ADDIS ABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL AND BIO-ENGINEERING

Characterization and Optimization of Iron (III) Modified Bentonite Adsorbent for Efficient Removal of Fluoride from Aqueous Solution

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A Thesis Submitted to
The School of Chemical and Bio Engineering, Addis Ababa Institute of Technology, Addis Ababa University

Presented in Partial Fulfilment of the Requirement for the Degree of Master of Science in Chemical Engineering (Process Engineering Stream)

Addis Ababa University
Addis Ababa, Ethiopia
June 2018

Addis Ababa University
Addis Ababa Institute of Technology
School of Chemical and Bio Engineering

This is to certify that the thesis prepared by Frehiwot Tesfamariam, entitled: “*characterization and optimization of iron (III) modified bentonite adsorbent for efficient removal of fluoride from aqueous solution”* and submitted in partial fulfillment of the requirements for the degree of Masters of Science (Chemical and Bio Engineering, Process stream) complies with the regulation of the university and meets the accepted standards with respect to originality and quality.

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DECLARATION

I declare that this thesis entitled “*characterization and optimization of iron (III) modified bentonite adsorbent for efficient removal of fluoride from aqueous solution”* has not been submitted in any form for another degree, diploma or an award at any university or other institution of the tertiary education. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due reference to the literature and discussions. Information taken from published and unpublished work of others has been acknowledged in the text and a list of references is given.

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

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Date: July 2018

ACKNOWLEDGMENT

First and foremost, I would like to thank God who has given me the strength, wisdom and health to complete this thesis. I sincerely would like to express my gratitude to my advisor Dr. Ing. Zebene Kiflie for his valuable guidance, encouragement and insights throughout the study. I would also like to acknowledge Dr. Beteley Tekola (Assi. Prof.) who has given me the title and supported me throughout my path. Furthermore, I would like to acknowledge AAIT, School of Chemical and Bio-engineering lab assistants for their technical support. I am deeply grateful for my family and friends for their continuous encouragement and endless moral support. Finally, I want to thank Addis Ababa City Government, Environmental Protection Authority for their cooperation in fluoride analysis.

ABSTRACT

The main objective of the research was to prepare Fe^{3+}-modified bentonite clay to be used as an adsorbent by optimizing the iron three loading through batch wise variation of agitation time, adsorbent dose, and iron three concentration for efficient removal of fluoride from aqueous solution. Physicochemical characterization of raw and Fe^{3+}-modified bentonite clay was done by X-ray diffraction, Fourier transformed infrared spectroscopy, Cation exchange capacity, and pHpzc. To investigate the performance of the prepared Fe^{3+}-modified bentonite adsorbent the effect of contact time, adsorbate concentration, adsorbent dosage and pH were evaluated. The adsorption capacity of fluoride by Fe^{3+}-modified bentonite was observed to be 3.37 mg/g at (26±2) ^{0}C temperature.

Design-Expert 7.0.0 three-level-full factorial RSM was applied for experimental design and statistical analysis of results. A total of 32 experiments were conducted at conditions of adsorbent dosage 1, 1.5 and 2 g, initial fluoride concentration 5, 15 and 25 ppm, and 15, 30 and 45 min of contact time. From the analysis of experimental results optimum conditions for efficient removal of fluoride were obtained at 2 g adsorbent dosage, 15 ppm adsorbate concentration and 15 min contact time which resulted 99.56% F^- removal. Kinetic studies revealed that fluoride adsorption fitted well to pseudo-second-order model and Freundlich adsorption isotherm. Fe^{3+}-modified bentonite showed a good stability in removing fluoride from natural fluoride containing water with > 66% F^- removal. The fluoride loaded adsorbent was reused and also regenerated using 0.5 M NaOH. Thus, this study has proved that Fe^{3+}-modified bentonite is a promising low cost adsorbent with high adsorption capacity of fluoride and can be a candidate for conventional de-fluoridation methods.

Key words: Adsorption; Batch experiments; Fluoride; Bentonite clay; Cation exchange capacity; Kinetics; Isotherm

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LIST OF ACRONYMES

AAS	Atomic Absorptive Spectrometry
AAU	Addis Ababa University
ANOVA	Analysis of Variance
CEC	Cation Exchange Capacity
EC	Electrical Conductivity
FT-IR	Fourier Transform Infrared Spectroscopy
Ppm	Parts per million
PZC	Point of Zero Charge
RSM	Response Surface Methodology
S/L	Solid to Liquid ratio
TDS	Total Dissolved Solids
WHO	World Health Organization
XRD	X-ray Diffraction

CHAPTER ONE

1. INTRODUCTION

1.1. Background

Water is one of the most important and indispensable natural resource present in earth. It nourishes and sustains life on earth and is available in abundance as a free gift of nature. Though the availability of water is abundant, amount of fresh water is very less. The earth's surface is covered with 71% of water. Out of which 96.5% is covered with oceans, 0.9 % with other saline water and 2.5% is fresh water (Buddharatna J. et al., 2014). Ground water is often contaminated by natural (geological formations, volcanoes activities, etc.) as well as man-made (industries, power plants, etc.) sources. Its contamination by fluoride is one of the major problems in Ethiopia.

Fluorine is 13th most abundant element on earth and it does not occur in the elemental state in nature because of its high reactivity. Fluorine accounts for about 0.3 g/kg of the earth's crust and exists in the form of fluorides in a number of minerals, of which fluorite (CaF_2), cryolite (Na_3AlF_6) and fluorapatite ($Ca_5(PO_4)_3F$) are the most common. It exists as the anion fluoride (F^-) in natural waters, with higher concentrations expected in ground waters (Dace et al. 2002).

According to UNESCO (Feenstra & Griffioen, 2007) more than 200 million people worldwide rely on drinking water with F^- concentrations exceeding the present World Health Organization guideline of 1.5 mg/l (WHO, 2008). In 2006, the WHO registered 28 countries were associated with exposure to high fluoride concentration in drinking water. Among these, the most affected were India, Ethiopia, and China (Farewell et al. 2006).

In the main Ethiopian Rift Valley about 14 million people rely on water sources that contain high concentrations of fluoride (Tekle-Haimanot R. et al., 2006). According to the report, 100 % of the hot springs, 75 % of the lakes, 54 % of the shallow wells and 35 % of the bore holes characterized in the main Ethiopian Rift Valley contain above 5.0 mg/L fluoride.

Daily intake of fluoride (primarily through drinking water and beverages but also via food) put a large part of the rural population in the Ethiopian Central Rift Valley at risk of dental and skeletal fluorosis. Excessive contamination of ground water by fluoride and its adverse effect on human health in many parts of the world has led to the importance of de-fluoridation studies.

