PREPARATION OF MODIFIED CLAY CERAMIC MATERIALS FOR FLUORIDE REMOVAL FROM DRINKING WATER

BY

LECHISA DABA GIDI

A THESIS SUBMITTED TO

SCHOOL OF APPLIED NATURAL SCIENCE APPLIED CHEMISTRY DEPARTMENT

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

OFFICE OF GRADUATE STUDIES

ADAMA SCIENCE AND TECHNOLOGY UNIVERSITY

ADAMA

SEP. 2017

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Subject: Thesis Submission

This is to certify that the thesis entitled **"Preparation of Modified Clay Ceramic Materials for Fluoride Removal from Drinking Water"** submitted in partial fulfillment of the requirements for the degree of Master's in Chemistry, the Graduate program of the department of Applied Chemistry and has been carried out by **Lechisa Daba Gidi, Id. No. GSS/0216/05**, under my/our supervision. Therefore, I/we recommend that the student has fulfilled the requirements and hence hereby he can submit the thesis to the department.

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DECLARATION

I hereby declare that this MSc. Thesis is my original work and has not been presented for a degree in any other university, and all sources of material used for this thesis have been duly acknowledged.

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This MSc. Thesis has been submitted for examination with my approval as thesis

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ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
C1	Clay, grog, saw dust and bone char mixture in volume ratio (5:1:1:1)
C2	Clay, grog, saw dust and bone char mixture in volume ratio (4:2:2:1)
C3	Clay, grog, saw dust and bone char mixture in volume ratio (3:3:3:1)
FT- IR	Fourier Transform-Infra Red
OSHO	Oromo Self Help Organization
Rpm	Revolution per million
TISAB	Total Ionic Strength Adjustment Buffer
WHO	World Health Organization
XRD	X-Ray Diffraction

Abstract

The present study shows the preparation of modified clay ceramic material for removal of fluoride from drinking water. The prepared adsorbent is characterized using XRD, FT-IR, and complete Silicate analysis. Batch adsorption studies were carried out which include the effect of initial pH of the solution, contact time, adsorbent dose and initial fluoride concentration on the adsorption capacity of modified clay ceramic material (C3).The fluoride efficiency was characterized using fluoride ion selective electrode. Fluoride adsorption was found to be pH dependent and 91.6 % of fluoride was removed at pH 3.0 and in the range of the WHO guideline for drinking water, at pH = 7.03, 73% of fluoride was removed. The equilibrium data have been analyzed by the Langmuir and Freundlich isotherm models. The adsorption kinetics has been investigated by the pseudo-first-order and pseudo-second-order kinetic models. The intra-particle diffusion was confirmed that adsorption of fluoride ion on this adsorbent was multi- step process involving adsorption on external surface as well as diffusion in to the interior surface. The modified clay ceramic material had good removal efficiency for the collected real water samples. It reduces the fluoride ion concentration of the real water samples to desirable fluoride ion containing drinking water. In comparison with other adsorbents from different countries, the adsorption capacity obtained for modified clay ceramic material fall in the range for those of adsorbents, which was shown in the earlier studies values.

Key words: Defluoridation, ceramic material, adsorbent, isotherm, and adsorption

1. INTRODUCTION

1.1. Background of the Study

Pure water is scarce and is not easily available to all parts of the society. People may consume polluted water and get sick periodically, often resulting in epidemic diseases. The water may be contaminated by natural process or by industrial effluents. One such contaminant is fluoride. Fluoride is an ion of the element fluorine. Fluorine is the most highly reactive element of halogen family. Most fluorides are reacting with monovalent cations such as Na and K to form NaF and KF respectively, are soluble in water, while the one formed with divalent cations such as CaF_2 and PbF_2 is generally insoluble. Fluoride (beyond 1.5 mg/L, WHO guideline) is "more toxic than lead and less toxic than arsenic" and is an accumulative toxic [1]. Contamination of drinking water by fluoride, due to its natural presence from dissolution containing rocks, or discharge by agriculture and industrial activities, such as steel, aluminum, glass, and electroplating [2-4] is one that affects human health and wellbeing.

The quality of drinking water is very important for public health and better life. Optimum fluoride concentration (about 1 mg/L) in drinking water is good for dental health and proper bone development. However, intake of excess fluoride (beyond 1.5 mg/L, WHO guideline) for long period can result in the incidental fluorosis. Low concentration of fluoride in drinking water has been considered beneficial to prevent dental fluorosis, skeletal fluorosis, and bone fractures [5].

The beneficial and harmful effects of fluoride is based on the possible ion exchange reactions between hydroxide and fluoride ions in the calcium hydroxyl-phosphate, the main skeletal structure compositional material, the replacement of hydroxide ions with fluoride ions, are given by equation which results in more acid resistant structure fluoroapatite.

$$[3Ca_3(PO_4)_2 2Ca(OH)_2] + 12F^- \rightarrow [3Ca_3(PO_4)_2 2CaF_2] + 12OH^- \quad \text{..... (eqn. 1)}$$

Fluoroapatite being more resistant to acid attack compared to hydroxyapatite a protective to the teeth enamel against acid from foods. This prevents dental fluorosis. Excessive fluoride intake however may enhance the reaction to go beyond replacement of hydroxide.

$[3Ca_3(PO_4)_2\ 2CaF_2] + 18F^- \rightarrow 3Ca_5F_{10} + 6PO_4^{3-}$ …….. (eqn. 2)

In this reaction, ion exchange occurs between phosphate and fluoride ions. The resultant compound, calciumdecafluoride, is a very hard and brittle material not appropriately suited for the functions of the skeletal structure [6]. The occurrence of high fluoride concentration in drinking water and the risk of fluorosis associated with using such water for human consumption is a problem faced by many countries, note by India, Sri Lanka, the Rift Valley countries in East Africa, Turkey and parts of South Africa [7].

Ethiopia is one of the 23 countries where the population suffers from the conception of fluoride rich drinking water [8]. In Ethiopia, around low land area, example Rift Valley zone, the concentrations of fluoride are greater than the WHO guideline value of 1.5 mg/L which have been found in ground waters, are recognized to be highest (10 mg/L) [9].

The most commonly used conventional methods for the removal of fluoride from drinking water are adsorption, ion exchange, precipitation, nano-filtration and Electrodialysis [10]. Among these methods, adsorption has been found to be superior to other techniques for fluoride removal based on essential cost, flexibility and maintenance. A large number of adsorbents have been studied for the removal of fluoride ions, including active alumina, calcite, fly ash, charcoal, layered double hydroxide, spent bleaching earth [10]. Among these adsorbents, activated alumina seems to be widely used because of its efficiency and low cost. However, the main disadvantage of active alumina is its residual aluminium and soluble aluminium fluoride complexes, the generation of sludge and narrow available pH (5.0 - 6.0) [10]. In addition, most of these materials are difficult to separate from liquid adsorption. So other implementation is required to treat drinking water in order to overcome these obstacles.

Ceramic adsorbents are solid phase of spherical shape materials, with high fluoride removal efficiency and sufficient mechanical strength to retain their physical integrity after long time adsorption, and these materials are robust, porous, and able to effectively remove fluoride in

subsequent operations and also avoid clogging during field applications. Ceramic adsorbents have been prepared by low cost effective materials consisting of clay soils, which is widespread in Ethiopia. Therefore, it has been required to implement appropriate water treatment procedures using these local resources that are accessible to the rural community with technically simple, cost effective, and easily transferable technology. So in this study a modified clay ceramic material has been prepared from the mixture of clay, grog, saw dust and bone char with various volume ratios for fluoride removal from drinking water and investigated in batch studies, and also the possibilities of utilizing it as a low cost defluoridation method and as a green chemical approach method.

1.2. Statement of the problem

Fluoride concentration in drinking water is a worldwide problem, especially a widespread problem in the East African Rift valley countries including the Ethiopian Rift Valley. Fluoride is very toxic, when it is taken in excess (3 .18 mg/L), leading to inhibition of infant's brain /mind development. It results in abnormal behaviors and reduces IQ in children. The permissible limit of fluoride concentration in drinking water is (1.0 - 1.5 mg/L) according to WHO guidelines. In Ethiopia, around Rift Valley, the concentrations of fluoride are greater than the WHO guideline value. Various methods of water treatments are present, but most of them are high cost of the media and running costs, difficult in operation, low potential for reuse, less number of useful cycles and has possibility of regeneration. Therefore, viable option is to look for low cost processes that can be built using local expertise and based on locally available and cost- effective coagulants or adsorbents. So clay, grog, saw dust and bone char are among the locally available ceramic material which can easily modified by firing to use as fluoride removal adsorbents from drinking water.

1.3. Objectives of the research

1.3.1. General objective

To prepare modified clay ceramic material adsorbent and investigate its fluoride removal efficiency from drinking water.

1.3.2. Specific objectives

To Prepare modified clay ceramic material

To determine the fluoride removal efficiency of the developed adsorbent

To investigate the effect of contact time, pH of the solution, dose of the adsorbent and initial fluoride concentration on its fluoride removal efficiency.

To characterize modified clay ceramic material

1.4. Significance of the Study

People who live in rural area and in some area of town are using ground water for drinking purpose. The drinking water might be contaminated by different contaminants. This study focus on one of the easiest method and the cheap material was made from locally available source that is used for the treatment of drinking water. The modified clay ceramic materials reduce the fluoride ion concentration and make the water suitable for drinking purposes in terms of its fluoride ion.

1.5. Scope of the Study

In this study modified clay ceramic materials were produced from locally available materials like clay, grog, sawdust, bone char and fired at different temperatures to investigate the effect of different parameters like contact rime, pH, adsorbent dose, and initial fluoride ion concentration and the was adsorbent characterized. The fluoride ion removal efficiency of the adsorbent was investigated in this work.

1.6. Limitation of the study

The limitation of this research work is the problem of having natural water sample sources which contains sufficient amount of targeted fluoride ion concentration to study the fluoride ion removal efficiency of the developed adsorbent. That is why the synthetic wastewater samples were prepared by using analytical grade chemicals for the fluoride ion test.

2. LITERATURE REVIEW

Fluorine is a common element, but it occurs as fluoride in nature because of its high activity, it exists in the form of fluorides in a number of minerals, of which fluorspar, cryolite and fluoroapatite are the most common. Fluorine is highly reactive and found naturally as CaF_2. Fluoride is a normal constituent of natural water samples. Its concentration, though, varies significantly depending on the water source. Although both geological and man-made sources contribute to the occurrence of fluoride in water, the major contribution comes from geological resources. Except in isolated cases, surface waters seldom have fluoride levels exceeding 0.3 mg/L. Examples are streams flowing over granite rich in fluoride minerals and rivers that receive untreated fluoride-rich industrial wastewater [11].

There is several fluoride bearing minerals in the earth's crust. They occur in sedimentary (limestone and sandstone) and igneous (granite) rocks. Weathering of these minerals along with volcanic and fumarolic processes is leading to higher fluoride levels in groundwater. Dissolution of these barely soluble minerals depends on the water composition and the time of contact between the source minerals and the water. Contamination of drinking water is one of the challenges the current society is facing. Fluoride is one of the most important contaminant of drinking water [11].

2.1. Health impacts of excess fluoride in potable water

Low dental fluorosis incidence rates demonstrate that fluoride concentrations of up to 1.0 mg/L in potable water is beneficial to the oral health of children and, to a lesser extent, adults. In several developed countries fluoridation of water supply is practiced if the natural concentration is below the desired level. Recently, however, fluoridation of drinking water has been questioned and many countries have expressed concerns over this practice due to the adverse health effects of fluoride [12].

2.1.1. Fluorosis

The intensity of fluorosis is not merely dependent on the fluoride content in water, but also on the fluoride from other sources, physical activity and dietary habits. Fluorosis is a disease

caused by excessive intake of fluoride, dental fluorosis (intake of F^- >1.5 mg/L) and skeletal fluorosis (intake of > 3 mg/L) [13].

2.2. Methods of treatment of excessive fluoride content

If fluoride concentration in a community's water supply is significantly and consistently beyond the permissible level, it is essential to consider remedial measures to combat fluorosis by using alternate water sources, improving the national status of population at risk and removing excess fluoride [14].

