewed by alkali/alum treatment. The total sorption capacity of GHB increased after regeneration and activation [33].

Kim et al. used pyrophyllite clay for defluoridation of water. This clay mainly consists of Si (74.03%) and Al (21.20%). The maximum adsorbent capacity of pyrophyllite clay was 0.737 mg/g with particle size less than 0.15mm. The equilibrium condition occurred in around 24 hours. The adsorption reaction was endothermic in nature. The fluoride was not sensitive to the pH range of 4 to 6. The clay calcined at 400°C gave 21% higher fluoride removal capacity compared to uncalcined ones [34].

Gogoi and Baruah investigated the defluoridation potential of acid activated kaolinite and raw kaolinite clay for defluoridation of water. The maximum adsorption of fluoride was obtained at pH of 4.0 with clay of 300 mesh size. The Langmuir maximum adsorption capacity of the acid activated clay for fluoride ranged between 0.0450 to 0.557 mg/g at temperature range of 25 to 30°C [56].

Treatment of water and wastewater containing fluoride ions requires a suitable and effective method. Membrane filtration, precipitation, nanofiltration, ion-exchange, electro coagulation, flotation, reverse osmosis and adsorption have been used for fluoride removal. Most of these methods have high operational and maintenance cost, low fluoride removal capacities, lack of selectivity for fluoride, undesirable effects on water quality, generation of large volumes of sludge and complicated procedures involved in the treatment.

Among these methods, adsorption is the most effective and widely used method because it is universal, has a low maintenance cost, and is applicable for the removal of fluoride even at low concentrations.



### 2.3.1 Adsorption method

There is a natural tendency for components of a liquid or a gas to collect often as a monolayer but sometimes as a multilayer at the surface of a solid material. This phenomenon is called adsorption [35].

In recent years, considerable attention has been focused on the study of fluoride removal using natural, synthetic and biomass materials. Here are some of the commercial adsorbents used in the adsorption and ion exchange method. Activated Alumina (AA), Activated bauxite (Hydrate of Al (OH)<sub>3</sub>), Zeolite (Na<sub>2</sub>Al<sub>2</sub>O<sub>3</sub>·nSiO<sub>3</sub>·XH<sub>2</sub>O), Activated carbon, Charcoal. Among the most frequently encountered commercial adsorbents are reviewed as follows.

Activated Alumina (AA): -Alumina (Al<sub>2</sub>O<sub>3</sub>) is practically insoluble in water. Its solubility in acid and alkali depends upon previous heat treatment, strong reagents do not easily attack it, and Alumina needs to be activated for the defluoridation process. There are different grades of activated alumina. The suitability of the grade for defluoridation depends upon the porosity and surface area of the alumina. Other considerations, which are also of importance, include the life of the activated alumina for defluoridation purpose [36].

The defluoridation capacity of activated alumina is independent of temperature. The adsorption of activated alumina obeyed Langmuir's adsorption isotherm indicating that the force of adsorption is governed by chemisorptions. However, fluoride removal by AA may also take place with decreasing pH and the extent of chemisorptions increase at a much higher rate. AA also adsorbs bicarbonate ions. Thus, the defluoridation capacity of AA decreases at increased concentration of bicarbonate. But chloride and sulphate ions have no effect on fluoride removal capacity. AA can be regenerated by 2% hydrochloric acid, 2% sodium hydroxide and 1% sulfuric acid. Fluoride removal efficiency is typically above 95%. A disadvantage of this process is that the regeneration steps result in an aqueous solution containing fluoride. On the other hand, if the spent alumina is discarded, the cost of the defluoridation increases. Apart from that, spent alumina may leach out fluoride ions when it is in contact with alkali [37].

Bone char. -Ms. Nutthamon Fangsrekam described the process of Defluoridation by bone char as the ion exchange and adsorption between fluoride in the solution and carbonate of the bone char [29]. The efficacy of the plant depends upon temperature and pH of raw water; duration for which the bone char is in contact with raw water. The maximum amounts of fluoride adsorbed per gram of bone char surface at 25° and 45° C are about 21.1, 22.4, and 25.7 μmol respectively. The optimum time for the adsorption to reach saturation is 9 hours and optimum pH of fluoride solution is between 7.00 and 7.50. Particle size has trivial effect on the adsorption of fluoride. If Calcium is present in the raw water, it precipitates out the fluoride. It is a highly economic technique

with a defluoridation percentage of 62 to 69]. Further, the efficiency of the bone char method of water defluoridation can be improved by pre-treating the raw water with Brushite and Calcium hydroxide [30]. Bonechar as the active ingredient and was functioning since 1948 in Britton, USA. It caused significant reduction of dental fluorosis in the local communities. Disadvantages of this technique are the bone char harbors bacteria and hence unhygienic. 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 may invite cultural and religious objections [31].

Brick pieces column - The basic principle of functioning of Brick piece column is same as that of activated alumina. The soil used for brick manufacturing contains Aluminium oxide. During burning operation in the kiln, it gets activated and adsorbs excess fluoride when raw water is passed through. Replacement of filter media is required once in three months if fluoride content in raw water is 2.50 mg/l. In places where high alumina content soil is available, brickbat filter may be one of the options [32].

Mud pot: -The raw pots are subjected to heat treatment as in the case of brick production. Hence the mud pot also will act as an adsorbent media. As per treatability results a marginal reduction in water fluoride level from 1.8 ppm to 1.5 and 1.4 ppm at the end of 2 days and 4 days respectively, which is practically not significant. The water pH was raised from 7.7 to 8.11 and 8.14 the end of 2 days and 4 days respectively, which is beyond the acceptable limits of alkalinity. The fluoride removal capacity will vary with respect to the alumina content present in the soils used for pot production, which is beyond the control of manufacturer. So, in a practical sense the use of mud pot for defluoridation is not promising. However, people can be advised to use mud pots to store water that is treated by other techniques, which results in partial defluoridation. Major advantages of mud pots are they are economic and readily acceptable for the rural communities [33].

Natural adsorbents - Many natural adsorbents from various trees were tried as defluoridation agents. Seeds of the Drumstick tree, roots of Vetiver and Tamarind seeds were few among them. The seeds of the drumstick tree (*Moringa oleifera*) adsorb fluoride from water. Drumstick seeds act as a coagulant. They have long been a traditional method for purification of turbid water in both India and Africa. Researchers at ...M. S. Swaminathan Research Foundation (MSSRF) had shown drumstick seeds to have remarkable defluoridation efficiency, which was higher than that of activated alumina. But, these results were not reproducible. The roots of Vetiver (*Cenchrus*

zizanoide) are another product that has traditionally been used for water purification. The roots were effective at defluoridation and could remove as much as 70% of the fluoride from a sample. The defluoridation efficiency was higher than activated alumina, and the price was comparable. But, the quantity of grass needed is so high that, a family would need to rise acres of Vetiver grass every year in order to provide enough material for defluoridation [36]. Tamarind seeds were successfully used for defluoridation by sorption. Since maximum defluoridation is achieved at an optimum pH of 7, post defluoridation pH adjustment is not required. Tamarind seeds, which are otherwise considered a kitchen waste, can be obtained at much cheaper price [34].

## 2.4 Adsorption characteristics of Clay

The term ,clay' is applied both to materials having a particle size of less than 2 micrometers and to the family of minerals that has similar chemical compositions and common crystal structural characteristics. The characteristics common to all clay minerals derive from their chemical composition, layered structure, and size. Most clay has the ability to soak up ions (electrically charged atoms and molecules) from a solution and release them when conditions change [38].

Clays are potentially good absorbers of anions since they contain crystalline minerals such as kaolinite, smectite and amorphous minerals such as allophane and other metal oxides and hydroxides which could adsorb anions such as [39].

The structure of the clay plays a very important role in determining the charge on the clay surface and type of exchange that can occur with ions in solution. In general, the more negative the surface charge, the better the sorption will be for positively charged metal ions. The pH parameter plays a dominant role in determining the adsorption capacity as pH modifies the charges on the clay mineral. Charges are generally positive under acid conditions and negative in an alkaline environment. An acid pH will favour adsorption of negatively charged ions while alkaline conditions will enhance adsorption of positively charged ions [40].

### 2.4.1 Kaolinite clay

Kaolinite group includes kaolinite, dickite, nacrite, and halloysite; formed by the decomposition of orthoclase feldspar (e.g. in granite). Dickite and nacrite are rather rare and usually are found mixed with kaolinite in deposits of hydrothermal origin [8]. The structure of the kaolinite group composed of units of one layer of silica tetrahedrons and one layer of alumina octahedrons. Kaolinite is called as 1:1 clay mineral due to the stacking of one layer of each of the two basic sheets

The schematic diagram of Kaolinite structure is given in Fig. 2.2. Kaolinite, dickite and nacrite possess similar chemical composition, and this kaolinite group has the molecular formula

$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ . The chemical composition of the kaolinite group majority is  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ . The differences in the kaolin minerals are the manner in which the unit layers are stacked above each other with the thickness of the unit layer around 7.13 [41].

Kaolinite, along with other clays, belongs to the phyllosilicate subclass of materials. In this subclass, rings of silica tetrahedrons are linked by shared oxygen to other rings in a two dimensional plane that produces a sheet like structure, this sheet is then attached to another structure made from aluminium octahedral rings, as shown in Figure 2.2 [42].