Treatment processes for fluoride contaminated aqueous solution include chemical precipitation, ion exchange, membrane separations (ultrafiltration, reverse osmosis, electro dialysis) and adsorption. Adsorption is considered to be the simplest and most cost effective technique relatively. The removal of fluoride ion from aqueous solutions using different adsorbents is currently of great interest (Bailey et al., 1999)

Adsorption is a process in which atoms, ions and molecules adhere on the surface of a material. Due to this, a layer of adsorbate (atoms to be adsorbed) is formed on the adsorbent (material which adsorbs). Adsorption is surface phenomenon. The process of adsorption arises due to presence of unbalanced or residual forces at the surface of liquid or solid phase. These unbalanced residual forces have tendency to attract and retain the molecular species with which it comes in contact with the surface. There are two types of adsorption; physical adsorption which involves adsorption of gases on solid surface via weak van der Waal's forces and chemical adsorption in which the gas molecules or atoms are held to the solid surface via chemical bonds. Several studies have identified adsorbents that are suitable for de-fluoridation, this include activated alumina, bone char, raw bauxite, activated carbon, natural clays etc.

Natural clays are abundantly available low-cost natural resources which are non-toxic to ecosystem. Clays have been good adsorbents because of the existence of several types of active sites on the surface, which include Bronsted and Lewis acid sites and ion exchange sites. Their sorption capabilities come from their high surface areas and exchange capacities (S. Babel and T.A. Kurniawan, 2003). The most common and effective type of clay used in water purification is bentonite.

Bentonite is an absorbent aluminum phyllosilicate, which is essentially impure clay consisting mostly of montmorillonite. Bentonite only forms in the presence of water. The structure of montmorillonite is a gibbsite layer sandwiched between two silica sheets to form the structural unit (Zakaria R. M. et al., 2009). The substitutions are mainly with in the octahedral layer (Mg^{2+}, Fe^{2+}) and to a much less extent with in the silicate layer (Al^{3+}, Si^{4+}).

For industrial purposes, two main classes of bentonite exist; sodium and calcium bentonite. (Lagaly G., 1995). Bentonite has proven to be a promising economic material for de-fluoridation of ground water due to due to its abundance, availability, and lower cost than chemicals fulfilling economic benefits of the operators as well as environmental concerns (Bellir K, Bencheikh-Lehocine M. & Meniai A-H., et. al., 2010).

1.2. Statement of the problem

Excessive fluoride exposure may cause irreversible demineralization of bone and tooth tissues, a condition known as Fluorosis. Fluorisis is endemic in at least 25 countries across the globe and has affected millions of people (Rao N. C. R., 2003). It is caused by high concentration of fluoride above 1.5 mg/l in drinking water (Ayoob S. & Gupta A. 2006). In Ethiopia, the regions that are facing excessive fluoride in ground-water are Afar, Oromia and Southern Nations and Nationalities Regional States. These regions are located in the Ethiopian Rift Valley part of the Great African Rift Valley (Tekle-Haimanot R. et al., 2006).

The high levels of fluoride occur due to the presence of high fluoride rocks and minerals in the vicinity of the aquifers. Fluoride levels greater than 1.5 mg/l have been found to be harmful to human health problems like pitting and loss of enamel, crippling skeletal fluorisis, non-skeletal effects such as kidney damage, infertility, birth defects, endocrine, thyroid and liver disorders and interference with metabolic processes (WHO 2008). Considering the fact that fluorisis is an irreversible condition and has no cure, it is imperative to treat such water before it is consumed. So, efforts are being made towards de-fluoridation of drinking water, combating the debilitating fluorisis and taking steps to prevent and control the diseases.

The different technologies used for removal of fluoride from water such as reverse osmosis, activated alumina, and synthetic resins are difficult to implement in Ethiopia due to their high operational and maintenance cost, the need for skilled manpower for system operation and maintenance, high electric power consumption and also 20-40% of water is lost in the process. (S. Kumar and K. Gopal, 2000). Simple and low cost technologies such as Nalgonda technique have been tried in Ethiopia but have proven in efficient due to g eneration of higher quantity of sludge, large amount of alum needed to remove fluoride, High residual aluminum is reported in treated water by some authors (Amrit Tewari and Ved Prakash Jalili 1986). Bone char is also another low cost adsorbent however 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-char may invite cultural and religious objections (M.J. Larsen and E.I.F. Pearce 2002).

Activated carbon is the most widely used absorbent due to its high capacity of adsorption and its effectiveness and versatility (Chen Y-M, Tsao T-M., & Wang M-K. 2011). However due to its disposal problem, difficulty of regeneration, slow adsorption kinetics and also the high cost resulted a search for cheap, effective adsorbents such as clay derivatives (Abd El-Latif MM et. al., 2010). In recent years, the use of clay materials to replace commercially available adsorbents has attracted much attention due to lack of toxicity, local availability (abundance), high cation exchange capacity (CEC), and chemical & mechanical stability (Murray H., 2002), environmental friendliness in addition to their reduced side effects, low cost and high adsorption capabilities and operational easiness (Chen Y-M et. al., 2011).

1.3. Objectives of the research

1.3.1. General objective

The main objective of this study is to characterize and optimize Fe (III) modified bentonite from locally available calcium bentonite clay to be used as an adsorbent for efficient removal of fluoride ions from aqueous solution.

1.3.2. Specific objectives

The specific objectives are:

- To prepare modified bentonite clay by optimizing the loading of Fe^{3+}.
- To characterize the physicochemical and mineralogical composition of the raw and modified bentonite clays using XRD, FTIR, CEC, and pHpzc analysis.
- To optimize and evaluate the F^- adsorption capacity of raw and modified bentonite clay in aqueous solution and in surface water.
- To study the main and interaction effects of variables (adsorbent dosage, adsorbate concentration and contact time) on F^- removal from aqueous solution using a response surface methodology (RSM).
- To study the reusability and regenerate modified bentonite.
- To investigate the adsorption kinetics and isotherms.

1.4. Significance of the study

This research has benefits for many Ethiopian communities which are affected by fluoride containing water. The Ethiopian government is in need for enhancing de-fluoridation methods that are efficient, economic and environmentally friendly for the sake of the people. Hence, this study should be significant in the sense that it will:

- Provide a means to exploit and manage local resources.
- Provide technically and economically feasible option for de-fluoridation processes through the modification of natural bentonite clays.
- Add knowledge and understanding of the modification process of bentonite clay by Fe (III) sulphate solutions.
- Provide a new potential of modified bentonite clay for efficient removal of fluoride from aqueous solutions.
- Provide useful knowledge on factors that might have impact on the removal efficiency.
- Create an understanding of the process that is simple to operate and maintain; which is also socially acceptable.

1.5. Scope of the study

The main focus of this research was directed towards the modification and characterization of bentonite clay. Through this study, the modification effects of bentonite clay by the impregnation of Fe^{3+} ion was investigated for the removal of fluoride ions from aqueous solution through batch experiments. The effect of contact time, adsorbent dosage, adsorbate concentration, and pH was studied. The characterization of the raw and modified bentonite clay before and after modification was evaluated by exploring the structural changes via a series of tests like X-ray diffraction, Fourier transformed infrared spectroscopy, Cation exchange capacity and pHpzc.