2.2.1. Defluoridation of water

When none of the above options is feasible or if the only solution would take a long time for planning and implementation, defluoridation of drinking water has to be practiced as the central treatment of water at the source and the treatment of water at the point of use that is, at the household level. In developed countries treatment at the source is the method adopted.

2.2.2. Defluoridation Methods

The process of removal of fluoride is generally termed as defluoridation. Numerous commercial methods have been described employing various materials for the fluoride removal since 1930 [15]. Defluoridation methods using inorganic and organic substances in many laboratories and field studies nowadays are summarized as follows. To conquer the hazardous wellbeing impact of fluorosis, different approaches for different defluoridation are like coagulation-precipitation, membrane separation processes, ion exchange, adsorption and others (Electrodialysis and Electrochemical).

2.2.2.1. Coagulation and Precipitation Method

Lime and alum are the most usually utilized coagulates for defluoridation of water. Expansions of lime prompt precipitation of fluoride as insoluble calcium fluoride and raise the pH value up to 11.0 - 12.0. As a first step precipitation happens by lime dossing which is trailed by a second step in which alum is added to bring about coagulation. At the point when the alum is added to water basically two reactions happens. In the first reaction alum reacts

with alkalinity's portion to deliver insoluble $Al(OH)_3$. In the second reaction, alum reacts with fluoride ions in the water. Best fluoride removal is proficient created at pH, of 5.5 - 7.5 [16]. Aluminium salt is utilized to remove fluoride from water. The dosage of fluoride relies up on the concentration of fluoride proportionality. The dosage of lime is by and large $1/20^{th}$ of the dose of alum. Lime serves to shape bigger and denser flocs for fast settling. Bleaching powder is included for cleaning at the rate of 3 mg/L. It is the most generally utilized defluoridation method especially at community level [17].

The bucket defluoridation system based Nalgonda technique has also been developed for household utilize [18]. The process is suitable for 20 Liters of water for one day utilization. The process produces water with leftover fluoride somewhere around 1 and 1.5 mg/L [19].

2.2.2.2. Membrane process

Membrane filtration processes are among advanced water treatment technologies that have been mainly employed in treatment of pure and ultra-pure water [20].

Reverse Osmosis and Nano Filtration are the well-known membrane technologies that can remove a large spectrum of contaminants from water such as pathogens, turbidity, heavy metals, salinity, natural and synthetic organic, and hardiness [21]. The two processes are highly qualifying water that includes disinfection during water treatment. Nano Filtration membranes operate at a low pressure and have lower capacity as compared to Reverse Osmosis membranes. Use of Electrodialysis plants in North Africa is employed in large scale water treatment of the fluoride brackish water for portable supply [22].

Electrodialysis is similar to Reverse Osmosis, except it was an applied direct current potential instead of pressure to separate ionic contaminants from water. Water does not physically pass through the membrane in the Electrodialysis process as such particulate matter is not removed. The Electrodialysis membrane is therefore not technically considered filters. The water quality from Electrodialysis treatment is compared to Reverse Osmosis, and may require post-treatment stabilization. The process tends to be the most economical for source of water with Total Dissolved Solid (TDS) level in excess of 4,000 mg/L. It is established that Reverse Osmosis and Electrodialysis have very high defluoridation capacities ($85 - 95^0/_0$) and

function effectively in any pH range. However, the water loss is high (20 – $30^0/_0$) for Electrodialysis, (40 – $60^0/_0$) for Reverse Osmosis, high capital cost and is energy intensive [23]. Membrane technologies often require special equipment, electrical energy and specialized training for operation as such the capital and operation costs are high. Low applicability is therefore envisaged for rural sectors of the developing countries where energy and trained human resource are often deficient.

2.2.2.3. Ion exchange

Defluoridation by bone char has been studied by several researchers [24] with remarkable efficiency. The removal process is considered to be ion exchange between fluoride ion the solution and carbonate of the apatite comprising of producing water with a residual fluoride concentration of less than 0.1 mg/L from an initial fluoride of 12.0 mg/L [25]. The materials are available locally and can also be processed locally by individual at household level for their own use or by a group of local people for selling to other local people. Precipitation of the bone char can also be done at a centralized station where by mass production and packing in labeled packets can be done.

The bones are charred in special kilns fueled by wood charcoal. Different sizes of the kiln have been fabricated and tested. Crushing and sieving devices have been developed [26]. Household and community scale bone char defluoridation systems have been developed and tested. The packed bone char and columns may then have been developed and tested.

The packed bone char production however needs bigger investment. The investment may involve capital for procurements of raw bones in large quantities, transportation of the raw bones to the processing station bigger kilns and powdered crushing and sieving devices. Other requirements may include packing materials and large number of plastic columns in to which the bone char is kept during defluoridation of water. Transportation and distribution of processed bone char and columns for local shops in fluorite area is another obvious cost. Since it is not easy for local people to know when to change the media of their household defluoridation, information on the initial fluoride concentration can be used to predict when the media be changed [26].

2.2.2.4. Adsorption Method

Among the unit operations in water and wastewater treatment adsorption occupies an important position. Adsorption operations exploit the ability of certain solids preferentially to accumulate specific substances from solution onto their surfaces [27]. Sorption, which is a general term, includes selective transfer to the surface, and into the bulk of liquid [28]. In a general adsorption process, the adsorbed solutes are referred to as adsorbate and the adsorbing agent is the adsorbent. Theoretically, the adsorption of solute on to solid particles normally takes four essential steps [29]. First, solutes diffuse through the fluid to an area near the solid particle surface, second, it diffuses to the external surface of the particle, third the solute diffuses to the pore wall, and then it adsorbs to the internal surfaces of the pore wall.

Adsorption process may be classified as purification or bulk separation, depending on the concentration in the feed fluid to the component adsorbed. Early applications of adsorption involved only purification, for example adsorption with charred wood to improve the taste of water has been known for at least five centuries. Adsorption methods can be implemented for the removal of fluoride due to physical, chemical, or ion exchange interactions with the adsorbents. Two types of contacting systems of adsorption are usually encountered, namely, the batch and fixed-bed processes. Batch type processes are usually limited to the treatment of small volumes of effluents whereas the bed column systems have the advantage of continuous operation up to the point of saturation [29].

Fixed-bed processes can be set up with relative ease and provide continuous treatment with a long breakthrough time, and they are widely used for small and large scale application. The criteria for selection of suitable sorbent are; cost of the media and running costs, ease of operation, adsorption capacity, potential for reuse, number of useful cycles and the possibility of regeneration. Some of the most frequently encountered adsorbents are reviewed in this section.

2.2.2.4.1. Activated Alumina

Activated alumina is a granular form of aluminium oxide (Al_2O_3) with very high internal surface area, typically in the range of 200 - 300 m^2g^{-1}. 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 [30]. The mechanism of fluoride removal from water is similar to those of a weak base ion exchange resin. Fluoride removal efficiency is high (typically > 95%), and is dependent on pH. Fluoride removal capacity is optimum in the narrow range of pH 5.5 to 6.0 [30].

Activated alumina can be regenerated with a solution of 1% sodium hydroxide which displaces fluoride ion from the alumina surface. This procedure is followed by rinsing with distilled water and then with 0.05 N sulfuric acid which neutralizes residual caustic left after the rinse step and also reactivates the alumina [31]. The problem with this method is disposal of regenerate waste. Defluoridation of water by activated alumina is the method of choice in developed countries. In Ethiopia a method based on adsorption by activated alumina has been practiced in Wonji-Shoa and Methara sugar estates since 1962 [30]. 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 its high cost of imported activated alumina.

2.2.2.4.2. Defluoridation using low cost materials

The removal of fluoride from water using commercial materials by adsorption, membrane separation, and ion exchange, techniques are expensive for developing countries, by virtue of which the search for a low defluoridation materials. Different low cost materials have been used in Tanzania and India. In these countries, the people have been using locally produced aluminum sulfate at household level in order to remove the fluoride from their drinking water. The process involves simple coagulation by mixing a given dose aluminium sulfate and filtering using cloth. In India another technique has been developed, based on the addition of alkali (lime) and aluminum sulfate. Also this method is claimed to cheap [32, 33].

In Sri Lanka, filter bed has been built from selected low temperature burnt clay (silicates, aluminates and hematite) at low cost and used for the separation of fluoride in household water [34]. It is reported that has reduced the fluoride content to acceptable level during its two-month operation. In Turkey, burnt locally available raw aluminium was used for a

preliminary test. It gave about 78% removal of fluoride while the commercial activated alumina removed about 92 % [35]. They reported that at low concentration fluoride by Illinois soils was described by both Langmuir and Freundlich isotherms. It was also suggesting that fluoride adsorption on to soils was due to the presence of the amorphous aluminium [36]. Bjorvatn et al studied the defluoridation of water using soil samples from Ethiopia. It was reported that five soil samples from high land areas around Addis Ababa was reduced the fluoride content of the water from about 15 to 1 mg/L. From this study, it was concluded that the highland soil may be useful for removal of excessive fluoride from drinking water [36]. Other materials such as spent bleaching earth, spent catalyst, rare earth oxides, bone, charcoal, seeds of drum stick plant (Moringa Oleifera) and activated carbon were studied as fluoride adsorbents [37]. Mahramanlioglu et al investigated the adsorption of fluoride using bleaching earth. They found that the removal of fluoride depends on the contact time, pH and adsorbent [38].

2.2.2.4.3. Clays and Soils

The first comprehensive study of fluoride adsorption onto minerals and soils was published in 1967 [39]. Since the above mentioned paper was published, several researchers studied the adsorption of fluoride. These studies include the use of Ando soils of Kenya [40], Illinois soils of USA [41], Alberta soil [42], illite-goethite soils in China [43], clay pottery [44], fired clay [45], and fired clay chips in Ethiopia [46].

The defluoridation of water using fired clay chips were studied in Ethiopia by researchers [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 tasted for defluoridation. The column defluoridates 6 L of tap water containing 10 mg L^{-1} fluoride to below 1.5 mg L^{-1}. Broken bricks also used as domestic defluoridator in Sri Lanka [48] and from this study the broken bricks could be used as filter media for concentration of fluoride in raw water around 2 mg/ L. Natural clays present a major advantage due to their abundance in nature. Since these ceramic materials are widely available in Ethiopia, it can be used as an alternative defluoridating material although its capacity is low as compared to other commercially available materials

such as activated alumina. Major drawbacks of using ceramic materials as an adsorbent are their low capacity and hydraulic permeability. Thus, these problems should be addressed properly before choosing a particular clay mineral for the removal of fluoride from drinking water. Since ground water forms a major source of drinking water in the different areas of Ethiopia both dental and skeletal fluorosis are public health problems, in addition to its social and economic problems. So far most of the ground water treatment methods cannot be applied in most developing countries, including Ethiopia, because the population is too poor to afford buying or paying for materials used by the methods for removing fluoride. Therefore, viable option is to look for low cost processes that can be built using local expertise and based on locally available and cost- effective coagulants or adsorbents.

2.2.2.4.4. Bone Char

Preparation of bone char in ceramic kilns as used in the northern part of Thailand is normally calcination rather than a charring process. This laboratory study shows that firing the cleaned bones up to 500^0C for 2h and then gradually opening the kiln gate and letting it cool down results in bone char of a good quality and with maximum fluoride removal efficiency of 91.8%. At higher temperature of calcination, the percentage was less, decreasing with increasing temperature. At 800^0C the percentage of fluoride removed was less than 50%. For comparison, the efficiency of normal bone char, which is heated in an electric furnace at 600^0C for 20 minutes, was only 69.4%. Thus calcination in ceramic kiln may be a promising process for use by local communities [49]. From many scientific studies reviewed, the two charring techniques are described:

1. Calcination is known as a process of high temperature heating in the presence of atmospheric oxygen. The end product being pure bone mineral, a compound related to hydroxyapatite. All organic materials are combusted to carbon dioxide.
2. Pyrolysis is a charring process with no or very limited access to oxygen. In the organic phase the bone is converted into inorganic carbon and graphite, which makes this bone char black whatever charring temperature is used.