Figure 2.2: Sheet structure of kaolinite clay

Although hundreds of chemical analyses of kaolinite have been made, there is still little known for certain about the exact composition of most, if not all of the samples. The idealized composition by mass for a kaolinite ( $\text{Al}_2(\text{Si}_4\text{O}_{10})(\text{OH})_8$ ), is the following: SiO<sub>2</sub>: 46.54 wt.%, Al<sub>2</sub>O<sub>3</sub>: 39.5 wt.% and H<sub>2</sub>O: 13.96 wt.%. However this is seldom if ever, found in nature. A basic kaolinite particle is composed of a silica layer bonded to aluminium oxide/hydroxide layers. The aluminium layer of kaolinite is often termed the gibbsite layer, as the layer has the same structure as gibbsite, an aluminium oxide mineral. Aluminium atoms are octahedral coordinated with oxygen atoms and hydroxyl groups, as can be seen in Figure 2.3. The alumina molecules are then octahedral interconnected to form a two dimensional layer [42].

Figure 2.3: Octahedral alumina group

Only two thirds of the octahedral positions in the gibbsite layer of kaolinite are filled by aluminium. The atoms are thought to be arranged so that two aluminiums are separated by a hydroxyl group above and below, thus making a hexagonal distribution in a single plane in the centre of the octahedral sheet. The reduction in the amount of aluminium present in the structure allows the

electrical neutrality of the particle to be maintained [42]. The structure of kaolinite results from the combination of the silica and alumina layers into a hexagonal sheet. In the layer common to the octahedral and tetrahedral groups, the silicon and aluminum share two thirds of the atoms, and they become single oxygen instead of hydroxyl groups, the other third remaining as hydroxyl groups, as can be seen in Figure 2.4.

(a) (b)

Figure 2.4 Kaolinite clay structure (a) Before and (b) After calcined

## 2.5 Principles of adsorption

Adsorption is a process that occurs when a gas or liquid or solute (called adsorbate) adheres on the surface of a solid or more rarely a liquid (adsorbent), forming a molecular or atomic film (adsorbate). Adsorbent solids are usually used in granular form, varying in size from roughly 2 mm in diameter to as small as 0.05 mm. The solids possess certain engineering properties depending upon the application to which they are put. If they are used in a fixed bed through which a fluid is to flow, for example, they must not offer too great a resistance to flow nor must they easily be carried away by the flowing stream. Adsorption is a very general phenomenon, and even common solids will adsorb gases and vapors at least to a certain extent. But only certain solids exhibit sufficient specificity and adsorptive capacity to make them useful industrial adsorbents [43]. Some substances adsorb fluoride ion by their surface, and it can exchange its negative ions such as sulfate for fluoride ions. This process depends on suitable conditions (pH, temperature, flow rate, grain size, etc.) [36]. The most common criteria for selection of suitable adsorbents are: cost of the medium and running costs, ease of operation, adsorption capacity, potential for reuse, number of useful cycles and the possibility of regeneration.

The extent of adsorption is proportional to specific area. Specific area cannot be that portion of the total area that is available for adsorption. Surface area is related to the grain size of the adsorbent. The choice of particle size is made by considering two sets of factors: 1) ease of mass transfer from the fluid to the surface, creation of as much interfacial surface area as possible and reduction of antiparticle diffusion path length, all of which favor smaller particles; and (2) maintenance of a low pressure drop, which favors larger particles [35]. Because hydrogen and hydroxide ions are adsorbed

quite strongly, the adsorption of other ions is influenced by the pH of the solution. In general, adsorption of typical pollutant from water is increased with decreasing pH [44]. The pH of the system is a very important parameter and determines the degree of protonation of the exchange sites and the degree of protonation of. The pH will therefore determine the specific charge of an exchange site and therefore ultimately also the adsorption tendency of the substrate [38].

The physicochemical nature of the adsorbent can have profound effects on both rate and capacity for adsorption. Whereas Solubility, molecular sizes, and charge (Ionic species) are considered in the case of adsorbate [45].

## 2.6 Adsorption Equilibrium and the Adsorption Isotherm

Adsorption is usually described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid). There are three types of isothermal adsorption are used to explain the adsorption process, i.e. Langmuir, Freundlich and Brunauer, Emmet and Teller isotherms.

### 2.6.1 Langmuir Isotherm

One of the simplest and most widely used isotherms is the Langmuir isotherm that was originally derived from adsorption kinetics by equating the rates of adsorption and desorption onto a flat surface. The Langmuir isotherm equation assumes that fixed individual sites exist on the surface of the adsorbent, each of these sites being capable of adsorbing one molecule, resulting in a layer one molecule thick over the entire active surface. The Langmuir model also assumes that the surface is homogeneous; the energy of adsorption is equal for all adsorption sites, all sites adsorb the adsorbate equally. Equilibrium is reached when the rate of adsorption of molecules onto the surface is the same as the rate of desorption of molecules from the surface. The rate at which adsorption proceeds is proportional to the driving force, which is difference between the amount adsorbed at a particular concentration and the amount that can be adsorbed at that concentration. At the equilibrium concentration this difference is zero [46].

Langmuir adsorption is defined in the following equation:

$$q = \frac{q_m b C_e}{1 + b C_e} \quad (2.1)$$

Where  $C_e$  (mg/L) equilibrium concentration of adsorbate in solution after adsorption,  $q_e$  (mg/g) the amount adsorbed at equilibrium,  $a$  (mg/g) is a temperature independent equilibrium constant related to maximum adsorption capacity (capacity parameter),  $b$  (L/mg) temperature dependent equilibrium constant related to energy of adsorption (affinity parameter). The adsorption affinity of the adsorbent for adsorbate can be assessed by comparing the constant,  $b$ . A high  $b$  value indicates that the

adsorbent has a high affinity for adsorbate and vice versa. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, RL, which describes the type of isotherm and is defined by following equation.

$$RL = \frac{K_f C_0}{1 + K_f C_0} \quad 2.2$$

Where b (l/mg) is the Langmuir constant and C<sub>0</sub> (mg/L) the initial concentration of solute. RL indicates the type of isotherm as follows:

Table 2.1 Equilibrium parameter, RL [43]

Value	Type of Isotherm
RL > 1	Unfavorable
RL = 1	Linear
0 < RL < 1	Favorable
RL = 0	Irreversible

### 2.6.2 Freundlich Isotherm

The Freundlich isotherm equation assumes that the adsorbent has a heterogeneous surface composed of adsorption sites with different adsorption potentials. This equation assumes that each class of adsorption site adsorbs molecules, as in the Langmuir equation. The Freundlich isotherm equation is the most widely used equation in adsorption from aqueous solution. In other words, for Freundlich isotherms to be valid, the adsorption must be purely a physical process with no change in the configuration of the molecules in the adsorbed state [47]. According to the Freundlich equation, the amount adsorbed increases infinitely with increasing concentration or pressure. This equation is, therefore, unsatisfactory for high coverage. At low concentration, it does not reduce to the Langmuir isotherm [47].

Freundlich proposed the equation:

$$q_e = k_f C_e^{1/n} \quad 2.3$$

Where C<sub>e</sub> (mg/L) is the equilibrium concentration, q<sub>e</sub> (mg/g) the amount adsorbed at equilibrium, and k<sub>f</sub> and n is the constants that are related to the adsorption capacity and the adsorption intensity, respectively. If 1/n is less than 1, it indicates favorable adsorption. If 1/n is much lower than 1, it indicates superior activity [48]. The Freundlich equation is basically empirical but is often useful as a means for data description. Data are usually fitted to the logarithmic form of equation. The

linear form of Freundlich equation is presented below. Values of  $k_f$  and  $n$  may be calculated by plotting  $\log q_e$  versus  $\log C$ . The slope is equal to  $1/n$  and the intercept is equal to  $\log k_f$

$$\log q_e = \log k_f + \frac{1}{n} \log C \quad (2.4)$$

### 2.6.3 Brunauer, Emmett, and Teller Isotherm

In 1938, Brunauer, Emmett, and Teller showed how to extend Langmuir's approach to multilayer adsorption, and their equation has come to be known as BET equation. The basic assumptions are that each molecule in the first adsorbed layer is considered to provide one site for the second and subsequent layers, that the molecules in the second and subsequent layers, which are in contact with other sorbate molecules rather than with the surface of adsorbent are considered to behave essentially as the saturated liquid, while the equilibrium constant for the first layer of molecules in contact with the surface of the adsorbent is different [43].

The BET equation assumes that the energy required to adsorb the first particle layer is adequate to hold the monolayer in place. The adsorption process can be described as adsorbed molecules on the surface sites and attachment of molecules to sites where occupied by adsorbed molecules. The resulting equation for the BET equilibrium isotherm is:

$$\frac{1}{q_e} = \frac{1}{Q_0} \left[ \frac{1}{C} + B \right] \quad (2.5)$$

whereas  $C$  is saturation concentration of the solution,  $Q_0$  is measured concentration of solution at equilibrium,  $Q_0$  number of moles of solute adsorbed per unit weight of adsorbent in forming complete monolayer on the surface,  $q_e$  number of moles of solute adsorbed per unit weight of adsorbent at concentration  $C$ , and  $B$  is the constant expressing the energy of the interaction with the surface.