CHAPTER TWO

2. LITERATURE REVIEW

2.1. Water resource

Water is a prime natural resource and a major constituent of all living beings. Water is available in two basic forms; surface-water and ground-water. Water is used for various purposes ranging from domestic, agricultural, industrial and allied purposes. Water is one of the fundamental needs on the globe. It is probably the only natural resource to touch all aspects of human civilization from agricultural and industrial development to cultural and religious values embedded in society. Over the past few decades, the ever growing population, urbanization, industrialization and unskilled utilization of water resources have led to the degradation of water quality and reduction in per capita availability in various developing countries. Due to various ecological factors, either natural or anthropogenic, the ground-water is getting polluted because of deep percolation from intensively cultivated fields, disposal of hazardous wastes, liquid and solid wastes from industries, sewage disposal, surface impoundments, etc. Thus, exploitation of safe water sources has been a global challenge for many countries like Ethiopia. The increasing demand of clean water has attracted much of the attention of government organizations and water industries to develop cost-effective technologies for water treatment.

2.2. Fluoride and Fluorisis

Fluoride is a salt of an element called fluorine. Fluorine is one of the most highly reactive element of halogen family. It does not exist as a free element. It exists in minerals, such as fluorspar, cryolite and fluor apatite and in water mainly as fluoride associated with monovalent cations, such as NaF and KF.

Fluoride is commonly observed in ground water due to natural and anthropogenic influences during its formation. Fluoride can get leached out and dissolved in ground water during the natural movement of water in the soil substrata.

High fluoride content is found mostly in calcium-deficient ground waters in many basement aquifers, such as granite, geothermal waters and sedimentary basins. Natural phenomenon includes mainly weathering of rocks, volcanoes and geothermal activities.

Excessive fluoride exposure may cause irreversible demineralization of bone and tooth tissues, a condition known as Fluorosis. Fluorisis is endemic in at least 25 countries across the globe and has affected millions of people (Rao N. C. R., 2003). It is caused by high concentration of fluoride above 1.5 mg/l in drinking water (Ayoob S. & Gupta A. 2006). The WHO guideline recommends the fluoride content in drinking water to be in the range of 1.0–1.5 mg/L (WHO 2008). Thus, management of excess fluoride in ground water is of prime importance.

The problem of fluorosis has a definite relationship with the following factors:

1. Fluoride concentration in drinking water
2. Period of exposure
3. Climatic factors such as temperature, pressure, etc.
4. Fluoride exposure from other sources and
5. Nutritional status

2.2.1. Chemistry of fluoride in water

The fluoride content of surface and ground-water is a function of many factors such as availability and solubility of parent fluoride minerals with which this water come in contact, rock porosity, velocity of flowing water, temperature of the interaction between the rocks and the water, pH of the water and concentration of calcium ions present in the water. When a fluoride compound is dissolved in water, the element fluorine will be present mainly as fluoride ions. However, depending on the ionic concentrations and pH of the solutions the fluoride is also present in solution as HF_2 and undissociated HF. Now if it is assumed that the calcium fluoride is representative of the natural fluorides while sodium fluoride that of artificial fluoride, these compounds dissolve in water under the equivalent conditions such that they ionize as shown in the following equations.

Calcium fluoride:

$\mathrm{CaF_2} \rightarrow \mathrm{Ca^{++}} + \mathrm{2F^-}$ .... (2.1)

$\mathrm{F^-} + \mathrm{H^+} \rightarrow \mathrm{HF}$ .... (2.2)

$\mathrm{HF} + \mathrm{F^-} \rightarrow \mathrm{HF_2}$ .... (2.3)

Sodium fluoride:

$\mathrm{NaF} \rightarrow \mathrm{Na} + \mathrm{F}$ .... (2.4)

$\mathrm{F^-} + \mathrm{H^+} \rightarrow \mathrm{HF}$ .... (2.5)

$\mathrm{HF} + \mathrm{F}^{-} \rightarrow \mathrm{HF}_2$ …………………………………………………………………………… (2.6)

In both these instances, fluoride is yielded as F^-, HF, and HF_2 and these will be chemically and physiologically identical with their equivalents irrespective of the two compounds they are derived from (Killedar D.J. & Bhargava D. S., 1998).

2.2.2. Fluoride containing water occurrence in the World

Fluoride occurs in ground water all over the world. Geographical areas around the world that have high concentration of fluoride include: Syria, Jordan, Egypt, Libya, Algeria and Morocco. It also includes the Rift Valley areas in Africa from Sudan through Kenya to Tanzania and Malawi. Another geographical area extends from Turkey through Iraq, Iran and Afghanistan to India, Northern Thailand and China (Mosonik 2015).

2.2.3. Fluoride containing water occurrence in Ethiopia

According to the Water Supply and Sanitation Directorate National Fluorisis Mitigation Project Office (2013), Ethiopia, the regions that are facing excessive fluoride in ground water are Afar, Oromia and Southern Nations and Nationalities Regional States (SNNPR).

Table 2.1: Fluoride content of water in various areas of Ethiopian Rift Valley

Sample sites	Fluoride (mg/l)
Gewane (town)	0.7-2.5
Abadir (farm)	4.0
Koka (town)	26
Alem tena (village)	9
Abernosa (village)	36
Jido (village)	33.6

Source: Tekle-Haimanot R. et al., 2006.

These regions are located in the Ethiopian Rift Valley part of the Great African Rift Valley (Tekle-Haimanot R. et al., 2006). Since the fluoride level of ground-water in the Rift Valley areas is high, the risk of fluorisis in Ethiopia is mainly observed in the rift valley areas and is spread over several regional states (Steenbergen F. V., Tekle-Haimanot R. & Aschalew S., (2011).

The high fluoride concentration in the ground-water of the Rift Valley are believed to be enhanced due to the high CO_2 pressure, hydrothermal heating, and low calcium and alkalinity in closed-basin lakes result from evaporative concentration.

2.2.4. Health effects of fluoride

Fluoride route to human is mainly through consumption of water, vegetables, fruit and milk. Water is considered to be the largest contributor for daily fluoride intake amounting about 75-90 %. Fluoride content in drinking water has always been a double-edge sword with both beneficial and detrimental effects on human health depending upon its concentration.

Table 2.2: health significance of consuming Fluoride

Fluoride (mg/l)	Impacts
<0.5	Dental caries
0.5-1.5	Optimum dental health, works against dental caries
1.5-3	Dental fluorisis, blackening and pitting of enamel and teeth from long term exposure, mottled enamel, roentgen graphic bone changes, polydipsia.
3-8	Skeletal fluorisis, damages fetus, increase in F^- concentration in milk, infant mortality due to calcification of blood vessels, lack of intelligence quotient in children, osteosclerosis, renal diseases, and elevated serum alkaline phosphates, stiffness of knees and hips, increased bone mineral density, bone and joint pains.
10-100	Gastroenteritis, skin irritation, deformation of bones and other skeletal abnormalities, thyroid changes, growth retardation, kidney damage, crippling fluorisis.