2.2.2.4.5. Carbon based sorbents

Some researchers used carbon as an adsorbent for fluoride removal. The potential sorption capacity of multi-walled carbon nanotubes was investigated as a means of removing fluoride from the drinking water of a number of regions in Iran and from experimental solutions [50]. A novel poly (aniline-co-o-aminophenol) modified carbon felt electrode reactor was designed and investigated for fluoride removal from aqueous solutions. Maximum fluoride uptake showed by zirconium impregnated coconut fiber charcoal and followed by groundnut shell and coconut shell charcoals due to its large surface area. Micro/nano-hierarchal web consisting of activated carbon fibers and carbon nano fibres impregnated with Al used as an adsorbent for fluoride removal from wastewater. At pH 5 - 8, Al-carbon nano fibres was used for treating the wastewater [50].

2.3. Characteristics of Clay materials

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 the ions later when conditions change [51]. Clays are potentially good absorbers of anions since they contain crystalline minerals such as kaolinite, smectite and amorphous minerals such as allophone and other metal oxides and hydroxides, which could adsorb anions such as F^- [52]. 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 the better the sorption will be for positively charged metal ion. Probability of one site being occupied is not dependent on the status of adjacent sites.

2.4. Adsorption Isotherms

The relationship between the amount of the substances adsorbed at constant temperature and its concentration in equilibrium solution is called adsorption isotherm. The equilibrium adsorption isotherms are of fundamental importance in the study of adsorption systems. The two well-

known adsorption isotherm models for surface coverage studies are Langmuir and Freundlich isotherm models.

2.4.1. Langmuir adsorption isotherm

The Langmuir isotherm model is most commonly used to quantify the amount of adsorbed on an adsorbent as a function of concentration at a given temperature.

Langmuir isotherm assumptions are:

. Intermolecular forces decrease rapidly with increase of distance and consequently predict the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent.

. Adsorption occurs at specific homogeneous sites within the adsorbent.

. Once adsorbate ion occupies active sites, no further adsorption can take at that site.

. All adsorption sites are identical and energetically equivalent.

.Probability of one site being occupied is not dependent on the status of adjacent sites.

Theoretically, the adsorbent has a finite number of sites for the adsorbate. Therefore, a saturation value is reached beyond where no further adsorption can occur.

Linear forms of the Langmuir equations are [53]:

$$\frac{Ce}{qe} = \frac{Ce}{Qe} + \frac{1}{bQe}, \quad \text{(eqn. 3)}$$

Where, q_e is the amount of fluoride adsorbed per unit mass of adsorbent (mg/g), Ce is the equilibrium concentration of the adsorbate (mg/L), and Qe and b represent maximum adsorption capacity and energy of adsorption, respectively. Langmuir parameters Q_e and b are determined from the slope and intercept of the linear plot $\frac{Ce}{qe}$ versus C_e respectively. The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless separation factor or equilibrium parameter, R_L, which is defined by:

$R_L = \frac{1}{1+bCo}$ ……(eqn.4)

where, C_o is the initial concentration of the adsorbate in the solution, b is the Langmuir's adsorption constant (L/mg). The value of R_L indicates the type of isotherm to be either favorable ($0<R_L< 1$), unfavorable ($R_L>1$) or irreversible ($R_L= 0$) [54].

2.4.2. Freundlich adsorption isotherm

The Freundlich isotherm equation takes into account repulsive interactions between adsorbed solute particles and also account for surface heterogeneities. The equation is adequate to describe non-linear adsorption in narrow range of adsorbate concentration. The logarithm form of the Freundlich isotherm is given as follows [55]:

$\text{Log } q_e = \frac{1}{n\log Ce} + \log K_f$, ……..……(eqn.5)

Where, q_e is the amount of fluoride ion adsorbed at equilibrium, C_e is the concentration of fluoride solution at equilibrium; K_f and $\frac{1}{n}$ are equilibrium constant indicates adsorption capacity of the adsorbent and adsorption intensity, respectively. Their values can be obtained from the intercept and slope of linear plots of log q_e versus log C_e. $\frac{1}{n}$ Value indicates the type of isotherm to be irreversible ($\frac{1}{n} = 0$), favorable ($0 < \frac{1}{n} < 1$), unfavorable ($\frac{1}{n} > 1$) [56]. The equilibrium adsorption capacity, q_e (mg/g) can be calculated using the mass balance equation given [54]:

$qe = V\frac{Co-Ce}{W}$, ……... (eqn.6)

Where, C_o and C_e is the initial and final equilibrium concentration of adsorbate (mg/L),

V is volume of the solution (L) and W is the dry adsorbent (g).

The amount of adsorbate adsorbed, q_e (mg/g) at any time can be calculated using equation:

$q_e = V\frac{Co-Ct}{W}$, ……(eqn.7)

Where, C_t is the concentration of adsorbate, (mg/g) at any time.

The percentage removal of adsorbate can be calculated using the following relationship [56]:

Percent (%) removal of Fluoride ion concentration $= \frac{(Co - Ce)}{Co} x100$…… (eqn.8)

Where, C_o and C_e is the initial and final equilibrium concentration of adsorbate, (mg/g), respectively.

The applicability of two adsorption isotherm (Langmuir and Freundlich) can be compared by evaluating the multiple regression correlation coefficients, R^2. In regression, the R^2 coefficient of determination is a statistical measure of how well the regression line approximates the real data points. R^2 is a number between zero and one that would give some information about the best fit of the model. If the value of R^2 close to zero suggests a poor model. If the value of R^2 is one indicates that the regression line perfectly fits the data. If the value of R^2 occurs outside the range 0 and 1, it is used to measure the agreement between observed and modeled value [58].

2.5. Kinetic of adsorption

The study of adsorption kinetics describes the rate of uptake of the adsorbate molecule or ion onto adsorbent, which determines the residence time required for design adsorption systems. This rate depends on the physic-chemical characteristics of the adsorbate and adsorbent, pH of the solution, temperature, and concentration of the solution. The adsorption kinetics shows the evaluation of the adsorption capacity though time and it is necessary to identify the adsorption mechanism in a given system. The following models are used to describe the adsorption kinetics behavior.

2.5.1. Pseudo-first- order equation

The adsorption kinetic describe by the Lagergren pseudo-first-order equation describing the adsorption rate based on the adsorption capacity. The differential equation is generally expressed as follows [57]:

$\frac{dq}{dt} = K_1(qe - qt)$ ..... (eqn.9)

Where, q_e and q_t refers to the amount of fluoride ion adsorbed per unit mass of the adsorbent at equilibrium time and any time, (mg/g), respectively and K_1 is the rate constant of pseudo-first- order adsorption (min^{-1}). Integrating Equation (9) by applying the boundary conditions $q_t = 0$ at t = o and $q_e = q_t$ at t = t gives:

$log\frac{qe}{(qe - qt)} = \frac{K1t}{2{,}303}$ .....(eqn.10)

Equation (10) can be rearranged to obtain the following linear equation form:

$\log(q_e - q_t) = \log q_e - \frac{K1t}{2.303}$,.....(eqn.11)

The rate constant, K_1 and equilibrium adsorption capacity, q_e can be predicted from the slope and intercept of the linear plots of log (q_e - q_t) versus t, respectively.

2.5.2. Pseudo- second- order equation

The adsorption kinetics may also be described by the pseudo- second- order equation. The rate of pseudo- second-order equation is dependent on the amount of solute adsorbed on the surface of adsorbent and the amount of adsorbed at equilibrium. The differential equation is given as follows [57]:

$\frac{dqt}{dt} = K_2 (q_e - q_t)^2$ .....(eqn. 12).

Where, K_2 is the rate constant of the pseudo- second –order equation (g/mg min.) and q_e is equilibrium adsorption capacity (mg/g).

Integrating equation (12) by applying the boundary conditions $q_t = 0$ at t = 0 and $q_t = q_e$ at t = t is simplified and rearranged to obtain linearized equation:

$\boldsymbol{\frac{t}{qt} = \frac{t}{qe} + \frac{1}{K2qe2}}$ ..... (eqn.13)

The values of q_t and K_2 can be determined experimentally from the slope and intercept of the plots of t/q_t versus t, respectively.

2.5.3. Intra- particle diffusion

To evaluate the rate-limiting of the fluoride adsorption onto modified fired clay ceramic material, the possible contribution of intra-particle diffusion on fluoride adsorption process was explored by using Weber-Morris model [59].

$$q_t = k_i t^{1/2} + C \quad \text{(eqn.14)}$$

Where, q_t is the amount of fluoride adsorbed at time t (mg/g), k_i is intra-particle diffusion rate constant (mg/g.h.$^{1/2}$), it can be calculated from the slope of the plot of q_t versus $t^{1/2}$ and C is intercept. The magnitude of the intercept, C is a measure of a thickness of adsorbed layer which gives an idea about the thickness of boundary layer i.e. the larger the intercept, the greater boundary efficiency. If a plot q_t versus $t^{1/2}$ is linear and passes though the origin, then intera particle diffusion is the sole rate determining.

3. MATERIALS AND METHODES

3.1. Materials and Apparatus

3.1.1. Instruments and Apparatus

Instruments and apparatus used in this study include: fluoride ion selective electrode (Orion Model 940 Expandable Ion Analyzer), XRD (Bruker D8 Advance Diffractometer), and FT-IR(Perkin Elmer, 65 Spectrophotometer FT-IR Spectrum), pH meter (mettle Toledo Mp220), electronic balance (OHAUS Switzerland), hot air oven (Contherm 260M), volumetric flasks (PYREX, UK), beakers, shaker (orbital shaker SOI, UK), centrifuge (K2 Series, CENTRION SCINTIFIC LTD West Sussex, UK), muffle furnace (BIBBY, Stuart), mortar and pestle, ceramic crucible**.**

3.1.2. Chemicals and Reagents

The research grade work chemicals used in this research include: sodium fluoride, hydrochloric acid (1%), sodium chloride (99.5%), sodium hydroxide, TISAB, potassium chloride, EDTA, glacial acetic acid, sodium citrate, and tap water; double distilled water for preparing various stock solutions and standard solution and other reagents for other purposes.

3.2. Methods and Procedures

3.2.1. Sampling of the raw materials

The raw material used for the preparation of modified clay ceramic materials such as: clay, grog, and saw dust were collected from Addis Ababa Kechene Women's Pottery Cooperation. The bone char powder was supplied from Modjo OSHO Fluoride Removal Technology Center.

3.3. Preparation of modified clay ceramic materials

Preparation of modified clay ceramic material adsorbent were done by modifying the method of preparation of ceramic material reported i.e. at less than 400^0C firing temperature the clay is soft and at above 600^0C the fluoride binding capacity of the clay also decrease, for saw dust

at less than 400^0C firing temperature no formation of charcoal and ash containing metals also at 500^0C and above firing temperature, the saw dust burn out of the mixture , for the bone char , above 500^0C firing temperature, reduces its fluoride removal capacity [60, 61, 62]. Batch adsorption experiments were carried out at laboratory of post graduate, Applied Natural Science of Adama Science and Technology University.

The collected clay, grog and saw dust were dried in open air by sun for 7 days. They were ground and sieved separately. These were then mixed with bone char in volume ratios (5:1:1:1), (4:2:2:1) and (3:3:3:1), respectively and represented by code C1, C2, and C3 for further experiments. These samples were mixed with tap water and three paste ceramic materials having the same shape and size were prepared from each sample, i. e. a total of nine equal pastes ceramic materials were prepared. The paste materials were dried by sun in open air for 2-3 days, and then fired for three hours in the muffle furnace at 400^0C, 500^0C, and 600^0C by taking one from each type, (C1, C2, and C3). These temperatures were selected based on the previous screening test. The fired ceramic materials were taken out of the furnace kept in desiccator and allowed to cool to room temperature for 12h; lastly they were ground and sieved to obtain nine powdered samples of modified clay ceramic materials with particle size 1.18 mm mesh for fluoride removal from drinking water.