### 3. MATERIALS AND METHODS

#### 3.1 Materials and Chemicals

The kaolinite clay which was collected from Gasay, Amhara region indicated in figure 3.1, was used for preparation of activated kaolinite clay powder for defluorination of groundwater. The raw clay was crushed using jaw crusher (BB51) and then sieved to <0.075, 0.075-0.15 and 0.15-0.30 mm diameter to determine the particle size. The kaolinite clay was weighed using digital balance (sartorius with 0.01mg sensitivity) and burnt at temperature of 800°C for 2 hours using the muffle furnace (L030H2CN) to remove the impurities and volatile matters from the clay. The clay was then activated by sulphuric acid ( $H_2SO_4$ ). The activated clay was washed by analytical grade sodium hydroxide (NaOH) and distilled water to neutralize and remove the acid from clay through vacuum filter. The different samples were dried at 105°C for 24 hrs using oven dryer (PH-030A). The surface area and functional group of activated clay was measured by BET (NOVA4000e) and FTIR. Liquid nitrogen was used as the adsorbate during determination of surface area (BET).

Fluoridated water was fetched from Aseyta specifically Afanbo ground water, which is found in Afar region and fluoride concentration before experiment was measured using photometer (ELE international) and the result is 4.7mg/l.

Figure 3.1 Kaolinite clay found in Gasay, Amhara Region

The fluorinated water then treated with activated clay and raw clay by a batch adsorption technique with the help of Hot plate (IKACMAGHS4) magnetic stirrer at speed of 300 rpm. The pH of the solution during experiment was controlled using pH meter (ELE international). Crucible was used for containing sample during burning of kaolinite clay powder, desiccator, magnetic stirrer, glass stopper and Erlenmeyer flasks are used for during analysis.

## 3.2 Characterization of Activated Kaolinite Clay

### 3.2.1 Analysis of Surface Area and Porosity of Adsorbent

Surface cleaning (degassing) was carried out using surface area and pore size analyzer which is called Branauer Emmet and Teller(model: NOVA 4000e).The sample of both raw and activated kaolinite clay adsorbent were added separately in a glass cell and heated under a vacuum for 24hr at 300°C. After degassing the glass cell, the samples were transferred to Dewar flask which contain liquid nitrogen and set up with computer to be analyzed. Then surface area, pore size and volume were analyzed by software, which is connected with instruments surface area and pore size analyzer BET (NOVA 4000e). Multilayer adsorption of nitrogen was measured as a function of relative pressure. It gives the idea of physical adsorption of gas molecule on the solid surface using absorption of N<sub>2</sub> gas on the solid materials. BET (surface area, pore size and volume) for both samples were analyzed.

### 3.2.2 Fourier Transform Infrared Analysis of Adsorbent

The Fourier Transform Infrared spectra were recorded for qualitative characterization of surface functional groups. Functional groups present in the activated and raw kaolinite clay were confirmed before and after adsorption by Fourier Transform Infrared (FTIR) spectroscopy using KBr pellet technique on JASCO model 4100. This analysis was conducted in AAU (Addis Ababa University), Department of Chemistry. Approximately 1mg of sample was mixed with 100mg of KBr and then grounded and pressed to prepare the pellets. The result obtained showing the wave lengths of the different functional groups in the sample which were identified by comparing these values with those in the library. FTIR spectra were obtained in the range of 400 to 4000 cm<sup>-1</sup> for both samples.

### 3.3.3. X-Ray Diffraction

XRD analysis was conducted in Material engineering department, ASTU (Adama Science and Technology University) Adama, Ethiopia. X-ray 7000 diffractometer SHIMADZU Corporation (Kyoto, Japan) were used to study the phase nature of raw and activated kaolinite clay. The kaolinite clay samples were fed into X-Ray Diffraction (XRD) analysis. Prior to analysis, the clay samples were ground to a powder form by simple pounding using a mortar and pestle due to its brittle nature. The ground samples were analyzed by Cu radiation with a scanning rate of 2° per minutes and scan range 10.000- 80.000 and using an acceleration voltage of 40 kV and current of 30 mA. An X-Ray Diffractometer is a mechanical device for obtaining x-ray intensities as a function of the angle between the incident and the diffracted beams. The resulting phase diagram called a diffractogram. The phase concentration is indicated by the peak height, with higher peak

representing higher concentration.

### 3.4 Determination of Adsorption Capacities

The batch experiments were conducted by mixing 100 mL of tap water collected from Afar region specifically Aseyta ground water having a concentration of 4.7 mg/L with raw and activated kaolinite clay for 30, 60, 90, 120 and 150 min in 250 mL glass bottles at 25, 40, 50, 60 and 70°C. After different mixing times, the mixtures of solution and adsorbent were agitated by using magnetic stirrer on 25, 40, 50, 60 and 70°C hot plate at 300 rpm. In this procedure a 100 mL of solution was added to a 250 mL glass bottle and the F<sup>-</sup> concentration measured after each time.

Preliminary tests were conducted in order to investigate the fluoride adsorption capacities of clay samples collected. From this study, clay samples with better adsorption capacity were selected.

The fluoride adsorption capacity and efficiency from the residual fluoride concentration was calculated by the following equations [57].

$$\% = \frac{C_0 - C_t}{C_0} \times 100 \quad (3.1)$$

$$q_e = \frac{(C_0 - C_t) \times v}{m} \quad (3.2)$$

Where  $C_0$  = initial fluoride concentration (mg/l)

$C_t$  = residual fluoride concentration at time (mg/l)

$m$  = mass of adsorbent (g)

$v$  = volume of the solution used in the batch (l)

$q_e$  = adsorption capacity (mg of fluoride removed/g of adsorbent)

Raw and activated kaolinite clay samples were selected in order to investigate the effect of different operating parameters on the fluoride adsorption potential of these clays. The investigation determines the effect of temperature, pH, contact time, adsorption dosage and particle size in order to determine whether how significant change in adsorption capacity can be induced by these factors.

### 3.5. Parameters affecting fluoride adsorption capacity

#### 3.5.1 Temperature

The effect of temperature on defluoridation was analyzed at 25, 40, 50, 60 and 70 °C and the adsorption capacities were determined and finally; the raw and activated kaolinite clay samples with the fluoride water solution were filtered and measured for each ranges

#### 3.5.2 PH

The effect of pH was analyzed for both raw and activated kaolinite clay samples. Initial pH of raw

water was prepared as 2, 4, 6 and 8. The desired pH was adjusted using 0.1M of NaOH and 2M H<sub>2</sub>SO<sub>4</sub> solution. Residual F<sup>-</sup> concentrations were determined after each contact time.

### 3.5.3 Clay Particle Size

To investigate the effect of particle size of the clays three different ranges of particle size (i.e. < 0.075, 0.075-0.15 and 0.15-0.3 mm diameter) mesh sizes were analyzed. Both raw and activated clay samples were considered. The same batch adsorption procedure was used.

### 3.5.4 Contact time on adsorption kinetics

One gram of the produced adsorbent samples were taken and shaken with 100 ml of fluoride rich water. The bottles were shaken at 30 minute intervals of 30 to 150 min at room temperature using magnetic stirrer at 100 rpm. At the end of each contact period the mixture was filtered using filter paper and the filtrate was stored in sample bottles in a refrigerator prior to analysis. The final concentration of the fluoride ion in the filtrates was measured by photometer. Adsorption kinetics and isotherms for each size of adsorption experiment was then analyzed.

### 3.5.5 Adsorbent Dosage

The substrate concentration in the range of 0.5 g-2.5g was used to analyze the effect. From the range with 0.5 interval substrate is prepared and then mixed with fluoridated water of 100 ml in conical flask for each. The conical flask was shaken for each 30, 60, 90, 120 and 150 min at each temperature in a magnetic stirrer at 100 rpm. Then the substrates were removed from the mixture by filtration and the concentration of the residual ions in the solution was determined. The amount of fluoride ions adsorbed from solution was determined by difference between initial and final concentration of fluoride.

## 3.6 Adsorption Isotherm Studies for Kaolinite Clay

### 3.6.1 Adsorption Isotherm Model

An adsorption isotherm is a curve relating the equilibrium concentration of a solute on the surface of an adsorbent,  $q_e$ , to the concentration of the solute in the liquid,  $C_e$ , with which it is in contact. The adsorption isotherm is also an equation relating the amount of solute adsorbed onto the solid and the equilibrium concentration of the solute in solution at a given temperature.

The relationship between  $q_e$  and  $C_e$  can normally be fitted to one or more equilibrium isotherm models. There are several isotherm equations available for analyzing experimental adsorption

equilibrium parameters. The most commonly used isotherms for the application of activated clay in water and wastewater treatment are the Freundlich and Langmuir isotherms [49, 50].

### 3.6.2 Langmuir Isotherm Model

The Langmuir isotherm model equation 3.3 was originally developed to describe and quantify adsorption on a set of distinct localized adsorption sites, and has been used to describe chemical adsorption. This model is based upon the following main assumptions [51]:

- Each active site interacts with only one adsorbate molecule.
- Adsorbate molecules are adsorbed on well-defined localized sites and the saturation coverage corresponds to complete occupancy of these sites.
- The adsorption sites are all energetically equivalent (homogeneous), and there is no interaction between adjacent adsorbed molecules.

Derivation of Langmuir Isotherm Model Equation: At equilibrium, the number of molecules being adsorbed will be equal to the number of molecules leaving the adsorbed state i.e.