Source: (Rao N.C.R. et al., 2003)

2.3. De-fluoridation

2.3.1. De-fluoridation methods

De-fluoridation is a process of removal of fluoride from drinking water. All the de-fluoridating methods may broadly be classified into two categories namely;

A) Additive methods and
B) Adsorptive methods.

In **additive methods**, certain reagents are added and optimum conditions for the de-fluoridation are maintained. A fluoride ion present in water reacts with the reagents added and forms an insoluble complex and will be removed as flocks.

In **adsorptive methods**, a bed of greater surface activity is chosen and fluoride containing water is passed through the bed. Due to surface activity, the fluoride ion gets preferentially adsorbed on the bed surface there by causing a reduction of fluoride ion in the exit stream (Patil A. R. & Kulkarni B. M., 1989). Adsorptive methods can be classified into four categories (Killedar D. J. & Bhargava D. S., 1998);

1. Adsorption method
2. Ion exchange method
3. Precipitation method
4. Miscellaneous methods

The precipitation coagulation method makes vast amount of sludge and may include leaching of undesirable components; membrane procedures are lavish and fouling is an escapable issue. Ion-exchange process requires longer reaction period and technique is exceptionally costly. Adsorption is considered to be the simplest and most cost effective technique though it has high concentration of total dissolved salts and drops in removal effectiveness after regeneration step. The removal of fluoride ion from aqueous solutions using different adsorbents is currently of great interest (Bailey S. E., et. al., 1999).

The choice of the de-fluoridation method to be used depends on:

A) **Efficiency:** whether the method can reduce the fluoride content to the desired level.
B) **Running of the plant:** this includes the level required for supervision, complexity of the operation and dependency on electricity.

C) **Cost:** cost of the process in the reference to running costs and establishment of the plant.

D) **Impacts:** possible negative impacts such as handling of dangerous chemicals, effects of wrong dosage of chemicals, inefficient fluoride removal and possible chemical residual in treated water.

E) **Supply:** supply of chemicals required for the process.

2.3.2. De-fluoridation process

De-fluoridation process should be economic, adoptable and acceptable by the community. Priority should be given to techniques, which utilize locally available materials as de-fluoridation agents. Generally, processes for treating fluoride containing water can be divided into three categories:-

1. Chemical process
2. Physical process
3. Biological process

Chemical process include chemical precipitation, chemical oxidation or reduction, formation of an insoluble gas followed by stripping, and other chemical reactions that involve exchanging or sharing of electrons between atoms.

Physical process include sedimentation, flotation, filtering, stripping, ion exchange adsorption and other processes that accomplish removal of dissolved and undissolved substances without necessarily changing their chemical structures.

Biological process are those that involve living organisms using organic or, in some instances, inorganic substances for food.

To summarize, the chemical process may give bad taste to water, requires high cost for importing the chemicals, the chemicals might have other side effects and fouling is an inescapable issue. Physical process is costly and time intensive process. Biological mechanism of fluoride uptake have lower removal efficiency. Adsorption process which belongs physical process has high concentration of total dissolved salts and drops in removal effectiveness after regeneration step. Based on the above mentioned reasons adsorption is relatively more preferable.

2.4. Adsorption

2.4.1. Definition

Adsorption is a process in which atoms, ions and molecules adhere on the surface of a material. Due to this, a layer of adsorbate (atoms to be adsorbed) is formed on the adsorbent (material which adsorbs). Adsorption is basically a surface phenomenon and includes the whole of volume of the adsorbent. Adsorption process takes place due to physical or van der Waals force (physisorption) and chemical (chemisorption) forces due to chemical bonds, between adsorbate and adsorbent.

Adsorption processes are used in drinking water treatment for the removal of taste and odor causing compounds, synthetic organic chemicals, color-forming organics, and disinfecting by-product precursors. Inorganic constituents, including some that represent a health hazard, such as perchlorate, arsenic, fluoride, and some heavy metals, are also removed by adsorption (Zakaria R. M. et al., 2009).

2.4.2. Adsorption mechanism

Adsorption is the bond of molecular species from bulk solution to a surface of a solid by physical and chemical forces. Adsorption procedures include the water's entry through a contacted bed where fluoride is removed by ion exchange or surface chemical reaction with the solid bed matrix. As contrast with different procedures of de-fluoridation, adsorption method is prominent because of its straightforwardness, accessibility of extensive variety of adsorbents and also flexible and suitable procedure for treating drinking water systems. The adsorption procedure can remove fluoride up to 90%. Adsorption is one of the preferred processes for de-fluoridation due to its high efficiency, fast and easy operation, simple and flexible design (Ozcan et al., 2005).

Fan X. (2003) enumerated the theoretical aspects of fluoride adsorption onto solid particles by three essential steps;

1. Diffusion or transport of fluoride ions to the external surface of the adsorbent from bulk solution across the boundary layer surrounding the adsorbent particle, called external mass transfer;
2. Adsorption of fluoride ions onto particle surfaces;

3. The adsorbed fluoride ions probably exchange with the structural element inside adsorbent particles depending on the chemistry of solids, or the adsorbed fluoride ions are transferred to the internal surface of porous materials (intra particle diffusion).

2.4.3. Factors affecting adsorption

2.4.3.1. Temperature

Adsorption increases at low temperature conditions. Since adsorption is an exothermic process it is inversely related to temperature.

2.4.3.2. Pressure

Adsorption increases with increase in pressure up to certain extent until saturation is reached. After saturation, has achieved no more adsorption will occur irrespective of the pressure applied.

2.4.3.3. Surface area

As adsorption is a surface phenomenon, increase in the surface area of an adsorbent will increase the active sites available and the rate of adsorption will be faster.

2.4.4. Adsorbent

2.4.4.1. Characteristics of adsorbent

Adsorbent is a solid substance that usually adsorbs gas, liquid or dissolved substance. They are used in the form of spherical pellets, rods, moldings, or monoliths. They must have high abrasion resistance, high thermal stability and small pore diameters, which results higher exposed surface area and hence high capacity for adsorption. The adsorbents must also have a distinct pore structure that enables fast transport of the gaseous vapors. A few adsorbent materials have been attempted in the past to check their possibilities and techno-economic feasibility as de-fluoridating specialists. Activated alumina, activated carbon, activated alumina coated silica gel and so on various adsorbent materials reported in literature (H. Kariyanna, 1987).

In recent years, the use of clay materials to replace commercially available adsorbents has attracted much attention due to their low cost, availability, high surface area, lack of toxicity and potential for ion exchange (Murray H., 2002). Their unique properties including high specific surface area and surface chemistry, a variety of surface and structural properties, chemical and mechanical stabilities give these materials a broad range of applications (Zhang L. et al., 2007).