3.3.1. Summary of Preparation of Modified Clay Ceramic Material

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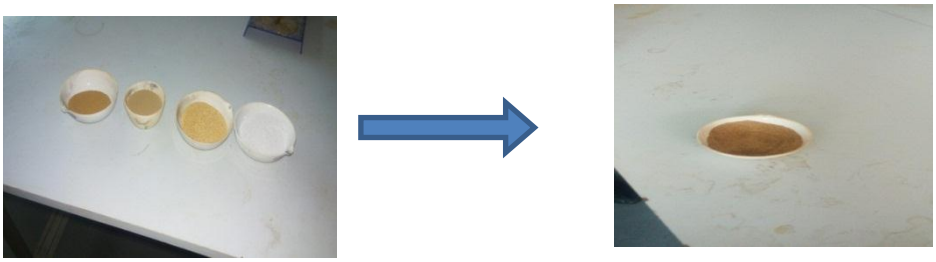

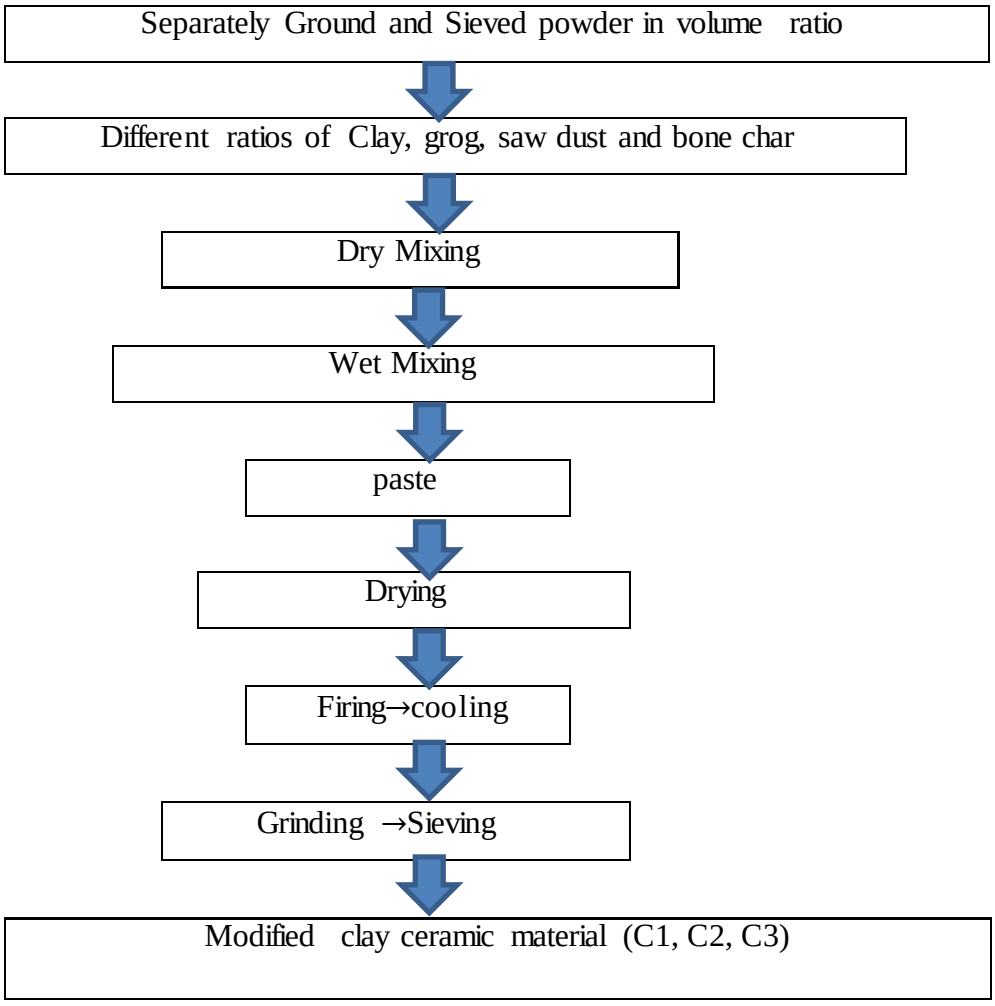

Figure1. Diagrammatic representation of the Preparation of Modified clay ceramic material

3.4. Determination of fluoride concentration

3.4.1. Reagent and standard solution

A stock solution of 1000 mg/L sodium fluoride has been prepared by dissolving 2.21 g of sodium fluoride in double-distilled water. Standards at a required concentration range (2.5 mg/L, 5.0 mg/L, 7.5 mg/L and 10.0 mg/L) have been prepared by appropriate dilution of stock solution, a 1000mg/L sodium fluoride, with double-distilled water.

3.4.2. Preparation of TISAB

500 mL of double distilled water, 7 g tri-sodiumcitrate ($Na_3C_6H_5O_7.2H_2O$), 56 g sodium chloride and 2 g EDTA (ethylenediaminetetraacetic acid) were added in 1000mL beaker and then stirred to dissolve. After the solution was dissolved, 57 g of glacial acetic acid was added in to it. And finally 5M sodium hydroxide was added until the pH reached 5.3, then transferred to 1000 mL volumetric flask and double distilled water was added to mark.

3.4.3. Calibration of the electrode

20 mL of fluoride solutions with different fluoride ion concentrations were prepared in constant intervals and 2 mL of TISAB was added to each solution. The potential readings of each concentration were taken and the graph of potential (E in mv) versus the logarithm of concentration ([Log c] in mg/L) was drawn. Then the slope of the graph and R^2 were calculated to check the accuracy of the measurement (Figure 2). Microsoft Excel program was used for all the calculations.

The prepared concentration of fluoride ions, (0.1 mg/L, 0.3 mg/L, 1 mg/L, 3 mg/L and 10 mg/L) were used for calibration Ion Selective Electrode. The slope should be 59.2 $\pm$3 mv and R^2 value close to 1 indicates good accuracy.

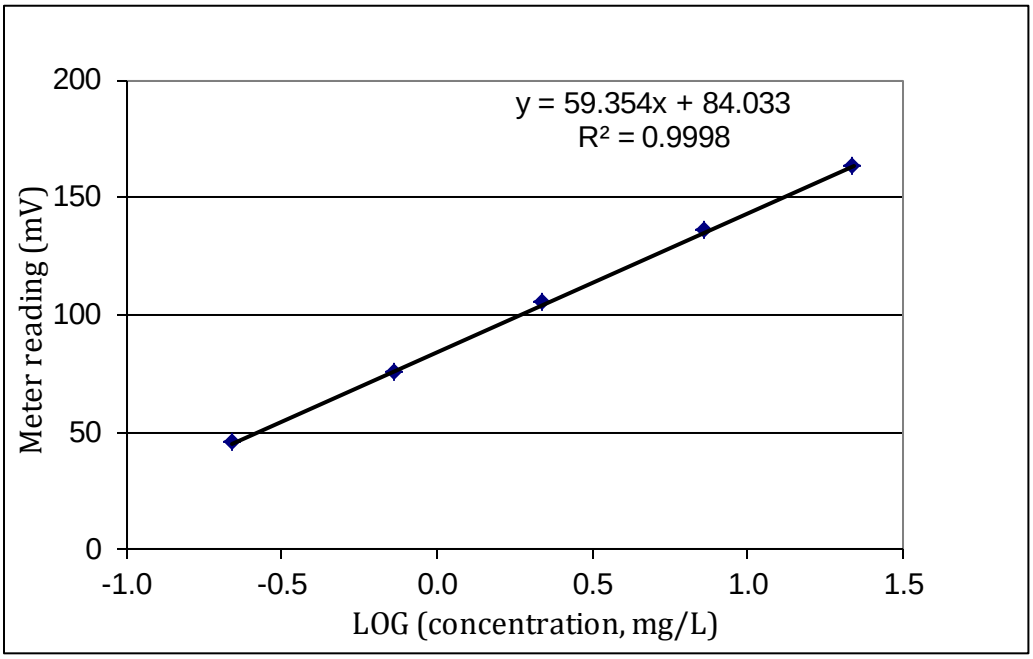

Figure 2. Plot of the potential readings versus the logarithm of fluoride concentration during calibration of the electrode

3.4.4. Sample Preparation and Fluoride measurement

10 mL of distilled water and 2 mL of TISAB were added in a 50 mL plastic beaker containing 10 mL of sample solution. The sample solution was stirred by a magnetic stirrer then the measurement was done by an electrode. The potential readings of all the samples were entered in an excel spread sheet program so that the potential reading would be converted to concentration. Microsoft Excel program was used to convert the mv potential readings to mg/L fluoride concentration.

3.4.5. Adsorption Procedure (Batch experiment)

The batch experiments were conducted by mixing 100 mL of the real water sample containing fluoride ion concentration of 3.12 mg/L collected from Didibsa village around Walenchit town. 5 g of modified clay ceramic material was mixed with it in 300mL glass bottles for 4h at room temperature. After 4h mixing, the mixture was centrifuged at 400 rpm for 10 minutes and decanted and then filtered using whatman No.1 filer paper. The final fluoride ion concentration measured after 4h, and again after 48h, was equal to 1.003 mg/L. No significant

reduction in F^- concentration was found for both measurements. So F^- did not react with adsorption vessels which imply that the remained 2.117 mg/L of F^- was adsorbed by the prepared adsorbent.

3.4.6. Determination of Adsorption Capacities

Preliminary tests were conducted in order to investigate the fluoride adsorption capacities of the prepared modified clay ceramic materials. In this study the adsorption capacities of the sample of modified clay ceramic materials (C1, C2, and C3) were conducted based on their firing temperatures. Then one sample with high percent removal efficiency was identified for the investigation of the effect of different operating parameters on it. The adsorption capacities were determined using the same adsorption experiment described as in section 3.4.5.

3.5. Investigation of the effect of various parameters on fluoride removal efficiency

3.5.1. Effect of pH

In this section, the effect of pH was investigated for the modified clay ceramic materials. Initial pH of raw water was prepared in the range of 3 to 8. The desired pH was adjusted using 0.1 M of NaOH and 1%HCl solution. Contact time, dose of the adsorbent and initial fluoride concentration remain constant.

3.5.2. Effect of contact time

By using, the batch adsorption procedures described in Section 3.4.5 the residual F^- concentrations was measured for different contact time of adsorption, 1, 2, 3,4 and 5h in order to investigate the effect of contact time. In this section the kinetic of the adsorption data was analyzed based on reaction kinetics of pseudo-first order and pseudo-second-order mechanisms. Also the possible contribution of Intra-Particle Diffusion on fluoride adsorption process was described as it was stated in the literature.

3.5.3. Effect of adsorbent dose

Adsorption efficiency (i.e. percentage of adsorption) and adsorption capacity (i.e. mg of fluoride removed per gram of adsorbent) were analyzed using 2.5, 5.0, 7.5, and 10.0 grams of

the modified clay ceramic material keeping contact time, initial fluoride ion and pH value constant.

3.5.4. Effect of initial fluoride concentration

The effect of initial fluoride concentration on the adsorption capacity was analyzed using different initial fluoride concentration ranging from 2.5 to 20 mg/L (2.5, 5.0, 10, 15, 20 mg//L). 5 grams of the modified clay ceramic materials were used at the constant contact time of adsorption and pH.

3.5.5. Adsorption Isotherm

The equilibrium data have been analyzed by the Langmuir and Freundlich isotherm models to determine the adsorption isotherms of modified clay ceramic materials. Untreated modified clay ceramic materials were considered at an initial raw water pH of 7.03, which is the desirable pH optimum for household system especially for drinking water adsorption. Adsorption isotherm has also been developed for modified clay ceramic materials heat treated at 400^0C. Data was generated by mixing a constant initial fluoride concentration of 5 mg/L with increasing dosages of adsorbents. The adsorption process was carried out for a contact time of 5h to ensure equilibrium.

3.6. Characterization of modified clay ceramic material

3.6.1. Complete Silicate Analysis

For determination of major and minor oxides complete silicate analysis (Analytical method LiBO2 Fusion, HF attack, Gravimetric, Colorimetric and AAS) of the adsorbent was done at Geological Survey of Ethiopian Geochemical Laboratory, Addis Ababa. The results of Silicate analysis were shown percent of the major and minor oxides in the prepared adsorbent (C3 fired at 400^0C).

3.6.2. XRD Analysis

The modified clay ceramic material was also analyzed by powder XRD and FT-IR. For XRD analysis the X-ray Diffractometer (Bruker D8 Advance Diffractometer) spectrum was recorded

from 10^0 to 80^0 with 2θ angles using CuKα (λ =1.54 Å) radiation operated at 40kV and 30 mA. The sample was powdered and scanned for diffraction angle of 2θ. The modified clay ceramic material was characterized by powder XRD at Addis Ababa University in Chemistry laboratory. The XRD technique has been one of the most prominent for the identification of crystal phase of the adsorbent.