- Rate of adsorption  $r_a$  is directly proportional to concentration in solution and available area for adsorption i.e.  $r_a = k_a C (A - A_{occupied}) = k_a C (A - K q) = C e^{-K(q - q_{max})}$
- Similarly, the rate of desorption  $r_d$  is directly proportional to number of molecules already adsorbed i.e.  $r_d = A_{occupied} = K q$

At equilibrium, rate of adsorption is equal to rate of desorption i.e.  $r_a = r_d$ , and solving for  $q$  gives:

$$q = \frac{A K C}{1 + K C} \quad (3.3)$$

Where,  $q$  ( $\text{mg g}^{-1}$ ) and  $k$  ( $\text{L mg}^{-1}$ ) are the Langmuir constants related to the capacity of adsorbent and energy of adsorption, respectively. This model is the most widely applied adsorption isotherm and has produced good agreement with a variety of experimental data [52].

### 3.6.3 Freundlich Isotherm Model

The Freundlich isotherm model equation is an empirical relationship, which describes the adsorption of the solutes from a liquid to solid surface. The Freundlich model equation 3.4 describes adsorption in terms of adsorbate concentration [53].

$$q = K_f C^{1/n} \quad (3.4)$$

Where,  $K_f$  and  $1/n$  are freundlich isotherm constants related to adsorption capacity and adsorption intensity respectively.

### 3.7 Experimental Design and Data Analysis

Full factorial design experiments with three factors corresponding to the following levels were carried out. The factors are temperatures (25, 40, 50, 60 & 70°C), PH (2, 4, 6, & 8) and particle size (<0.075, 0.075-0.15 & 0.15-0.3). The effects of these factors on fluoride removal were performed by keeping one factor (particle size) same value and varying the other's value (temperature and pH value) for each particle size. After finding of relatively best fluoride removal temperature and pH value, adsorbent dosage and contact time were performed by varying particle size. The data were analyzed using design expert software, entered into Microsoft excel worksheet and then summarized as well as analyzed.

## 4. RESULTS AND DISCUSSION

### 4.1 Characterization of Kaolinite Clay

#### 4.1.1 Fourier Transform Infrared

The major functional groups present in kaolinite peaks were revealed by the FTIR analysis. Four samples were analyzed and these are raw kaolinite (before and after adsorption) and activated kaolinite (before and after adsorption). Both samples showed same major peaks but their transmittance percentage intensity showed a wide range of difference. The major peaks are 1066, 593, 3481, 2964, 447, and 1659  $\text{cm}^{-1}$ . The band position is compared with the Gadsden (1975), absorption bands observed at 3481  $\text{cm}^{-1}$  and 1659  $\text{cm}^{-1}$  could be corresponding to the OH vibration mode of the hydroxyl molecule. The bands between 3450 and 3670  $\text{cm}^{-1}$  are attributed to the OH stretching mode. In the 500  $\text{cm}^{-1}$  and 1000  $\text{cm}^{-1}$  region, main functional groups were Si and Al-OH. The region at 780-798  $\text{cm}^{-1}$  is due to Si-O-Si inter tetrahedral bridging bonds in Si and OH deformation band. When we compare the samples, the activated kaolinite showed lowest pick due to the replacement of the fluoride ion on the active surface of the adsorbent. The decrease in the intensity of transmittance in fluoride activated clay after adsorption at 3694 and 3620  $\text{cm}^{-1}$  indicates the exchange of OH from a surface [54]. Similar observations have been made by Boehm et al.

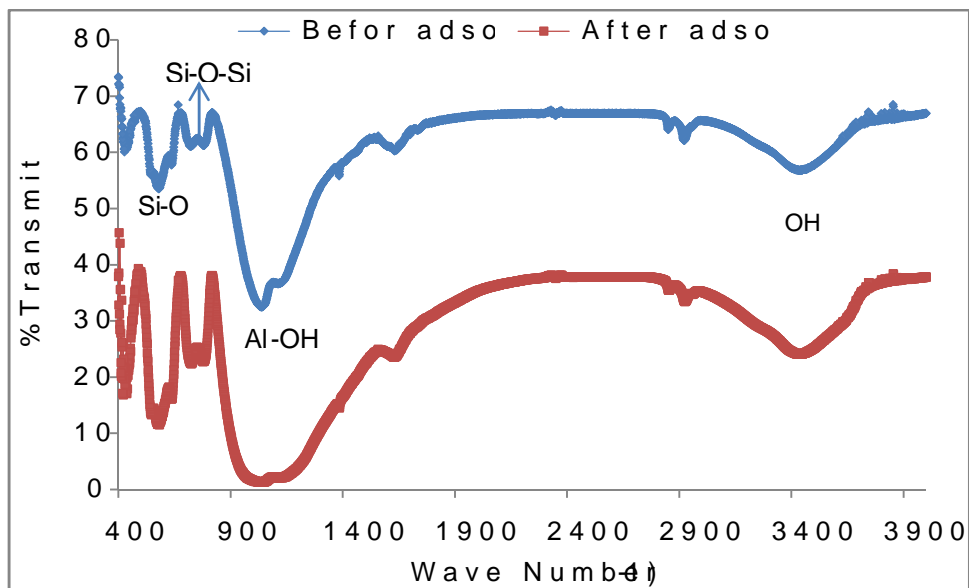


Figure 4.1 FTIR result of activated clay before and after adsorption of fluoride

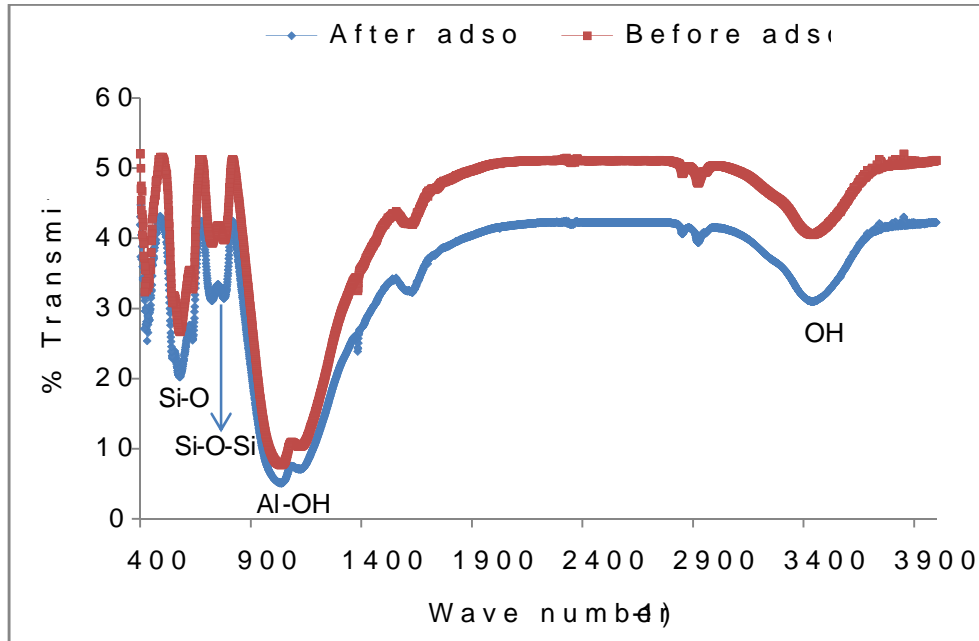


Figure 4.2 FTIR result of raw clay before and after adsorption of fluoride

#### 4.1.2 Brunauer, Emmett, and Teller

The BET was performed on activated and raw kaolinite clays to evaluate the surface area and pore volume. As the BET results are presented in table 4.2, smaller particle size had the largest surface area and activation of clay further increases the surface area of the adsorbent via removing impurities or impurity from the surface of the adsorbent.

Table 4.1 Summary of BET surface area results of different particle size of adsorbents

Particle size (mm)	Surface area of AC (m <sup>2</sup> /g)	Cumulative pore volume of AC (cm <sup>3</sup> /g)	Surface area of RC (m <sup>2</sup> /g)	Cumulative pore volume of RC (cm <sup>3</sup> /g)	Surface area of AC from literature (m <sup>2</sup> /g)	Surface area of AC from literature (m <sup>2</sup> /g) [S. Meenakshi, et al.]
<0.075	10.598	4.72*10 <sup>-3</sup>	5.258	-	9.121	32.43
0.075• 0.15	7.489	3.43*10 <sup>-3</sup>	3.312	1.75*10 <sup>-3</sup>	-	-
0.15• 0.30	7.396	3.56*10 <sup>-3</sup>	2.504	-	-	-



### 4.1.3 X-Ray Diffraction

X-ray diffraction analysis was used to determine morphology and the degree of crystallinity of raw kaolinite clay samples. A 2 theta range of  $0^{\circ}$  to  $70^{\circ}$  is usually adequate to cover the most important regions of the XRD pattern, and each peak represents at least one diffraction ray. The relative intensities of the peaks are related to the level of sample crystallization and are determined by the type and position of all atoms in the unit cell. The widths of the peaks are related to the size of crystallite, i.e. they can give an indication of the crystalline quality of the sample.

Figure (4.3) clearly indicates the formation of raw kaolinite clay samples as the major peaks of identification on XRD pattern were located at  $2\theta = 14.085^{\circ}$ ,  $17.86^{\circ}$ , and  $32.15^{\circ}$ . The XRD pattern also indicates that the peak in the range of  $15-35^{\circ}$  which is an indication of degrees of crystalline. The small zigzag peak refers to presence of amorphous material, the highest XRD peak is observed at exactly  $17.86^{\circ}$  and other peaks are also very sharp. It is shown to be fully crystalline. Similar results on XRD patterns on raw kaolinite clay were reported by Diaz-Nava et al.