Most industrial adsorbents fall into one of three classes:

- **Oxygen-containing compounds** – Are typically hydrophilic and polar, including materials such as silica gel and zeolites.
- **Carbon-based compounds** – Are typically hydrophobic and non-polar, including materials such as activated carbon and graphite.
- **Polymer-based compounds** – Are polar or non-polar functional groups in a porous polymer matrix.

Characteristics of a good adsorbent;

1. The adsorbent must be available locally.
2. The cost of the adsorbent must be economic.
3. The materials should not give any other side effect.
4. The method of operation must be easy.
5. The materials should be readily acceptable by the users.

Table 2.3: Advantages and Disadvantages of Adsorbents

Adsorbent	Advantages	Disadvantages
Activated carbon	High surface area	High cost
Bio-sorbents	High adsorption capacity	High market cost
Agricultural and industrial by-products	Available in abundance	Sorption properties depend on origin
Bentonite	High surface area, high cation exchange capacity and low cost.	Needs modification for adsorption of anions.
Zeolite	High ion exchange capacity and surface area.	Complex sorption mechanism.

2.5. Natural clays

2.5.1. Definition

Clays are lamellar aluminosilicates possessing a wide range of physicochemical properties such as swelling, adsorption, ion exchange and surface acidity (Yang T. et al., 2006). Natural clays are acquiring prominence as low-cost adsorbent over the last few decades due to their local and abundant availability and capability to undergo modification to enhance the surface area, adsorption capacity and range of applicability (Monvisade P., And Siriphannon P., 2009).

2.5.2. Modification of clay minerals

The chemical nature and pore structure of clay materials generally influence their adsorption capability. In order to increase their adsorption capacity, modification of the pore structure of clay materials can be conducted chemically as well as physically. Modification can alter the clay structure to enlarge its surface area, therefore increasing the adsorption capacities (Dai J.C. & Huang J.T., 1991). The chemical composition of clay minerals varies depending upon the origin influencing the layer charge, cation exchange capacity, adsorption capacity and morphology. These factors play a significant role in the modification of natural clays (Steudel A. et al., 2009). Inorganic acids, bases, salts and surfactants have been used for modification of clay minerals. A combination of chemical and physical treatment processes have also been employed to modify the surface and structure of clay minerals.

2.5.2.1. Types of modification of clay minerals

There are various methods for modification of clay minerals, such as, acid activation (Steudel A. et al., 2009), treatment with cationic surfactant (He H. et al., 2006), clay rubber composite (Dai J.C. & Huang J.T., 1991), thermal treatment (Al-Asheh S., Banat F. & Abu-Aitah L., 2003), polymer addition, pillaring by different types of poly (hydroxo metal) cations, intraparticle and interparticle polymerization, de-hydroxylation and calcination, delamination and re-aggregation of semetics, and lyophilisation, ultrasound and plasma (Paiva, et al., 2008), adsorption and ion exchange with inorganic and organic cations, binding of inorganic and organic anions (mainly at the edges) and grafting of organic compounds (Liu P. et al., 2007).

Modification of clay minerals can generally be classified into three;

- **Hydrophobic modification: -** the cations residing between the layers are exchangeable with quaternary ammonium ions like acetyl-tryalkyl-ammonim or acetylvinyl-diakyl ammonium. This process converts the hydrophilic surface of the layer into a hydrophobic one thereby improving the compatibility of nanoclay into polymer matrix. Presence of encapsulation by a polymer by in-situ polymerization.
- **Intercalation: -** this is a physical process by which a macromolecule like a dye or polymer is “inserted’’ in the gallery. Such molecule is flanked by two clay layers and is immobilized and shielded. Width of the gallery is however not much affected during intercalation.
- **Exfoliation**: - this is delaminating process where the gallery is expanded from its normal size of 1nm to about 20nm or higher. Thus there is a clear disruption of the layers which get spatially separated apart bringing about nanoscale dispersion in the polymer matrix. Thus exfoliated clays represent true nano materials.

2.5.3. Bentonite

Bentonite is an aluminium phyllosilicate clay material consisting mostly of montmorillonite. It was named by Wilbur C. Knight in 1898 after the Cretaceous Benton Shale near Rock River, Wyoming (Hosterman J.W. & S.H. Patterson, 1992). Bentonite is a material derived from the alteration, over geological periods, of glassy material emitted from volcanoes (tuff or ash), or from the alteration of silica bearing rocks such as granite and basalt; this requires hydration (taking up or combination with water) and a loss of alkali’s, bases, and possibly silica, with the preservation of the textures of the original volcanic glass. Depending on the nature of formation, bentonite can have a variety of accessory minerals in addition to its constituent mineral montmorillonite. These minerals may include attapulgite, kaolin, mica, and illite as well as minerals like quartz, feldspar, calcite and gypsum.

2.5.3.1. Bentonite in Ethiopia

Bentonite clay resources in Ethiopia are found in Afar and Oromia regions. They are easily accessible, as they are located near the main road. The main occurrences in Afar are located at Ledi, Gewane, Hadar and Warseiso. These sediments were deposited near the western margin of the central part of the Afar depression, which throughout the tertiary and quaternary was an area of subsidence and intermittent volcanism. Bentonite clay of Pleistocene age is also found at Gidicho Island (bottom locality on map below), Lake Abaya, in association with diatomite, with a total estimated resource of five million tons (Knot, 1983).

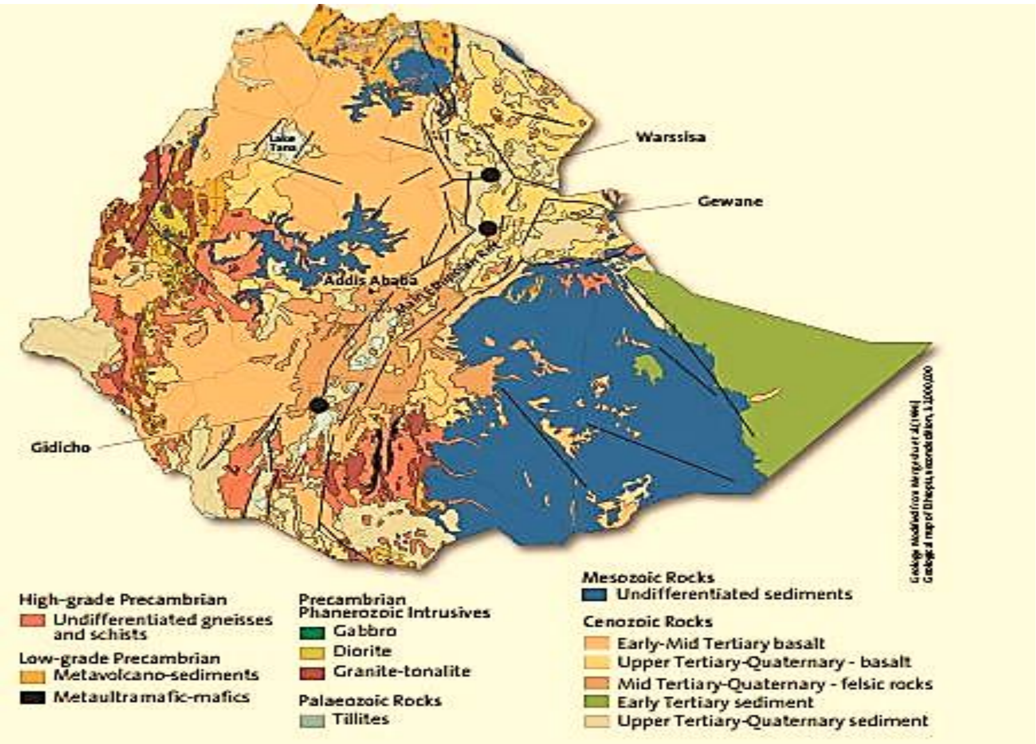


Figure 2.1: Simplified geological map of Ethiopia showing bentonite deposits

Source: *www.mome.gov.et* (Ministry of Mines of Ethiopia)