3.6.3. FT-IR Analysis

For the FT-IR analysis the FT-IR (Perkin Elmer, 65 Spectrophotometer FT-IR Spectrum) instrument was used and detected the surface functional groups at the scanning range of 4000 – 400 cm^{-1}. The small amount of the adsorbent sample was placed on the KBr plates. The plates were placed in to the sample holder and a spectrum was run. The FT-IR spectrum of modified clay ceramic material was characterized and analyzed at (Addis Ababa University, Chemistry laboratory) and illustrated. FT-IR analyzed was done to understand the concept of bonding between the metal with adsorbent by doing the comparison of the position of different peaks and their intensities in the spectra and also identify the type of functional groups exist in the adsorbent.

3.7. Data Analysis and interpretation

All data generated during the experiments were analyzed using the Microsoft Excel, origin-8, Window program and the linear regression values were computed as required. The average percentage of fluoride adsorbed for modified clay ceramic materials has been calculated. The average adsorption capacity and efficiency of modified clay ceramic materials treated at different parameters mentioned were calculated and the average triplicate measured values of residuals fluoride concentration was determined. The results of the data analysis and residual plot were done for the experiments.

4. RESULT AND DISCUSSION

4.1. Adsorption capacities of the adsorbents (C1, C2 and C3)

In this paper, the modified clay ceramic material with volume ratios of clay, grog, saw dust and bone char (3:3:3:1), C3 fired at 400^0C, was selected and its adsorptive capacity for removal of fluoride ion from drinking water was also investigated. The adsorption capacities and efficiency of the adsorbents were discussed based on values given in Table 1 and also calculated from the residual fluoride concentration using the equations given in literature (eqn.6 and eqn.7)

Table 1. Average values of adsorption capacity and percent of adsorption of C1, C2, C3 (fired at temperatures of 400^0C to 600^0C) with (adsorbent dose = 10 g, initial fluoride concentration = 9.12 mg/L, contact time = 1h, and pH value of the solution = 6.7) .

Firing Temperature (^{o} C)	Samples	Measured values of C_e(mg/L), (triplicate measurements values)			Average values of C_e (mg/L) (Mean $\pm SD$)	Average Percent of F^- removed	Average values of q_e(mg/g)
		C_e 1	C_e 2	C_e 3			
400	C1	0.850	0.853	0.847	0.851 ± 0.202	90.68	0.0827
	C2	0.701	0.690	0.702	0.702 ± 0.301	92.32	0.0842
	C3	0.580	0.559	0.541	0.56 ± 0.131	93.86	0.0856
500	C1	1.528	1.586	1.788	1.53 ± 0.184	83.22	0.0759
	C2	0.710	0.762	0.808	0.76 ± 0.531	91.67	0.0836
	C3	0.678	0.480	0.581	0.58 ± 0.03	93.64	0.0854
600	C1	0.601	0.543	0.662	0.601 ± 0.143	93.42	0.0854
	C2	0.887	0.892	0.890	0.89 ± 0.201	90.24	0.0823
	C3	0.583	0.382	0.776	0.58 ± 0.18	93.64	0.0852

The rate and capacity of F^-binding in the modified clay ceramic materials were varied with the firing temperatures and mixture components. At all firing temperatures (Table 1), C3 was the highest in fluoride removal capacity from the drinking water, specifically C3 fired at 400^0C. At 400^0C firing temperature the clay was with more OH^-functional groups and became strong by the

grog in the mixture [60]. The saw dust was more in amount and also converted to charcoal, then to ash, containing oxides of Si, Al, Fe, Ti, Ca, $MgSO_3$ and alkalies along with mixed oxides, at 400^0C firing temperature that made the saw dust increase in its removal capacity of fluoride ion from the water [61]. For bone char 400^0C firing temperature is the optimum temperature to increase the adsorbent fluoride removal capacity [62]. So based on value obtained (Table 1), **t**he modified clay ceramic material (C3 fired at 400^0C) was the identified and selected adsorbent.

4.2. Investigation of the effect of various parameters on adsorbent C3 fired at 400^0C

4.2.1. Effect of pH on removal efficiency of the adsorbent (C3 fired at 400^0C)

It was well documented in literature that pH of water significantly affect fluoride uptake capacity. In order to see this effect, experiments were conducted for the sample identified.

Figure 3.Shows the influence of initial solution pH on the fluoride removal efficiency of the selected adsorbent.

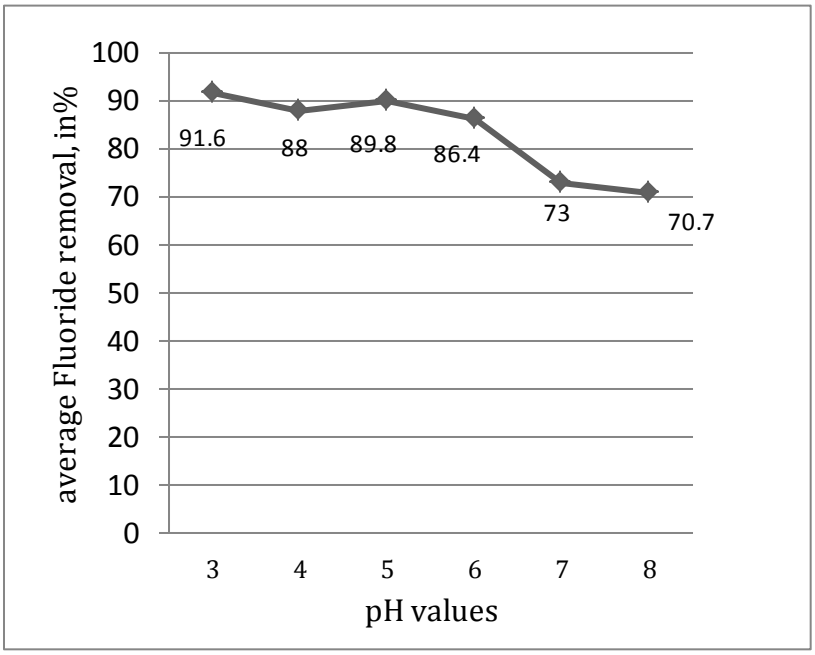

Figure 3. Plot of Percent removal of fluoride ion versus pH on modified clay ceramic material at (contact hour = 4h., dose = 5 g, and initial fluoride concentration = 5 mg/L)

The result (Figure 3) shows that higher adsorption capacity was observed at lower pH values (acidic media) because the surface is highly protonated in acidic medium and therefore in acidic

medium fluoride removal is attributed and it has a decreasing tendency as the pH was increased. Previous study revealed that the concentration of positively charged components of the clays (i.e. oxides of silicon, aluminium and iron) were increased with decreasing pH and hence they can readily adsorb the negatively charged fluoride ion [63]. Thus, decrease in the adsorption capacity in the basic region was due to the decrease in positive charges of the clay and increase in competition of $F^-$with the OH^-as both have the same charge and ionic radii [64]. Maximum adsorption of fluoride was found to be 91.6 $^0/_0$ at the pH = 3. From the WHO guideline drinking water with a neutral pH value 7.0 to 8.5 was desirable for adsorbents to remove fluoride ion [65]. In this range desirable conditions, pH = 7.03, the prepared clay ceramic material can remove 73% fluoride ion from drinking water. The removal efficiency fell as the pH went above 5.0. The sharp reduction in the amount of fluoride adsorbed under alkaline pH conditions is due to competition from hydroxyl ions for adsorption sites even though the oxide surface was positively charged [66].

4.2.2. Effect of equilibration time

The effect of contact time between the adsorbent and fluoride ions could be observed in Figure 4. The effect of contact time between the adsorbent and fluoride ions was studied at the one hour time intervals up to 5 hours. In this case, the equilibrium was attained at 4h; the sorption percentage altered from 55.4% at one hour to 72.8% at 4h, at which point it raised ground. Faster initial adsorption rate was possibly due to the availability of sufficient vacant adsorbing sites in presence of higher fluoride concentration gradient. Afterwards, the F^- uptake rate by the adsorbent was decreased significantly due to limited vacant adsorption sites available.

This perhaps owing to the fact once a certain amount of fluoride ions gets adsorbed on this adsorbent within a given time; no more binding of fluoride ion was occurred afterwards. Further the achievement of highest binding capacity within 4h proposes that a minimum contact time was adequate enough for the taking away of fluoride from water by these adsorbents. The fluoride ion was reached equilibrium at 4h, and 72.8% of fluoride ion was adsorbed, after that there was a decrease in amount of fluoride ion adsorbed by adsorbent. Hence, 4h contact time was chosen as the optimum time for further inspection.

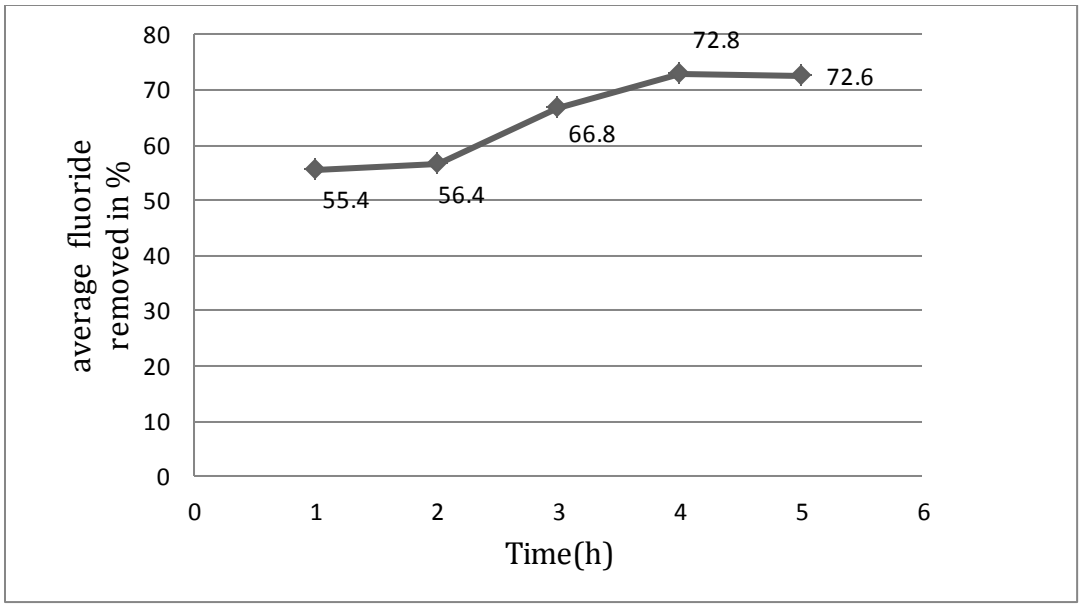

Figure 4. Plot of percent removal of fluoride ion on modified clay ceramic material (C3 fired at 400^0C) versus contact time (at pH = 7.03, dose = 5 g, and initial fluoride concentration = 5 mg/L)

4.2.3. Adsorption kinetics in batch experiments

According to the kinetic data obtained from the experiments, various models have been used to throw light on the mechanisms of adsorption and potential rate controlling steps. In this experiment, the pseudo-first-order, and pseudo-second-order models were used to test the mechanism of fluoride adsorption on modified clay ceramic material. From the data, q_e (calculated) and q_e (experimental) values were not in agreement with each other for the pseudo-first- order. Therefore, that indicates the adsorption of fluoride on modified clay ceramic material was not a first-order reaction. So the experimental data were analyzed using only a pseudo-second order Lagergren equation (eqn.13 given in literature).

The plot $\frac{t}{qt}$ versus t giving R^2 = 0.986 which was shown in Figure 5 and the values of q_e2 and the constant K_2 calculated from the slope and intercept of the plots were given in Table 2.

Figure 5. Shows that R^2 values are higher than those obtained from the first-order kinetics, in addition, theoretical and experimental q_e values are almost in agreement. Therefore, it was possible to prove that the adsorption process using modified clay ceramic material followed the second-order kinetic model.

This further suggests that the adsorption process is of a chemisorption type that would possibly involve exchange or sharing of electrons between the adsorbent and adsorbate.