Figure 4 -3: XRD plot of raw kaolinite clay

## 4.2 Batch Fluoride Adsorption Parameter Effects

### 4.2.1 Temperature

The dependence of fluoride adsorption by kaolinite clays was studied over temperatures of 25, 40, 50, 60 and 70°C. The percentage of adsorption of fluoride ion at 1 hour was found to be 42.3, 50.2, 56.4, 55.5 and 52.6 for raw clay and 57.2, 61.27, 68.2, 67.02 and 63.5 for activated clay respectively. The plot of percent fluoride removal by the clays at the five different temperatures is given in figure 4.4. The increase in percentage of fluoride adsorption at higher temperature confirms the endothermic nature of the process because at higher temperature the interaction between fluoride ion and adsorbent increased with temperature. The first portion (25°C • 40°C) of the adsorption process corresponds to external surface adsorption or instantaneous adsorption stage. The second (40°C • 50°C) gradual linear portion follows the gradual adsorption stage and reaches a maximum adsorption stage in this stage (50°C) which represents the equilibrium stage. In this model, the clay mineral is treated as being surrounded by a boundary layer film of water molecules through which the fluoride ion must diffuse prior to adsorption on the clay surface. The second portion of figure 4.4 indicates predominantly intra-particle diffusion where the diffusive transport of fluoride occurs through the internal pores of adsorbent. The third position of the curve (50°C • 70°C) shows the decrease in the rate of diffusion reaching equilibrium. The observation about enhanced fluoride adsorption rate by the adsorbent with increase in temperature until it reaches equilibrium is in perfect agreement with earlier findings [55].

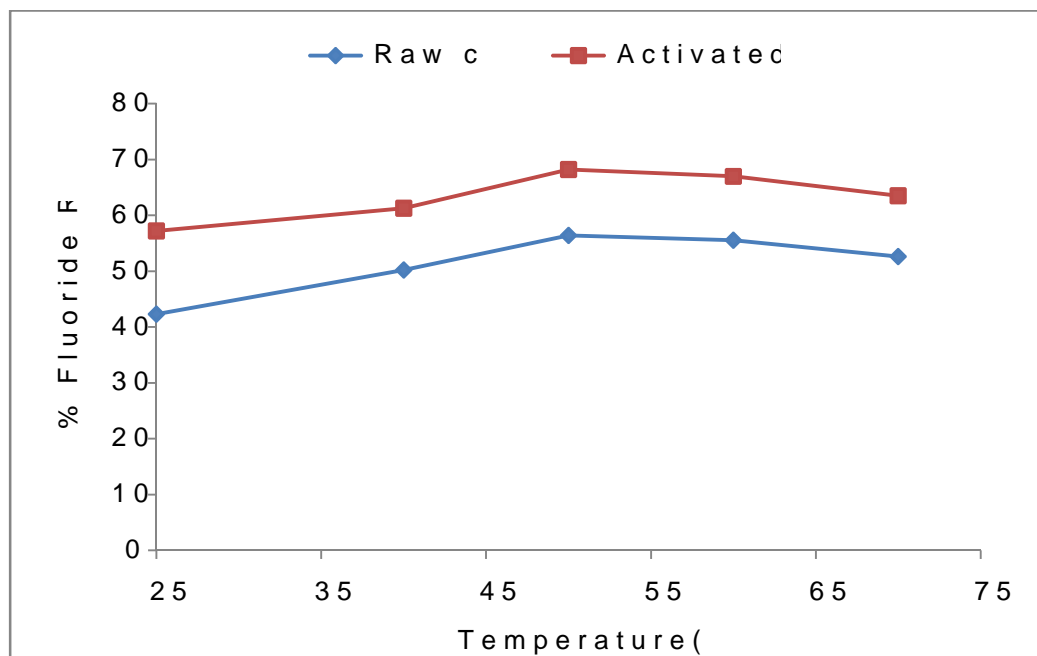


Figure 4. 4 Effects of Temperature on fluoride removal

#### 4.2.2 pH

The effect of pH on percent removal of fluoride on raw kaolinite clay and activated kaolinite clay adsorbent was studied at various pH values of 2, 4, 6, and 8 at temperatures of 25, 40, 50, 60 and 70°C and particle size of <0.075, 0.15, 0.3 mm and adsorbent dosage of 1 g (any assumption) for 1 hour. As it can be seen from figure 4.5 the curves have the same trend for both adsorbent that percent removal of fluoride increased from 45.9 to 56.4 and 57.2 to 68.2 at a pH value of 2 up to a pH value of 4 for raw kaolinite clay and activated kaolinite clay respectively. Similar trend also observed for both adsorbent as the percent fluoride removal decreased from 56.4 to 30.4 and 68.2 to 41.06 for raw kaolinite clay and activated kaolinite clay respectively as the solution pH was increased from 4 to 8. This is due to the fact that the clay contains  $\text{Al}(\text{OH})_3$  which act as anion on the active site of the adsorbent; increase in the pH value led to increase in the number of negatively charged sites (the hydroxyl ions  $\text{OH}^-$ ) on the adsorbent as a result the percent of fluoride removal decreased. This is probably due to the competition for adsorption sites between fluoride and hydroxyl ions at the clay surface. These results provide more support to previous findings that the adsorption of anions on clay minerals decreases as the pH of the solution increases [56]. The decrease in adsorption of fluoride with increase in pH has been explained on the basis of decrease of positive charge on the clay mineral [56]. At lower pH, the positively charged surface on adsorbent does not favor the sorption of anionic ( $\text{F}^-$ ) solution due to the electrostatic repulsion appears between positively charged particles of solution and adsorbent surface which leads to maximum attraction between fluoride and adsorbent active sites. Similar trend was observed by Karthikeyan et al. At all pH, the percent removal of fluoride on activated kaolinite clays greater than that on raw kaolinite clay. In both cases the optimum percent removal of fluoride for adsorbents was obtained at a pH value of 4.

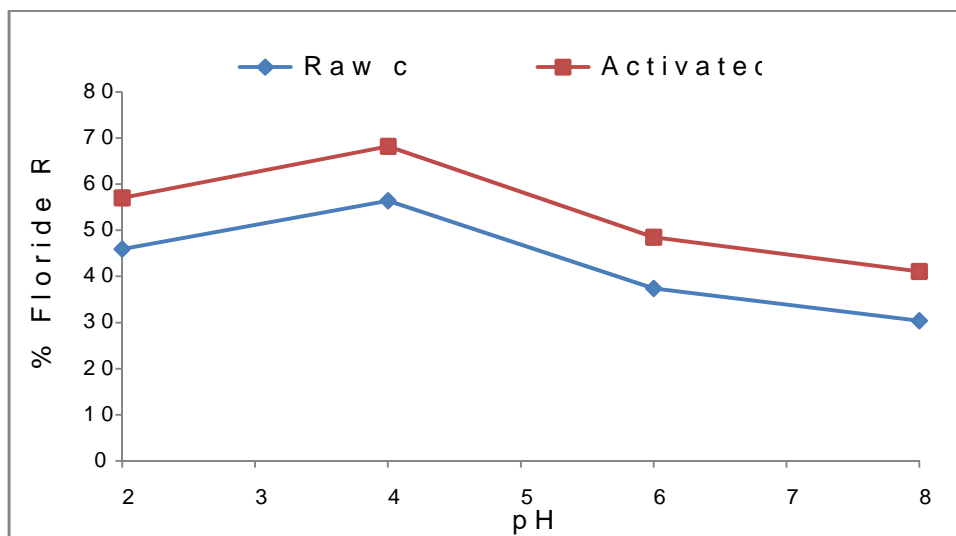


Figure 4.5 Effects of pH on fluoride removal

### 4.2.3 Clay particle size

The percentages of fluoride removal by the sample with different particle sizes were studied. The defluoridation experiments were conducted using raw and activated kaolinite clay with three different particle sizes of <math>0.075</math>, <math>0.075</math>, <math>0.15</math> and <math>0.15</math>-<math>0.30</math> mm diameter at temperature of 25, 40, 50 60 and 70°C, and pH value of 2, 4, 6 and 8 and adsorbent dosage of 1 gram for 1 hour. As seen in the figure 4.6, higher percentage (56.4 and 68.2) of adsorption by raw and activated kaolinite clay respectively with smaller particle size was observed. This is due to the availability of more specific surface area on the adsorbent surface [57]. The fluoride removal efficiency of the sample with 0.075 mm diameter registered higher efficiency due to larger surface area. Hence, the material with particle size of 0.075 mm diameter has been chosen for further experiments. From figure 4.6, at all particle size ranges, the percent removal of fluoride on activated kaolinite clay is greater than that on raw kaolinite clay because activation of the raw clay increases the porosity of adsorbent by removing the impurities like ferrous oxide, sodium, magnesium present in the adsorbent.