Table 2.4: Location and resource of bentonite deposits in Ethiopia

Area (province)	Name of deposits	Easting	Northing	Resource (million tons)
Afar	Gewane Bentonite	40° 38' 05"E	10° 17' 50"N	126
Sidamo	Gidicho Bentonite	37° 56' 00"E	06° 24' 00"N	5
Afar	Warsissa Bentonite	40° 39' 00"E	11° 22' 20"N	10.5

Source: www.mome.gov.et (Ministry of Mines of Ethiopia)

2.5.3.2. Structure of Bentonite

Bentonite, 2:1 type clay, is a natural silicate mainly composed of montmorillonite. The basic structure of bentonite is made up of two silica tetrahedral sheets with an intermediate aluminum octahedral sheet (Vimonses V. et al., 2009).

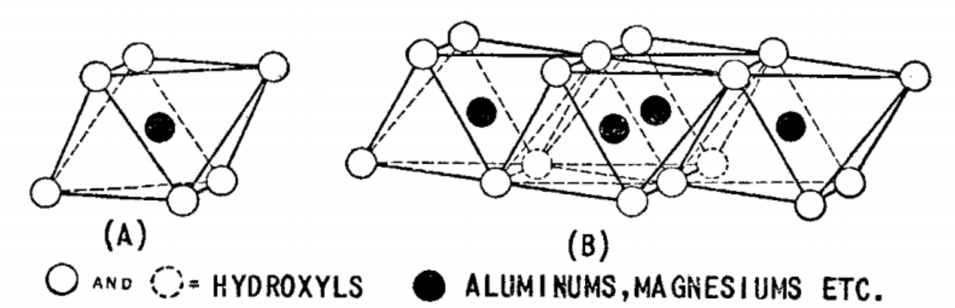


Figure 2.2: Diagrammatic sketch showing (A) single octahedral unit, and (B) portion of an octahedral sheet structure

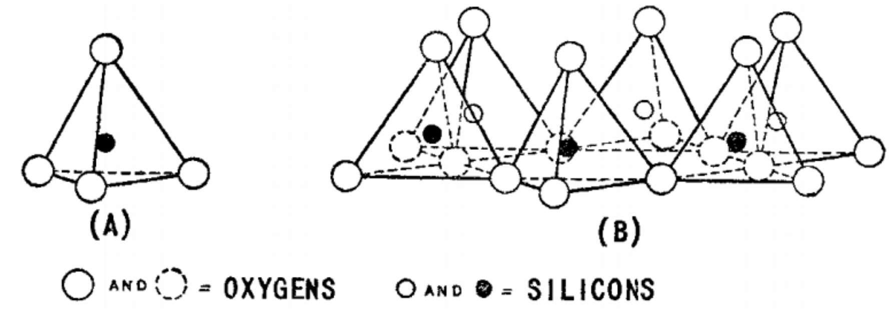


Figure 2.3: Diagrammatic sketch showing (A) single silica tetrahedron, and (B) portion of a silica tetrahedral sheet structure

Chemical composition of pure montmorillonite is used as the reference in assessing analytical data of the studied bentonite samples. Neaman et al. (2003) gives the following stoichiometric formula for purified montmorillonite:

$Na_{0.18}Ca_{0.10}$ $(Si_{3.98}Al_{0.02})$ $(Al_{1.55}Fe^{3+}_{0.09}Fe^{2+}_{0.08}Mg_{0.28})$ O_{10} (OH) $2 \bullet nH_2O$

Exchangeable Tetrahedral Octahedral site H_2O^+ H_2O^-

The charge between the octahedral and tetrahedral sheets is not balanced due to its isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet and generally Mg^{2+} for Al^{3+} in the octahedral sheet (Ozcan A. S. & Erdem B., 2005). The substitution of these ions of lower valence induces a permanent negative charge in the lattice structure. The negative charge is balanced by treating it with cations such as sodium, calcium or magnesium. These cations are exchangeable cations in the lattice structure due to loose binding (Vimonses V. et al., 2009). Depending on the exchangeable cations, commercial bentonites are known as Ca-bentonite or Na-bentonite (Babaki H., Salem A. & Jafarizad A., 2008).

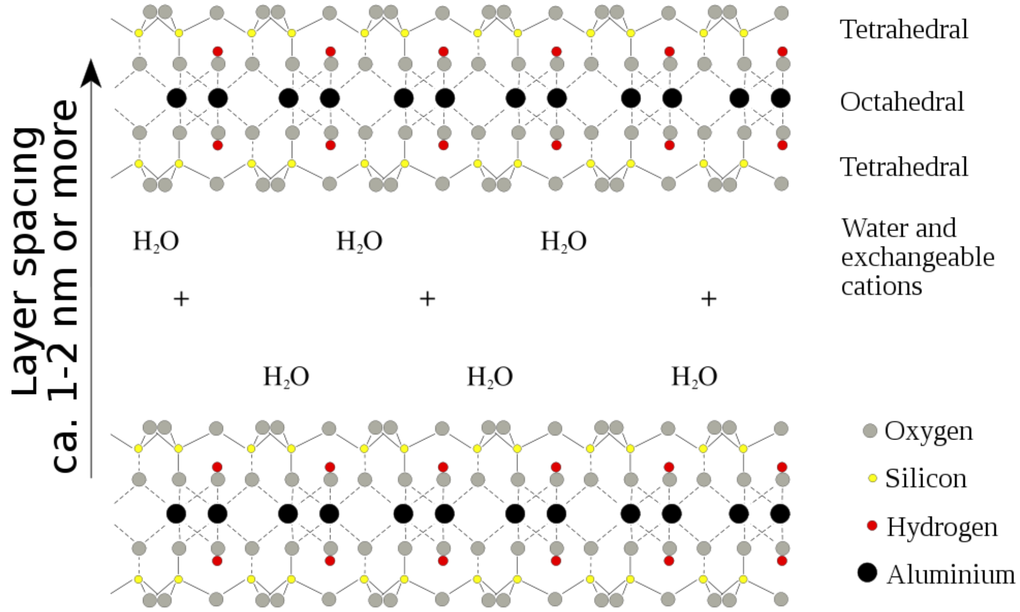


Figure 2.4: Diagrammatic sketch of the structure of montmorillonite

2.5.3.3. Types of Bentonite

2.5.3.3.1. Sodium bentonite

Sodium bentonite expands when wet, absorbing as much as several times its dry mass in water. It has single water layer particles which contain Na^+ as the exchangeable ion. It is often used in drilling mud for oil and gas wells and boreholes for geotechnical and environmental investigations (Hosterman J.W. & S.H. Patterson, 1992). The property of swelling also makes sodium bentonite useful as a sealant, since it provides a self-sealing, low permeability barrier. It is used to line the base of landfills, for example. Various surface modifications to sodium bentonite improve some rheological or sealing performance in geo-environmental applications, for example, the addition of polymers (Theng B.K.G., 1979).