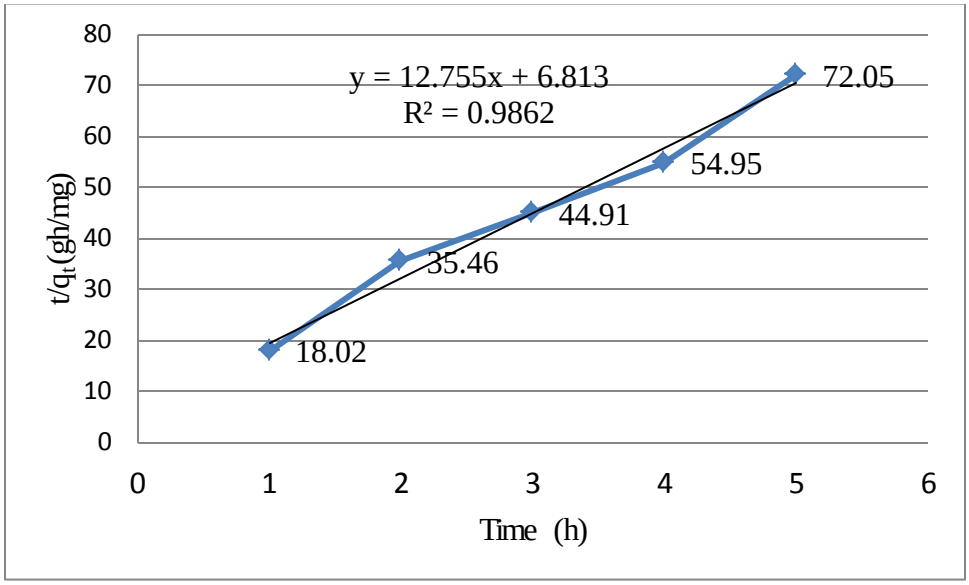

Figure 5. Plot of pseudo- Second-order kinetic modeling of fluoride adsorption on modified clay ceramic material adsorbent

4.2.4. Intra-Particle Diffusion

The possible contribution of Intra-Particle Diffusion, fluoride adsorption process was described as it was stated in the literature. As shown in Figure 6, the linear portion of plot was not passing through the origin, which indicates the fluoride adsorption on this adsorbent was a complex procedure. Both the surface adsorption as well as intra-particle diffusion contributes to the rate determining step. This indicates that although intera particle diffusion was involved in the adsorption process, it was not the sole rate limiting step. This also confirms that adsorption of fluoride ion on this adsorbent was multi- step process involving adsorption on external surface as well as diffusion in to the interior surface [67].

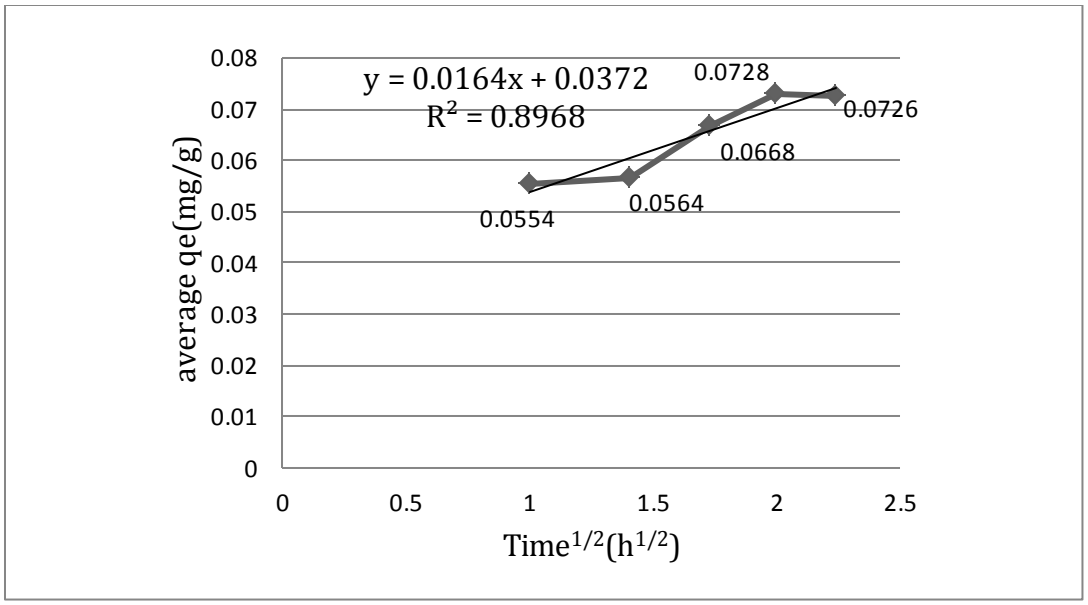

Figure 6. Plot of intra- particle diffusion of Fluoride ion on modified clay ceramic material

Table2. Values of pseudo- first-order, pseudo-second- order, and intra particle diffusion

	pseudo- first-order			pseudo-second- order			intra- particle diffusion		
C_o(mg/L)	q_e(mg/g)(calc.)	K_1 (1/h.)	R^2	q_e(mg/g) (calc.)	K_2[g/(mg h.)]	R^2	k_i(mg/g. $min.^{1/2}$)	C	R^2
5.0	$3.47x10^{-3}$	13.2	-0.169	0.0742	52.6	0.986	0.0164	0.0372	0.896

4.2.5. Effect of Adsorbent dose on Adsorption Capacity and Efficiency

The experimental result shows that all the modified clay ceramic exhibited decreased adsorption capacity and increased adsorption efficiency with increased adsorbent dosage (Figure7). It seems that increasing of fluoride removal efficiency with an increase in adsorbent dosage was due to the increased in availability of F^- binding sites. The decrease in capacity is due to the depletion of fluoride in the solution with increasing dose of adsorbent. Also when the dose is smaller, the number of fluoride ions is relatively higher compared to the availability of adsorption sites [68].

As it was observed on Figure 7, the percentage removal of fluoride was increased from 37.6% to 85% with an increase in adsorbent dose from 2.5 g to 10 g (2.5, 5, 7.5, and 10 g). The dose of adsorbent became higher and higher, more active sites over-lapping have been take place that might reduce the removal efficiency. Higher doses of the adsorbent will increase the amount of adsorbent and cost of recovery, without introducing a significant benefit in the amount of fluoride removed. This dose (10 g) may also be sufficient to reduce the amount of fluoride (9.12 mg/L, Table 1) to the desirable standard in dirking water (below 1.5 mg/L).

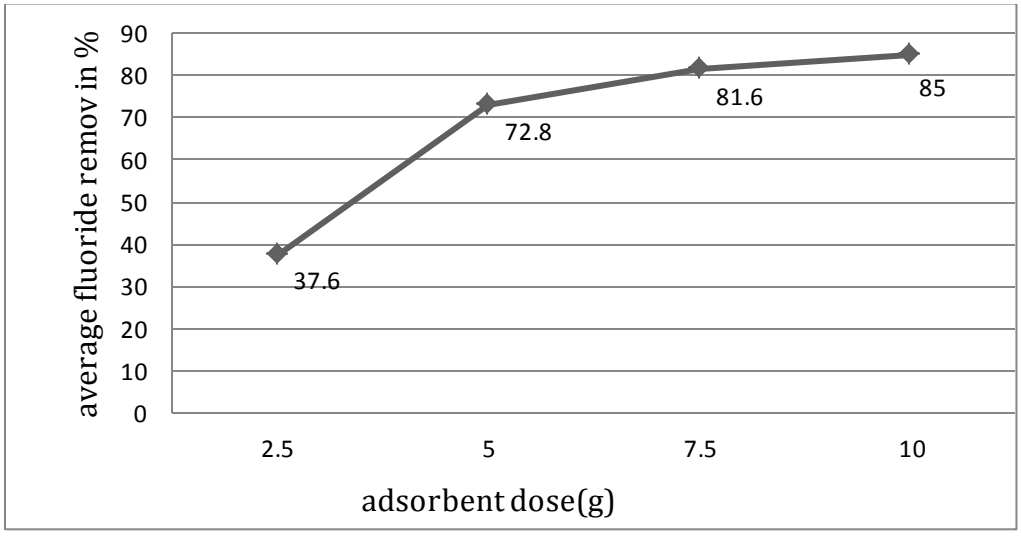

Figure 7. Plot of percent removal of fluoride ion on modified clay ceramic material (C3 fired at 400^0C) versus dose (at pH = 7.03, and contact time = 4h, initial fluoride conc. = 5 mg/L)

4.2.6. Effect of Initial Fluoride Concentration

The result of the effect of the initial fluoride concentration (Figure 8.) shows that, for a fixed mass of adsorbent, the fluoride removal capacity increased with increasing initial concentration. The increase in adsorption capacity with increase in initial fluoride concentration was due to increased diffusion of fluoride to adsorption sites and utilization of less accessible active sites of the adsorbent.

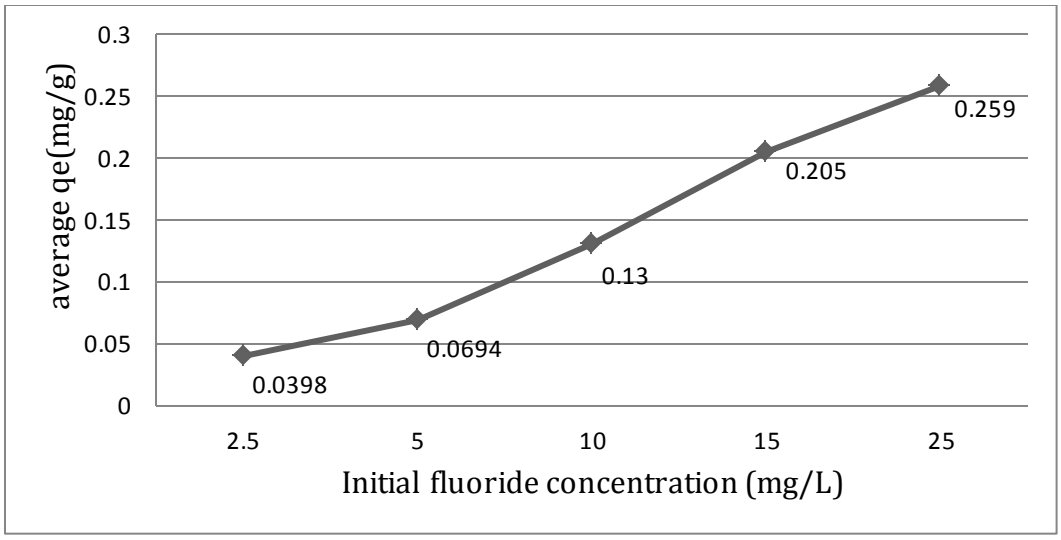

Figure 8. Plot of adsorption capacity versus initial fluoride concentration on modified clay ceramic material (C3 fired at 400^0C) (dose = 5 g, contact time = 4h, at pH = 7.03).

4.2.7. Adsorption Isotherm

Many studies show, adsorption isotherm curves for F^- adsorption onto metal oxide surfaces can be well represented by Langmuir model. Langmuir derived the model based on some reasonable assumptions like uniform adsorption surface, monolayer adsorption, and constant temperature and also assumed equal rates of adsorption and desorption at equilibrium. Using the Langmuir equation as given in literature (eqn. 3):

Plotting $\frac{Ce.}{qe}$ vs Ce the Langmuir constants, Q_e and b can be determined from the slope and intercept of the line.

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless separation factor or equilibrium parameter, R_L which is defined by (eqn.4 in literature):

So to confirm the favorability of the Langmuir adsorption process, R_L values at different adsorbate initial concentration were calculated (Table 3). The R_L value = 0.118, lie between 0 and 1 which confirm that the adsorption process of fluoride ion on modified clay ceramic material is favorable.