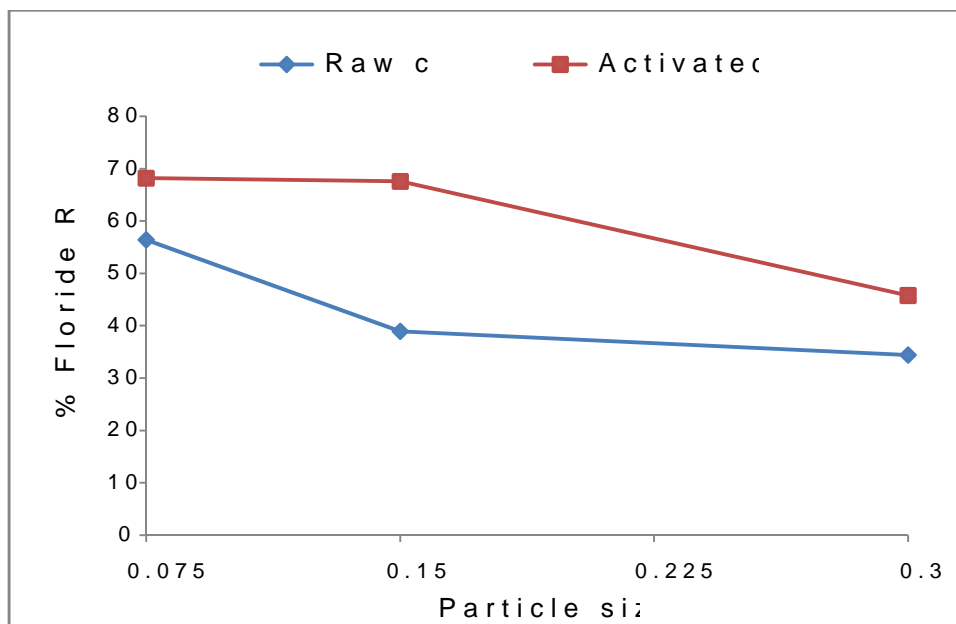


Figure 4. 6 Effects of particle size on fluoride removal

### 4.2.4 Contact time on fluoride removal

Figure 4.7 shows adsorption efficiency and contact time on the efficiency of the system at temperature of 50°C (best result from experiment at  $t=60$  min) and pH value of 4 (best result at  $t=60$ ) and adsorbent dosage of 1 gram for 1 hour. The experimental results on the contact time revealed that as the time increases, percent removal increases rapidly, but gradually approaches a constant value exhibiting

the attainment of equilibrium. The sorption reaction depicted in figure 4.7 indicates that it followed a pattern of the two phases. First phase was the rapid phase where the rate of removal was very rapid and this had occurred in initial 60 minutes. This may be due to instantaneous adsorption reaction in which fluoride ions were adsorbed rapidly on to the surface of the raw and activated kaolinite clay due to specific chemical interaction (or affinity) of adsorbent active site and fluoride ion. After 60 minutes, the rate of adsorptive uptake decreased due to lesser adsorption as a result of migration of fluoride ions from the film/boundary layer to enter pore/capillary surfaces and due to non availability of sorption sites. From the figure 4.7, similar trends were observed for contact time and sorption efficiency of raw and activated kaolinite clay. But percent removal of raw clay increased from 18.6 to 54.4 for the first 60 minutes while that of activated clay increased from 42 to 68.2. After 60 minutes there was no much decrease in percent removal of fluoride after 60 minutes for adsorbents, an equilibrium time of 60 minutes was taken and this was employed in subsequent experiments [58].

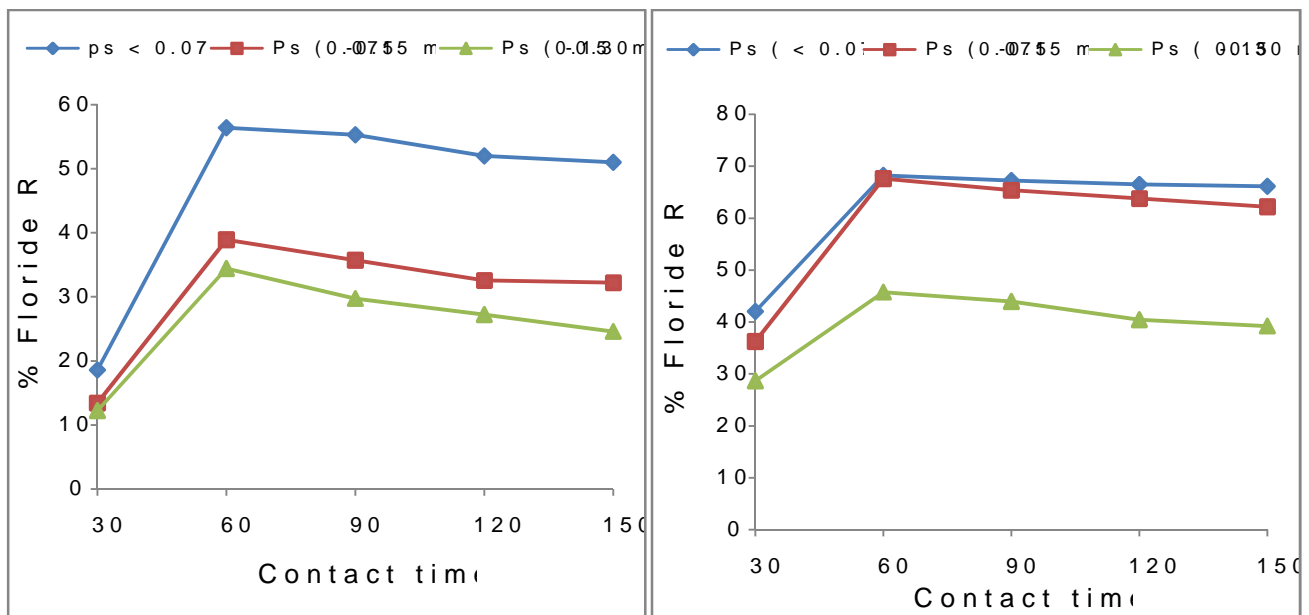


Figure 4.7 Effects of contact time on (a) Raw clay (b) Activated clay

#### 4.2.5 Adsorbent dosage

The effect of adsorbent dosage on fluoride adsorption on raw and activated kaolinite clay at contact time of 60 min, temperature of 50°C and PH value of 4 for 1 hour was studied (best results at 1g). The results were presented as percent fluoride removal vs adsorbent dosage. Figure 4.8. The percent fluoride removal increased from 23 to 61.4 for raw clay and from 35 to 74.1 for activated kaolinite clay for 0.5 • 1.5 gram of adsorbent dosage. The increase in adsorption capacity with increase in dosage is obvious, because any adsorption process depends upon the number of active sites. The same

explanation holds good for the increased percent removal of activated clay than raw clay. However, it can be seen from Figure 4.8 that after the dosage of 1.5 gram the adsorbent used, there was no noticeable change in the percent removal of fluoride due to the overlapping of active sites at higher dosage, thus reducing the net surface area. Thus, optimum dosage for maximum fluoride removal as a function of dosage was considered 1.5 gram for both raw clay and activated clay samples. These results were in consistent with the experimental result done by [59] as higher dosage of adsorbent causes overlapping of active sites.

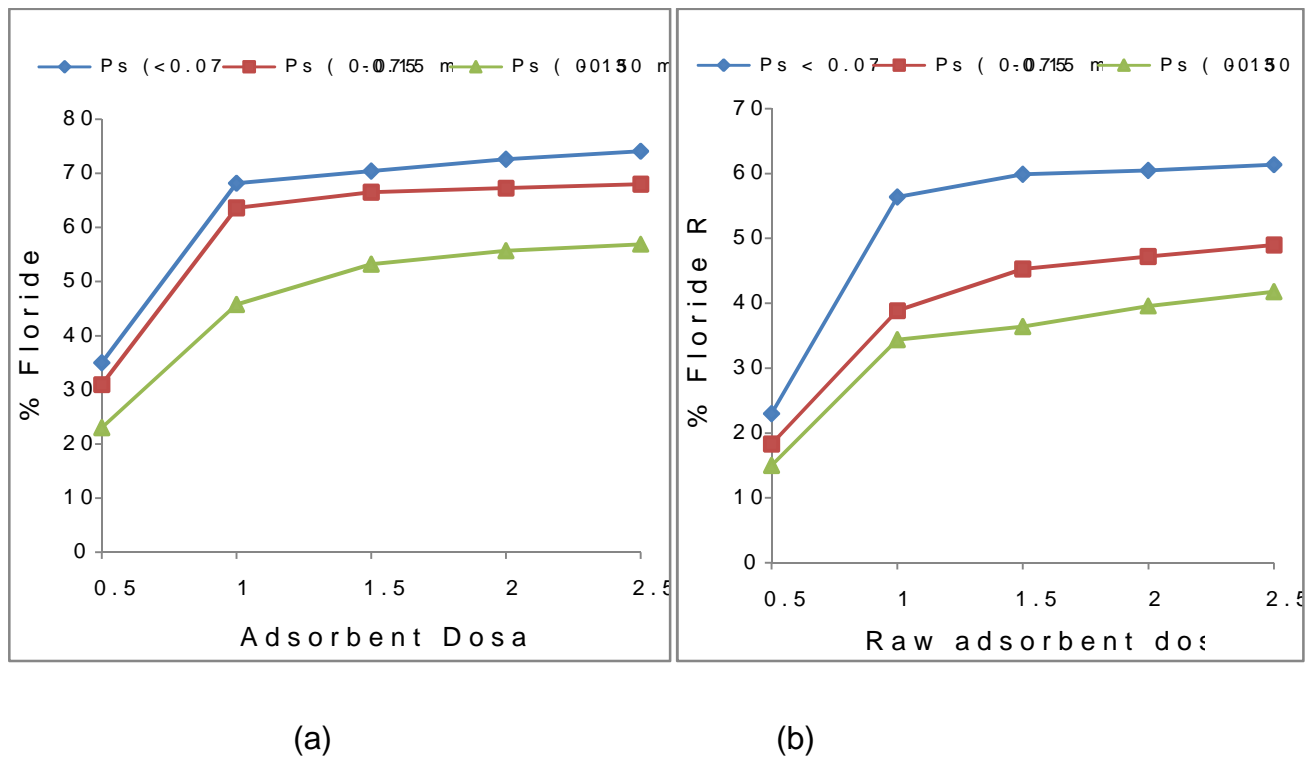


Figure 4. 8 Effects of adsorbent dosage on (a ) Raw clay (b) Activated clay fluoride removal

### 4.3 Adsorption Isotherm

Langmuir and Freundlich isotherms are used in adsorption to understand the extent and degree of favorability of adsorption. These two most common isotherm models were tested in the present study to analyze equilibrium data of solute between adsorbent and solution. The parameters obtained from these different models provide important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent.