2.5.3.3.2. Calcium bentonite

Calcium bentonite is a useful adsorbent of ions in solution, (Lagaly G., 1995) as well as fats and oils. It is the main active ingredient of fuller's earth, probably one of the earliest industrial cleaning agents (Robertson R.H.S., 1986). It has a double water layer with Ca^{2+} as the exchangeable ion. Calcium bentonites have the greatest market as bonding agents in foundry molding sands. Their higher green strengths are unique among mineral binders considering the small amount of bentonite necessary to impart adequate strengths.

By blending calcium and sodium bentonite, foundry-men develop favorable strength characteristics throughout all phases of the casting procedure and keep a mixture which is compatible with other sand additives such as the cellulose products.

2.5.3.4. Properties of Bentonite

The widespread use of bentonite can be attributed to its physical and chemical properties such as small particle size, high porosity, large surface area and high cation exchange capacity (Doulia D. et al., 2009). The ability of bentonite to swell in water is due to the expanding of its lattice-like structures by capillary pressure, pushing apart the stable film around each particle (Hascakir B. & Dolgen D., 2008). The bentonite has excellent adsorption capacity and its adsorption ability is determined by the chemical nature and pore structure (Koyuncu H., 2008). The porous structure of bentonite is broadly classified into three categories as micropores, mesopores and macropores. Micropores are smaller than 2nm, between 2nm and 50 nm are mesopores and larger than 50nm are macropores. The physico-chemical properties such as adsorption capacity largely depend on the presence micro and mesopores; and, the effect of macropores is found to be insignificant (Babaki H., Salem A. & Jafarizad A., 2008).

2.5.3.5. Application of Bentonite

Bentonite is widely used in various industrial products and processes such as pharmaceuticals, cosmetics and drilling fluids to modify the rheology and control the stability of systems (Faur-Brasquet C., et al., 2002). It is used as a plasticizer in ceramics, as an emulsifying agent in asphaltic substances, as thickener and extender for paints, as adhesive in concrete mixtures, horticultural sprays and insecticides, adsorbent in removal of dyes and heavy metals and in bleaching earth in refining oils and fats (Pushpaletha P., Rugmini S. & Lalithambika M., 2005)

CHAPTER THREE

3. MATERIALS AND METHODS

3.1. Materials

3.1.1. Equipment and Instruments

The following equipment were used for the study.

Table 3.1: List of equipment and instruments

Instrument	**Model**	**Use**
Jaw crasher		Size reduction (1st)
Mortar and pestle	5657 HAAN	Size reduction (2nd)
Sieve	Retsch, AS200	To sieve sample
Drying oven	Memmert 100-800	To dry sample
Analytical balance	EP214C	To weigh sample
Incubator Shaker Series	New Brunswick Scientific Excella E24	To mix the bentonite with the iron solution
Vacuum filter		To filter washed and modified bentonite
Filter paper	Whatman	To filter samples
pH meter	Jenway 3505	To measure pH
Centrifuge	UNIVERSAL 320 R	To separate the adsorbent from the liquid.
Digital reading pipettes	ACURA 825/835	To take sample in small scale
Thermometer		To measure temperature
Conductivity meter		To measure conductivity of the filtrates.
Refrigerator		To store samples

3.1.2. Chemicals and Reagents

All chemicals which are listed in table (3.2) were analytical reagent grade and bought from different chemical stores in Addis Ababa.

Table 3.2: List of chemicals and reagents

Chemicals and Reagents	**Use**
Distilled water	Used for washing raw bentonite, preparation and dilution of solutions
Iron three sulphate	Used for modification of raw bentonite
Ammonium acetate	To extract exchangeable cations
Nitric acid	To preserve the samples
Potassium chloride	To determine the surface chemistry (pH_{PZC})
Sodium fluoride	To prepare aqueous solution
Sodium hydroxide and hydrochloric acid	To adjust pH
Bentonite (local)	Used as adsorbent

3.2. Methods

3.2.1. Collection and pretreatment of raw Bentonite

Bentonite was used as an adsorbent for the study. Bentonite was collected from Ethiopian Mineral, Petroleum and Biofuel Corporation. This bentonite originally came from Afar region, Gewane area. Sample was crushed, screened and washed with distilled water then dried in an oven at a temperature of 105 ^{0}C for 12 h. to remove moisture and volatile organics from the clay while protecting its characteristics. Then the dried raw bentonite was crushed again with jaw crusher and further size reduced using mortar and pestle. The powdered raw bentonite was sieved and the particle size between 32-63 μm was retained. Previous studies by Dai J.C. & Huang J.T., (1991) concluded that smaller particles of medium were more effective than larger ones because of greater available surface area and consequently high adsorption capacity. After that, the powdered bentonite was weighed and preserved in an air tight plastic bag for the next step.

3.2.2. Preparation of fluoride solutions

A 1000 mg L^{-1} sodium fluoride stock solution was prepared by using deionized water. Standards at a required concentration range were prepared by diluting an appropriate amount of stock solution with deionized water.

3.2.3. Preparation of Fe^{3+} working solution

A stock solution of 2000 ppm Fe^{3+} was prepared by dissolving 7.16 g of $Fe_2(SO_4)_3.xH_2O$, in 0.005 M H_2SO_4 solution to prevent immediate precipitation of Fe^{3+}. Working solutions were prepared from this stock solution through appropriate dilutions for the batch experiments.