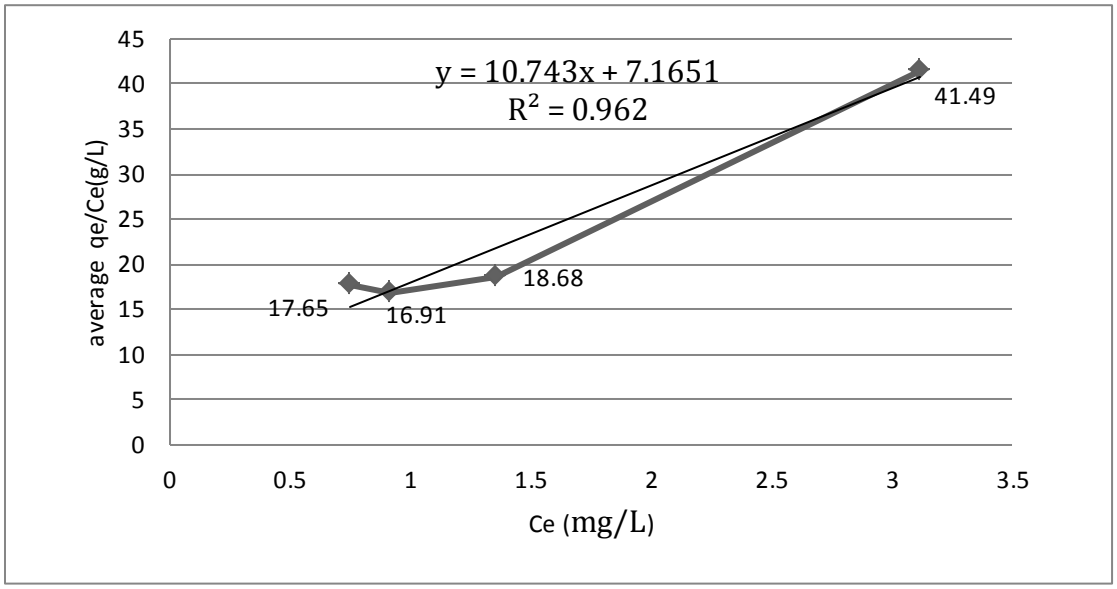

Figure 9. Plot of the Langmuir Adsorption Isotherms for fluoride ion concentration on modified clay ceramic material (C3 fired at 400^0C) (dose = 5 g, Initial fluoride conc. = 5 mg/L, contact time = 4h, pH = 7.03).

The results shown in the Figure 9 indicates that all experimental fluoride adsorption isotherm data have well fitted to the Langmuir isotherm, and the related correlation coefficients (R^2 = 0.962) (Figure 9.). Adsorption capacity (Q_e = inverse of slope of the Langmuir isotherm line) of 0.093 (Table 3.) was obtained for modified clay ceramic material (C3 heat treated at 400^0C).

Table3. Results of the Langmuir Adsorption Isotherms Studies at room temperature for adsorption of fluoride ion on modified clay ceramic material

Langmuir isotherm parameters					
Adsorbent	Equation	Q_e (mg/g)	b (L/mg)	R^2	R_L
C3 fired at 400^0C	y =10.743x + 7.165	0.093	1.50	0.962	0.118

The Freundlich isotherm takes in to account repulsive interaction between adsorbed solute particles and also account for surface heterogeneities. The equation is adequate to describe non-linear adsorption in narrow range of adsorbate concentration. The log form of the Freundlich isotherm equation (eqn.5) was used as stated on literature.

As 1/n value is between 0 and 1, (0<1/n <1), i.e. (1/n = 0.372) Freundlich isotherm is also favorable. The value of correlation coefficients, (R^2 = 0.962) for Langmuir isotherm is higher in comparison to that obtained for Freundlich isotherm. For the Freundlich model, the value of correlation coefficient (R^2) was 0.744. Hence, it can be concluded that Langmuir isotherm model is more suitable for adsorption of fluoride ion than Freundlich isotherm on the basis of the experimental study.

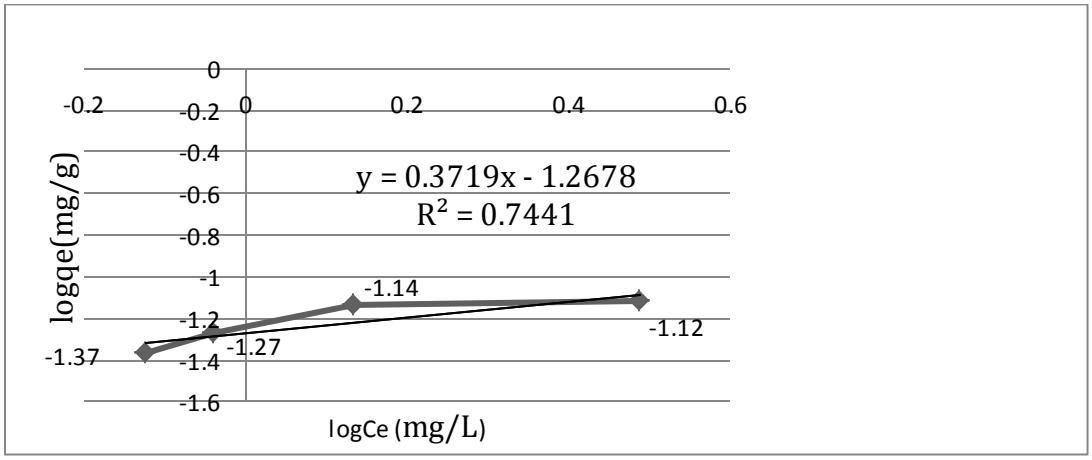

Figure10. Plot of the Freundlich adsorption isotherm for fluoride ion concentration on modified clay ceramic material (C3 fired at 400^0C) (dose = 5 g, Initial fluoride conc. = 5 mg/L, contact time = 4h, pH = 7.03).

Table 4. Results of the Freundlich Adsorption Isotherms Studies at room temperature for adsorption of fluoride ion on modified clay ceramic material

The Freundlich adsorption isotherm parameters				
Adsorbent	Equation	K_f (mg/g)	1/n	R^2
C3 fired at 400^0c.	Y = 0.372x – 1.268	0.534	0.372	0.744

4.2.8. Application to the Real Water Samples

The adsorption process was done (at temperature of 24 ± 2^0C, rotation speed of 400rpm for 10 min, optimized contact time of 4h, dose of adsorbent = 5 g, and at optimized pH of the real

water sample = 7.03). Real samples of water were collected from different locations of Oromia region East Showa district, near the way of car road from Adama to Harer, enterance to Welachit town around Didibsa, and around Maki town, Sarity ground water with fluoride ion concentration of (3.12 ± 0.03) mg/L, and (10.5 ± 0.03) mg/L, respectively, which were more than permissible limit of WHO. After adsorption the fluoride ion concentration of the two samples were measured and it was found that the fluoride ion concentration was decreased by modified ceramic material to (1.003 ± 0.124) mg/L and (3.040 ± 1.293) mg/L, respectively (appendix table 9). The modified clay ceramic material had good removal efficiency for collected real water samples.

4.3. Characterization of Modified Clay Ceramic Material

4.3.1. Complete silicate analysis for determination of major and minor oxides

Table 5. The results of Silicate analysis, in percent

Sample studied	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	P_2O_5	TiO_2	H_2O	LOI
C3	51.42	20.32	11.64	9.40	1.24	1.00	0.20	0.08	2.46	0.27	0.09	0.54

The Silicate analysis results of the prepared adsorbent (C3 fired at 400^0C) as indicated in table 5 shows the modified clay ceramic material adsorbent is the composition of 51.42% SiO_2, 20.32% Al_2O_3, 11.6% Fe_2O_3 and 9.40% CaO as major amount. The adsorbent modified clay ceramic material contain large amount of silica (SiO_2) which indicates mainly it composes sandy clay. Due the presence relatively, 11.64% iron oxide (Fe_2O_3), the adsorbent material contains red clay.

4.3.2. XRD patterns for Modified Clay Ceramic Material (C3 fired at 400^0C)

The XRD technique has been one of the most prominent for the identification of crystal phase of the adsorbent. Figure 11a and b show the X-ray diffraction pattern of modified clay ceramic material before and after adsorption of fluoride ions. It is clear that the XRD patterns crystal structure of the modified clay ceramic material has not been significantly changed after the adsorption process. According to the XRD analysis (Figures 11a. and b.), multiple peaks were observed and indicates the presence of various oxides phases (SiO_2, Al_2O_3, Fe_2O_3 and CaO as

dominant oxides (table 5.), this indicates heterogeneous surface sites for adsorption. This may not also indicate that fluoride had caused crystalline phase transformation of the modified clay ceramic material [69]. The possibility of calcium fluoride, ferric fluoride and aluminium fluoride being formed by the reaction of fluoride with soluble or exchangeable cations in at or near neutral pH, has been reported before [70]. A surface complex formation model (ligand exchange model) has been proposed [71] to describe fluoride adsorption on metal oxides as:

$MO^- + H^+ \leftrightarrow MOH$……..…… (eqn.15)

$MOH + H^+ \leftrightarrow MOH_2^+$……..……..…… (eqn.16)

$MOH + F^- \leftrightarrow MF + OH^-$ ……..… (eqn. 17)

$MOH_2^+ + F^- \leftrightarrow MF + H_2O$……(eqn.18)

Where, M represents the metal ion (Si, AI, Fe, Ca etc.) and MOH_2^+, MOH and MO^-were groups generated in the process of the fluoride adsorption.

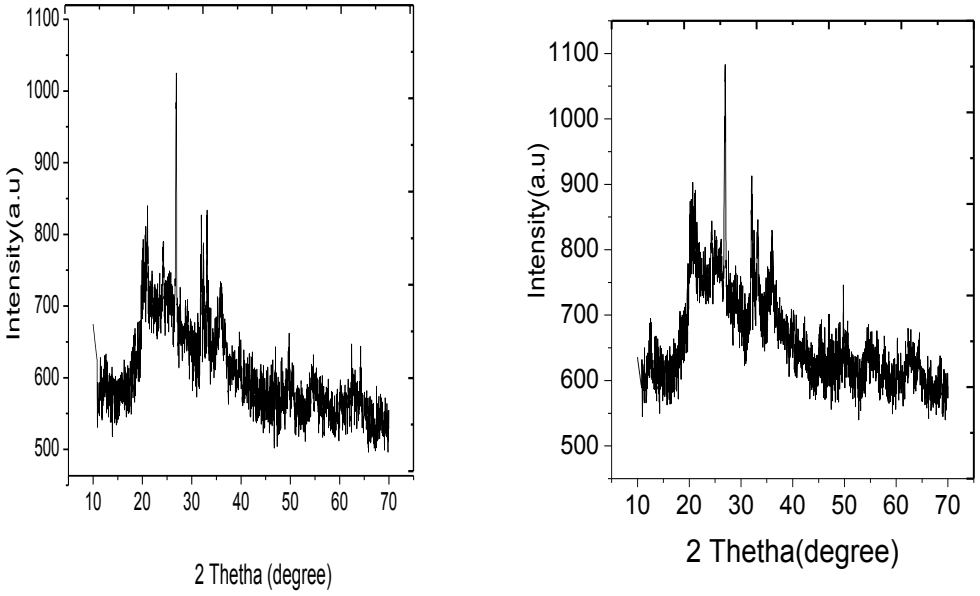

Figure 11. XRD analysis of C3 fired at 400^0C, a) before adsorption, b) after adsorption

4.3.3. FT-IR spectrum for Fluoride Adsorption

FT-IR identify the type of functional groups exist in the adsorbent. Figure 12a and b, the shift in stretching frequency observed between 3600 and 4000 cm^{-1} to between 3600 and 3800 cm^{-1} are assigned to the involvement of hydroxyl groups. The two peaks at 3620 and 3696 cm^{-1} were associated with the strong Hydrogen bonded -OH stretching groups (Figure 12b.) [72], the

adsorption bands at 3430 cm^{-1} show the characteristics of –OH group. FT- IR spectrum revealed that the -OH groups on the adsorbent surface were involved in the sorption of fluoride. Anion exchange and electrostatic interaction were suggested as the main mechanisms involved in the sorption of fluoride on adsorbent.