Langmuir adsorption parameters have been determined by transforming the Langmuir equation into linear form as in equation

$$- = - + \text{---}$$

The values of  $q_m$  and  $K_L$  have been computed from the intercept and slope of the Langmuir plot of  $1/q_e$  versus  $1/C_e$  respectively. As well as the values of correlated coefficient ( $R^2$ ) have been computed from both models.

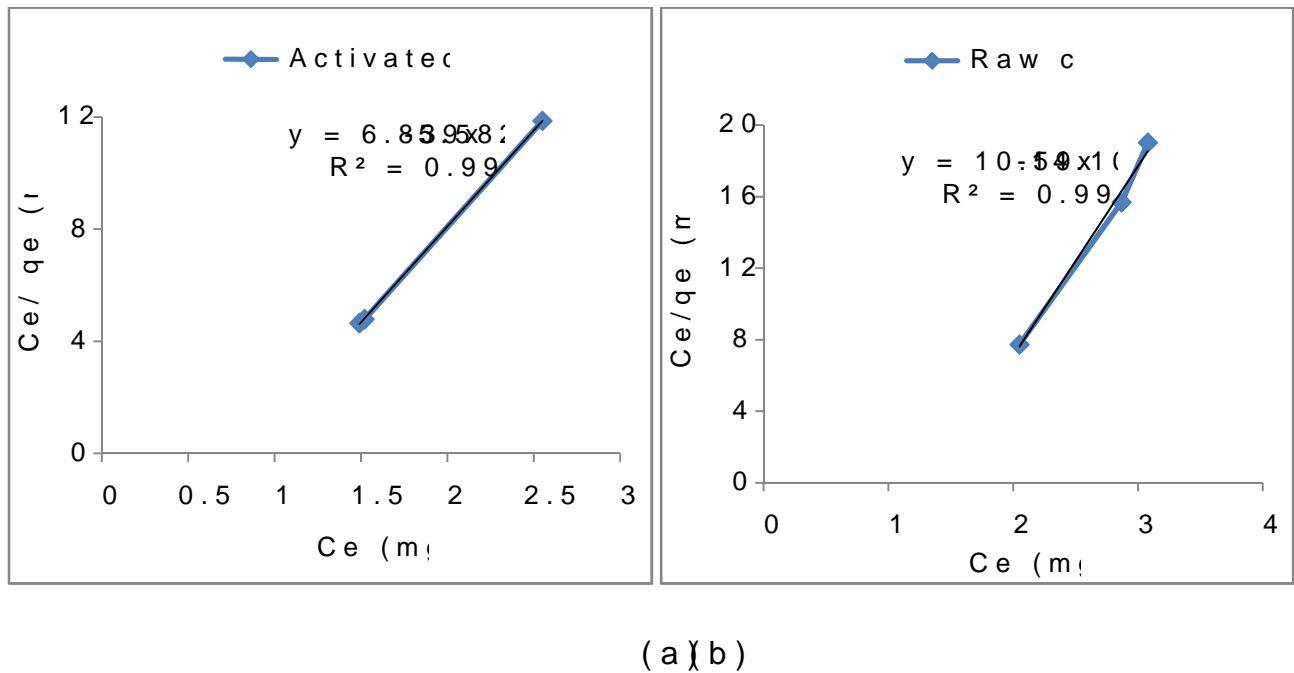


Figure 4.9 Langmuir isotherms for (a) Activated clay (b) Raw clay adsorbent removal

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant called separation factor, also called equilibrium parameter, which is defined by equation. The value of indicates the type of isotherm to identify its favorability adsorption according to assign in Table 4.3 [60].

Table 4.2 Types of Separation Factor, RL of Langmuir Isotherm [60]

Value	Types of Isotherm	Obtained Result	
		AC	RC
>1	Unfavorable	-	-
= 1	Linear	-	-
$0 < < 1$	Favorable	0.35	0.136
= 0	Irreversible	-	-

$$= \frac{1}{1 + (K_L C_e)} \quad (4.1)$$

Where,  $K_L$  is the Langmuir constant related to the energy of adsorption (L/mg) and  $C_0$  is the highest initial fluoride concentration (mg/L). The calculated value of  $K_L$  for powder of activated clay and raw clay adsorbent were 0.35 and 0.136, respectively. So, the value of  $K_L$  is between 0 and 1 for activated and raw clay adsorbent indicating that the equilibrium adsorption has been favorable.

Freundlich adsorption isotherm the parameters of this model also have been studied. Linear form of the Freundlich equation is as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4.2)$$

Freundlich isotherm model plot  $\log q_e$  versus  $\log C_e$ . The applicability of the Freundlich adsorption isotherm has been analyzed, using the same set of experimental data.

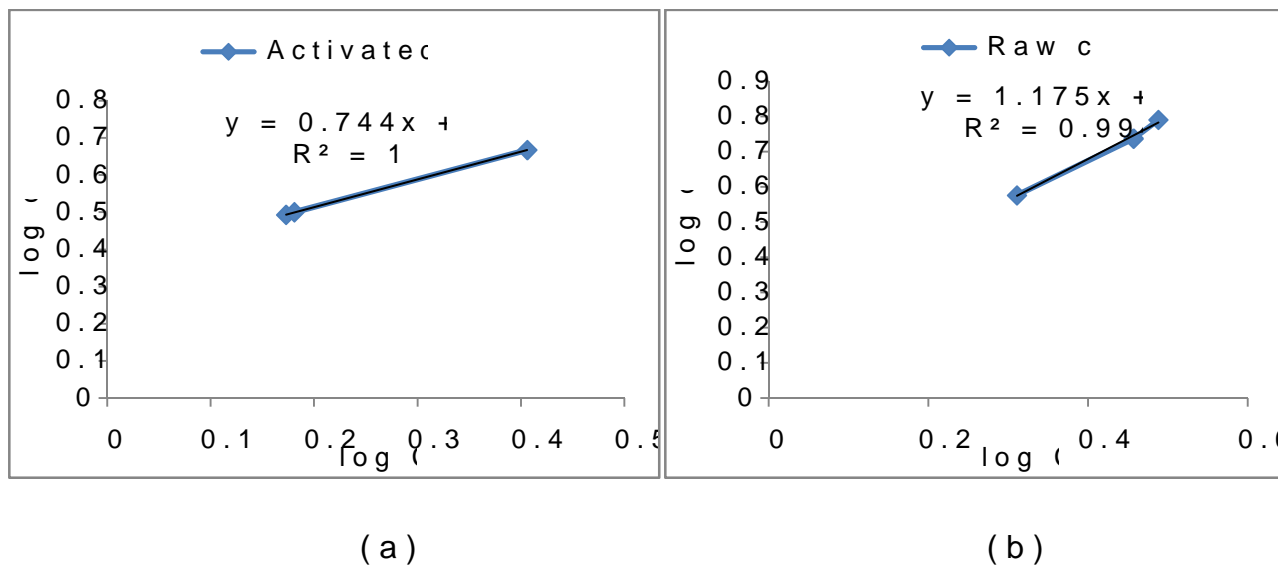


Figure 4.10 Freundlich isotherms for (a) Activated clay (b) Raw clay adsorbent removal

Table 4.3 Langmuir and Freundlich isotherm model for adsorbent AC and RC

Types of adsorbent	Langmuir Isotherm Parameters			Freundlich Isotherm Parameters		
	$q_m$ (mg/g)	$K_L$ (L/mg)	$R^2$	$K_f$ (mg/g)	$n$	$R^2$
Activated clay	0.179	0.817	0.9999	2.315	1.34	1
Raw clay	0.070	1.348	0.9906	1.617	0.85	0.9943

The favorable adsorption of this model can be characterized; the magnitude of the exponent  $n$  gives an indication on the favorability of adsorption. It is generally stated that values of  $n$  as



intensity,  $n$  in the range 2 to 10 represent good, 1 to 2 moderately difficult, and less than 1 poor adsorption characteristic [6]. In the present study, the values of 1.34 and 0.85 for activated clay and raw clay adsorbent respectively i.e. 1 to 2 indicating that the adsorption process is moderately adsorption for activated clay and less than one indicating that the adsorption process is poor adsorption for raw clay.