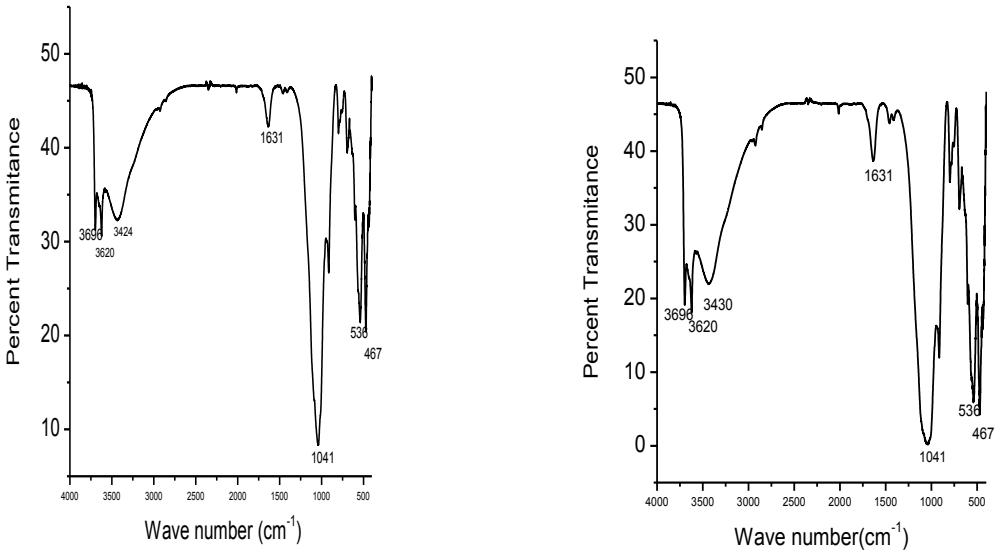

Figure 12. FT-IR analysis of C3 fired at 400^0C, a) before adsorption, b) after adsorption

The change of stretching frequency of fluoride treated modified clay Ceramic material confirm the chemical modification.

4.4. Comparison between various adsorbents used for fluoride removal

The adsorption capacity of different clays, soils and also other adsorbent types from other studies have been compared with the values obtained by this study. The values were presented in Table.7. The comparison gives rough indication of F^- adsorption trends for a wide variety of clays, soils and other adsorbents from different countries. The adsorption capacities obtained for modified clay ceramic material fall in the range for those of mentioned adsorbents listed in the table, which showed values in the earlier studies

Table 6. Comparison between various adsorbents used for fluoride removal.

Adsorbent name description.	Adsorption capacity(mg/g)	Reference
$Al(NO_3)_3$ in soil pot	0.46	[73]
Activated carbon	1.11	[74]
Calcite	0.39	[75]
Red mud	$6.28x10^{-3}$	[76]
Charcoal	$8.8x10^{-5}$	[76]
Muger clay(Ethiopia	0.19	[77]
Clay pot (Ethiopia)	0.07	[77]
Modified clay ceramic materials	0.093	This thesis

5. CONCLUTIONS AND RECOMENDATIONS

5.1. Conclusions

This study shows that the modified clay ceramic material with ratio of clay, grog, saw dust and bone char, 3:3:3:1, respectively (C3 fired at 400^0C) was found to have better potential adsorbents for F^- from drinking water. The XRD and the complete Silicate analysis were found that the prepared adsorbent was composed of the oxides of metals like Si, Al, Fe, Ca also the presence of OH^- functional groups were indicated by FT-IR analysis.

The pH of the solution was found to be the most important factor affecting adsorption potential. Results obtained show that better adsorption was achieved in the acidic range, pH = 3 to 7 with maximum adsorption efficiency (91.6%) at pH = 3 and (73%) at pH = 7.03, but according to the WHO guideline, drinking water with a neutral pH value 7.0 to 8.5 is desirable for adsorbents to remove fluoride ion. So, the investigation of the effect of all parameters were done at pH = 7.03. The fluoride adsorption capacity was increased with increasing initial fluoride concentration. Both Langmuir and Freundlich models were tested for the adsorption isotherm studies and the experimental results indicated that Langmuir model was more favorable for the removal of fluoride ion. The kinetic studies showed that the adsorption reaction of fluoride removal can be well described by a pseudo - second-order rate equation. The modified clay ceramic material had good removal efficiency for the collected real water samples. It reduces the fluoride ion concentration of the real water samples to desirable fluoride ion containing drinking water. In comparison with other adsorbents from different countries, the adsorption capacity obtained for modified clay ceramic material fall in the range for those of adsorbents, which was shown in the earlier studies values

5.2. Recommendations and future works

In this paper only three different volume ratios of component mixtures were prepared and one was identified and considered for the absorption process. So other different ratio component mixture of adsorbents should be identified and assessed with geologist and other related specialist. It is recommended for this modified clay ceramic material adsorbent the effect of coexisting ions in the water such as Cl^-, CO_3^{2-}, PO_4^{3-}, SO_4^{2-} and

column experiments should be studied further in full scale to determine optimum domestic defluoridation column parameters (batch type, bed height, flow rate, particle size). The regeneration should be studied and its procedure should be optimized and safe disposal methods of exhausted adsorbents and regenerates should be identified.

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APPENDICES

Lists of Appendix Tables

Table1. Average values of Percent of adsorption, adsorption capacity of modified clay ceramic material with value of pH vary, at (dose = 5 g, contact time = 4 h, initial fluoride concentration = 5 mg/L)

pH values	measured Values of C_e (mg/L) (triplicate)			Average C_e (mg/L) (Mean ±SD)	Average percent of adsorption	Average q_e(mg/L)
	C_e 1	C_e 2	C_e 3			
3	0.459	0.397	0.422	0.422±0.027	91.6	0.0916
4	0.556	0.645	0.602	0.60±0.364	88	0.0880
5	0.509	0.490	0.531	0.510 ±0.019	89.8	0.0898
6	0.811	0.677	0.815	0.682 ±0.045	86.4	0.0864
7	1.090	1.339	1.600	1.341 ±0.060	73.0	0.0730
8	1.642	1.501	1.568	1.570 ±0.069	70.7	0.0707

Table 2. Average values of percent of adsorption, adsorption capacity, and q_t (mg/g) with contact time (dose of adsorbent = 5 g, pH of the solution = 7.03, initial F^- concentration = 5 mg/L)

Contact time (h.)	measured Values of $C_{e(}$ mg/L) (triplicate)			Average C_e(mg/L) (Mean±SD)	Average Percent of adsorption	Average q_t(mg/g)
	Ce 1	Ce 2	Ce 3			
1	2.231	1.969	2.490	2.230 ±0.820	55.4	0.0554
2	2.302	2.178	2.061	2.18±0.120	56.4	0.0564
3	1.657	1.423	1.901	1.661 ±0.401	66.8	0.0669
4	1.341	1.362	1.388	1.362 ±0.001	72.8	0.0728
5	1.362	1.408	1.380	1.38±0.005	72.6	0.0726

Table 3. Average values of percent of adsorption, adsorption capacity, q_t (mg/g) and t/q_t with contact time(dose of adsorbent = 5 g, pH of the solution = 7.03, initial F^- concentration =5 mg/L)

Contact time (h.)	measured Values of C_e (mg/L) (triplicate)			Average C_e(mg/L) (Mean±SD)	Average percent of adsorption	Average q_t(mg/g)	t/q_t(g h./mg)
	Ce 1	Ce 2	Ce 3				
1	2.231	1.969	2.490	2.230 ±0.820	55.4	0.0554	18.02
2	2.302	2.178	2.061	2.18±0.120	56.4	0.0564	35.46
3	1.657	1.403	1.901	1.661 ±0.401	66.8	0.0669	44.91
4	1.341	1.362	1.378	1.362 ±0.001	72.8	0.0728	54.95
5	1.362	1.408	1.380	1.38±0.005	72.6	0.0726	72.05

Table 4. Average values of percent of adsorption, adsorption capacity, q_t (mg/g) and $t^{1/2}(h^{1/2})$ with contact time (dose of adsorbent = 5 g, pH of the solution = 7.03, initial F^- concentration =5 mg/L)

Contact time (h.)	measured Values of C_e (mg/L) (triplicate)			Average C_e(mg/L) (Mean±SD)	Average percent of adsorption	$t^{1/2}(h^{1/2})$	Average q_t(mg/g)
	Ce 1	Ce 2	Ce 3				
1	2.231	1.961	2.490	2.230 ±0.820	55.4	1	0.0554
2	2.302	2.178	2.061	2.18±0.120	56.4	1.41	0.0564
3	1.657	1.403	1.901	1.661 ±0.401	66.8	1.73	0.0668
4	1.341	1.362	1.378	1.362 ±0.001	72.8	2	0.0728
5	1.362	1.408	1.380	1.38±0.005	72.6	2.24	0.0726

Table 5. Average values of adsorption capacity and Percentage of adsorption of the best adsorbent with different dose(contact time= 4h, pH of the solution = 7.03, initial F^- concentration = 5 mg/L)

Adsorbent dose(g)	measured Values of C_e (mg/L) (triplicate)			Average C_e(mg/L) (Mean±SD)	Average percent of adsorption	Average q_e(mg/g) values
	Ce 1	Ce 2	Ce 3			
2.5	3. 142	3.122	3.096	3.12±0.000	37.6	0.0752
5	1.283	1.357	1.440	1.36±0.071	72.8	0.0728
7.5	1.068	0.793	0.917	0.92±0.071	81.6	0.0544
10	0.880	0.749	0.621	0.75±0.130	85	0.0425

Table 6. Average values of adsorption capacity and Percentage of adsorption of the best adsorbent with different initial fluoride ion concentration (dose of adsorbent = 5 g, pH of the solution = 7.03, contact time = 4h)

C_o (mg/L)	measured Values of C_e (mg/L) (triplicate)			Average C_e(mg/L) (Mean±SD)	Average percent of adsorption	Average q_e(mg/g)
	C_e 1	C_e 2	C_e 3			
2.5	0.901	0.509	0.121	0.511 ±0.291	79.96	0.0398
5	1.593	1.532	1.407	1.533 ±0.067	69.4	0.0694
10	3.480	3.502	3.458	3.48±0.016	65.2	0.130
15	4.040	4.758	5.440	4.762 ±0.544	68.67	0.205
20	7.042	7.030	7.014	7.031 ±0.02	64.85	0.259

Table 7. Average values of the Langmuir adsorption Isotherms for fluoride ion concentration on modified clay ceramic material (dose of adsorbent = 5 g, pH of the solution = 7.03, contact time = 4h)

Dose of adsorbent(g)	measured Values of C_e (mg/L) (triplicate)			Average C_e(mg/L) (Mean$\pm SD$)	Average q_e(mg/g)	Average C_e/q_e(g/L)
	Ce 1	Ce 2	Ce 3			
2.5	3. 142	3.122	3.096	3.12 ± 0.000	0.0752	41.49
5	1.283	1.357	1.440	1.36 ± 0.071	0.0728	18.68
7.5	1.068	0.793	0.917	0.92 ± 0.131	0.0544	16.91
10	0.880	0.749	0.621	0.75 ± 0.130	0.0425	17.65

Table 8. Average values of the Freundlich adsorption isotherm for fluoride ion concentration on modified clay ceramic material (dose of adsorbent = 5 g, pH of the solution = 7.03, initial F^- concentration =5 mg/L)

Dose of adsorbent(g)	measured Values of C_e (mg/L) (triplicate)			Average C_e(mg/L) (Mean$\pm SD$)	logC_e(mg/ L)	Average q_e(mg/g)	logq_e(mg/g)
	C_e1	C_e 2	C_e 3				
2.5	3. 142	3.122	3.096	3.12 ± 0.000	0.49	0.0752	-1.12
5	1.283	1.357	1.440	1.36 ± 0.071	0.134	0.0728	-1.14
7.5	1.068	0.793	0.917	0.92 ± 0.131	-0.04	0.0544	-1.27
10	0.880	0.749	0.621	0.75 ± 0.130	-0.124	0.0425	-1.37

Table 9. Measured Values of C_o (mg/L), C_e (mg/L), percent of F^- removed, and q_e (mg/g) of sample C3 fired at 400^0C(using dose of adsorbent = 5 g, contact time = 4h, pH of the real water adjusted =7.03).

Collected real water sample	Initial F^- concentration C_O (mg/L)	Triplet measured final F^- concentration, C_e (mg/L)		Average Percent of F^- removed	Average Adsorption capacity, q_e(mg/g)
Diddibsa real water sample	3.121	1	0.471	67.8%	0.0678
		2	1.206		
		3	1.324		
		Mean	1.003		
		SD	0.124		
Sarity real water sample	10.501	1	4.260	71.04%	0.0710
		2	3.176		
		3	1.684		
		Mean	3.040		
		SD	1.293		