## 5. CONCLUSION AND RECOMMENDATION

### 5.1 Conclusion

A series of defluoridation experiments conducted showed that the amount of fluoride removed is affected by factors like temperature, pH, particle size, adsorbent dose and contact time. The results

of present investigation reveal some important observation of fluoride adsorption and the following specific conclusion can be drawn

Activation and calcination of an adsorbent can significantly increase its adsorption capacity increasing its surface area and pore volume due to removal of volatile matter from the surface of adsorbent.

Characterization results of FTIR analysis of the clay samples revealed that the clay has Si, Al-OH and OH functional groups. The Al-OH and OH functional groups found in the clay play an important role in exchanging the fluoride ion present in the water through adsorbing over the surface of the adsorbent.

Smaller particle size exhibit larger surface area and found to have the highest fluoride removal capacity. It can be concluded from XRD that the raw kaolin material is fully crystalline.

Adsorption exhibits an increase in adsorption rate at higher temperature and this confirms the endothermic nature of the process.

The adsorption process is a surface phenomenon. The sample with smaller particle size diameter have higher fluoride removal efficiency due to larger surface area.

As the contact time between adsorbate and adsorbent increases, it is noticed that the percentage of fluoride removal also increases up to equilibrium point (60 min) and there was no noticeable change in the percent removal of fluoride. It was observed that a fluoride removal of 75 % occurred in 6 min with a fixed amount of activated clay (1 g/L).

The amount of fluoride adsorbed per mass of the adsorbent was found to be in the range of 1.5 gram adsorbent for each adsorption medium. This may be attributed to the formation of stable aluminum fluoride complexes at high initial fluoride concentration.

Though, the adsorption process follows both Langmuir and Freundlich model, the preferred isotherm seems to be Langmuir model that the adsorption mechanism involves mechanisms of an initial rapid adsorption of fluoride on the surface of the adsorbent followed by slower diffusion of the fluoride into the interior of the adsorbent.

## 5.2 Recommendation

- Ø In this thesis only the potential kaolinite clay from Debretabawere selected for the production and characterization the adsorbent addition, other potential Ethiopian kaolinite clay sites for adsorption of fluoride should be identified and assessed with geologist and other related specialist because kaolinite clay is found in some part of Ethiopia like Dejen, Shakiiso, Bombowha and Kombolcha.
- Ø The potential of the produced kaolinite clay adsorbent on its capacity as fluoride removal from water was studied by using batch wise operation was recommended that adsorbent should be studied further in column experiment in full scale to determine optimum removal rate column parameters (bed height, flow rate, particle size).
- Ø Regardless of these of kaolinite for the production of adsorbent in different conditions, no attempt has been made to date to produce adsorbent from Ethiopian natural kaolin. The raw kaolin is mainly consumed by domestic ceramic factories. Apart from this, Ethiopian kaolin has not been evaluated for other applications such as the production of adsorbent.

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Appendix A: BET result of activated clay for particle size of <0.075mm diameter

Appendix B: BET result of activated clay for particle size of 0.075 -0.15mm diameter





Appendix D: BET result of raw clay for particle size of <0.075mm diameter

Appendix E: BET result of raw clay for particle size of 0.075 -0.15mm diameter

Appendix F: BET result of raw clay for particle size of 0.15 -0.3mm diameter

Appendix G: Design expert for different factors on percentage removal of Fluoride

Run	Block	Particle size	R	Temp.	% F removal	% F
					RC	removal AC
1	Block 1	0.0750.15	6	40	28.939.7	
2	Block 1	<0.075	8	25	24.4	35.9
3	Block 1	0.150.3	6	40	6.1	17.2
4	Block 1	0.0750.15	6	25	24.25	35.32
5	Block 1	0.0750.15	4	60	55.9	66.8
6	Block 1	<0.075	8	60	5.7	16.8
7	Block 1	0.0750.15	2	25	16.5	27.2
8	Block 1	<0.075	4	40	50.2	61.27
9	Block 1	<0.075	4	60	55.53	67.02
10	Block 1	0.0750.15	2	60	38.5	49.57
11	Block 1	0.150.3	4	50	34.4	45.74
12	Block 1	<0.075	2	40	32.3	43.4
13	Block 1	0.150.3	4	60	31.9	45.1
14	Block 1	0.150.3	4	25	17.02	28.08
15	Block 1	0.0750.15	4	50	38.967.6	
16	Block 1	0.0750.15	8	50	22.3	37.65
17	Block 1	0.0750.15	4	25	14.0425.3	
18	Block 1	<0.075	6	60	37.2	47.8
19	Block 1	<0.075	2	25	28.08	38.93
20	Block 1	0.0750.15	2	50	17.8	29.4
21	Block 1	0.0750.15	6	50	44	55.1
22	Block 1	0.0750.15	8	60	1.7	35.53
23	Block 1	0.150.3	6	25	3.61	14.04
24	Block 1	<0.075	8	50	30.4	41.06
25	Block 1	0.150.3	2	40	14.225.3	
26	Block 1	0.0750.15	8	40	18.0829.14	
27	Block 1	0.0750.15	6	60	39.7	50.85
28	Block 1	<0.075	2	60	41.752.7	
29	Block 1	<0.075	8	40	27.6	38.7
30	Block 1	<0.075	4	50	56.4	68.2
31	Block 1	0.150.3	2	60	14.04	25.1
32	Block 1	<0.075	4	25	56.3	57.2
33	Block 1	<0.075	6	40	34.6	45.7
34	Block 1	0.150.3	6	50	14.04	25.3
35	Block 1	<0.075	6	50	37.4	48.5
36	Block 1	0.0750.15	2	40	24.2	34.8
37	Block 1	0.150.3	2	25	8.29	19.36
38	Block 1	0.150.3	8	60	1.9	12.97
39	Block 1	0.0750.15	4	40	49.360.85	
40	Block 1	0.150.3	2	50	24.25	25.74
41	Block 1	<0.075	6	25	20.85	31.7
42	Block 1	0.150.3	8	25	4.04	14.68
43	Block 1	0.150.3	8	40	46.1	12.2
44	Block 1	<0.075	2	50	45.9	57.02
45	Block 1	0.0750.15	8	25	10.4	20.8

46	Block 1	0.15-0.3	4	40	27.8	38.9
47	Block 1	0.15-0.3	8	50	7.8	18.93
48	Block 1	0.15-0.3	6	60	10.85	21.94

Appendix H: Effect of temperature on activated and raw clay for particle size < 0.075 mm at PH value of 4 and 1 gm adsorbent dosage for 1 hour

Temperature (°C)	Initial fluoride concentration mg/l	% Fluoride removal for AC	% Fluoride removal for RC
25	4.7	57.2	42.3
40		61.7	50.2
50		68.2	56.4
60		67.02	55.53
70		63.5	52.6

Appendix I: Effect of particle size on activated and raw clay at PH value of 4, Temperature 50°C and 1 gm adsorbent dosage for 1 hour

Particle size	Initial fluoride concentration mg/l	% Fluoride removal for Activated clay	% Fluoride removal for Raw clay
<0.075	4.7	68.2	56.4
0.075• 0.15		67.6	38.90
0.15• 0.30		45.74	34.40

Appendix J: Effect of PH on activated and raw clay for particle size < 0.075 mm at temperature of 50 °c and 1 gm adsorbent dosage for 1 hour

PH	Initial fluoride concentration mg/l	% Fluoride removal for AC	% Fluoride removal for RC
2	4.7	57.02	45.90
4		68.2	56.40
6		48.5	37.40
8		41.06	30.40

Appendix K: Effect of contact time activated and raw clay for different particle size at PH value of 4, temperature of 50 °c and 1 gm adsorbent dosage for 1 hour

Contact time (min)	% Fluoride removal for Activated clay			% Fluoride removal for Raw clay		
	<0.075	0.075• 0.15	0.15• 0.30	<0.075	0.075• 0.15	0.15• 0.30
30	42	36.2	28.65	18.6	13.46	12.23
60	68.2	67.6	45.7	56.4	38.90	34.4
90	67.2	65.4	45.90	55.3	55.7	29.75
120	66.5	63.8	40.6	52.0	32.6	27.23
150	66.1	62.15	39.20	51.0	32.25	24.60

Appendix L: Effect of adsorbent dosage for different particle size at PH value of 4, temperature of 50 °c and 1 gm adsorbent dosage for 1 hour

adsorbent dosage(g)	% Fluoride removal for Activated clay			% Fluoride removal for Raw clay		
	<0.075	0.075• 0.15	0.15• 0.30	<0.075	0.075• 0.15	0.15• 0.30
0.5	35	31	23	23	18.3	15
1	68.2	63.6	45.74	56.4	38.90	34.4
1.5	70.4	66.5	53.20	59.90	45.3	36.40
2	72.6	67.3	55.70	60.5	42.20	39.60
2.5	74.1	68.0	56.90	61.4	49.00	41.80

Appendix M: Equilibrium concentration and Equilibrium adsorption capacity of activated and raw clay for different particle size at PH value of 4, Temperature 50 °c, adsorbent dosage of 1 gram for 1 hour.

Particle size (mm)	Activated clay			Raw clay		
	<0.075	0.075• 0.15	0.15• 0.30	<0.075	0.075• 0.15	0.15• 0.30
Ce (mg/l)	1.49	1.52	2.55	2.05	2.87	3.08
Qe (mg/g)	0.321	0.318	0.215	0.265	0.183	0.162