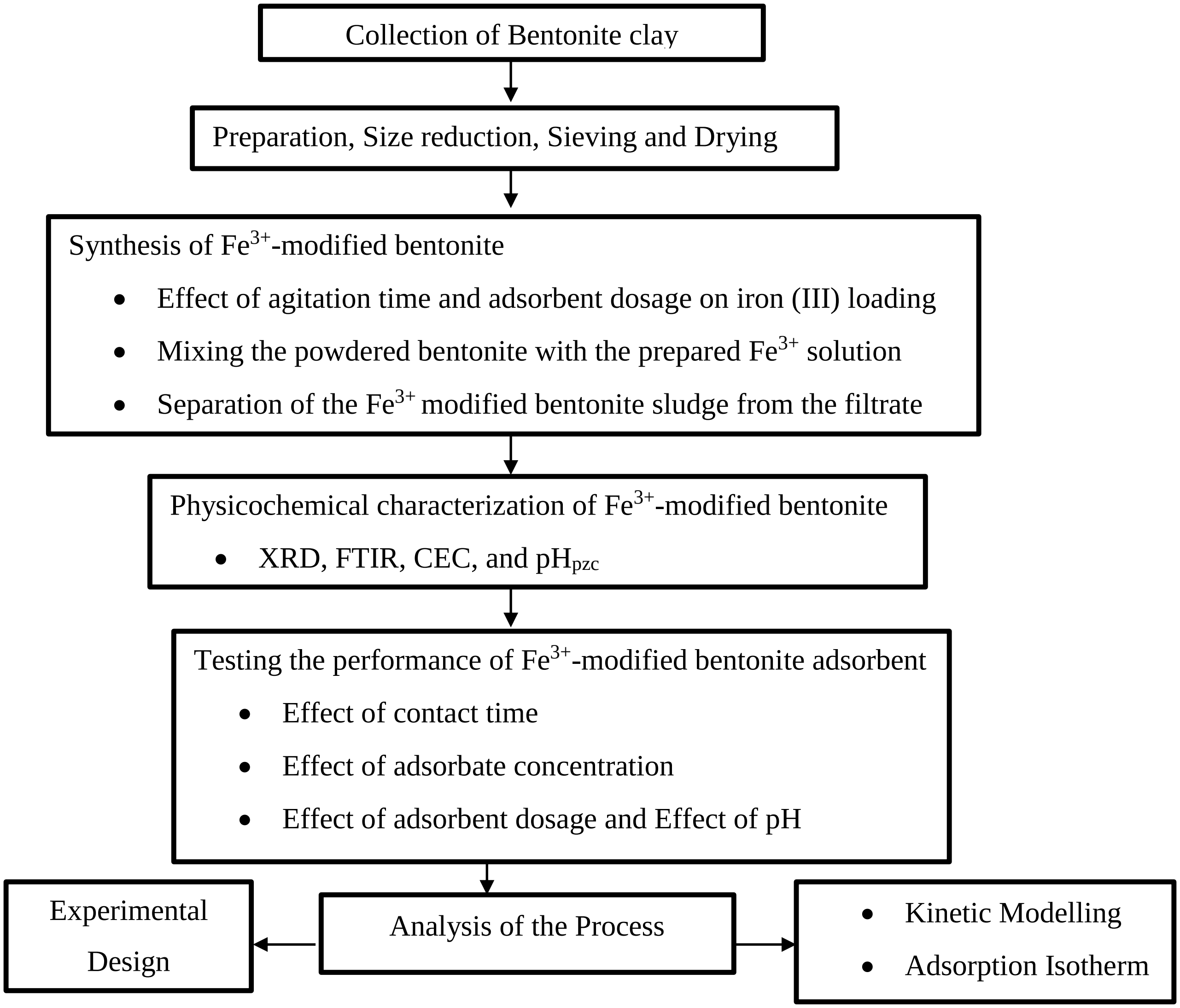


Figure 3.1: Frame work of the experiment

3.2.4. Batch adsorption tests for iron (III) loading

In order to study the effect of different controlling parameters like pH, contact time, adsorbent dosage and adsorbate concentration, on de-fluoridation capacity of raw and modified bentonite, adsorption studies were carried out through batch process. The main advantage of batch process is the simplicity of equipment needed, flexibility and relatively inexpensive.

3.2.4.1. Effect of agitation time on iron (III) loading

7 samples of 100 ml (50 ppm Fe^{3+}) working solution were pipetted into 7, 250 ml Erlenmeyer flask. 0.1g of washed powdered bentonite was added into each flask. The mixtures were then agitated for 1, 3, 5, 10, 30, 60, and 180 min at 250 rpm Masindi (2014). The pH, TDS, EC and temperature were measured before and after agitation in order to determine the optimal agitation time for loading Fe^{3+} onto bentonite clay.

3.2.4.2.Effect of adsorbent dosage on iron (III) loading

7 samples of 100 ml (100 ppm Fe^{3+}) working solution were pipetted into 7 bottles of 250 ml volume and varying mass of bentonite added. The mass of bentonite that was used include 0.2, 0.3, 0.5, 0.8, 1, 3 and 5 g. The mixture was then agitated at optimal agitation time obtained from previous experiment at 250 rpm Masindi (2014). The pH, TDS, EC and temperature were measured before and after agitation. The mixture of the optimum point was then filtered and two drops of concentrated HNO_3 acid was added. The samples were then kept at 4ºC until analysis. The analysis of Fe^{3+} of the optimum point was done by using Atomic Absorption Spectrometer at College of Natural Science, Department of Chemistry, AAU. HNO_3 is added to the samples for two purposes: one, at the time of sample collection, to reduce pH< 2. Below pH 2, precipitation, adsorption to container wall and microbial degradation are minimized. Though any acid will serve this purpose, HNO_3 is preferred because of its oxidizing nature. Adding HNO_3 converts metal ions into their nitrate salts, which are highly soluble. Secondly, sample digestion is required before AAS analysis. The purpose is destroy the matrix, which otherwise interfere during atomization.

3.2.5. Preparation of Fe^{3+}-modified bentonite for de-fluoridation experiments

The Fe^{3+} modified bentonite adsorbent for the de-fluoridation experiment was synthesized by mixing Fe (III) sulphate solution and raw bentonite using the conditions optimized in previous experiments. The mixture was then transferred to an erlenmeyer flask in order to avoid spillage during agitation. After that the mixture was agitated on a table shaker and then filtered. The solid residue left on the filter paper was dried for 12 hours at a temperature of 105°C in an oven. The material was then grounded to powder and used for subsequent de-fluoridation experiments. The experiment was repeated certain times to generate enough Fe^{3+}-modified bentonite for subsequent experiments.

3.2.6. Characterization of raw and Fe^{3+}-modified bentonite

3.2.6.1. X-ray diffraction (XRD)

X-ray diffraction helps to study the deposition of Fe^{3+} on the surface of bentonite clay. It is an experimental method that provides details which will help to understand the structures of minerals and other crystalline matter on an atomic scale. It thus establishes relationships between the crystal structure and the physical and chemical properties of the material under investigation (bentonite clay).

XRD was used to determine the mineralogical composition of the raw and Fe^{3+} modified bentonite. X–ray diffraction (XRD) patterns was recorded with D8 Avance XRD of Brucker powder diffractometer with Cu-Kα (λ=1.540593-1.544414 Å, 40 KV and 15 mA) radiation having a continuous scanning mode with speed of 10 deg/min. X-ray diffractograms of raw and Fe^{3+} modified bentonite powders were obtained for the 2θ angles ranging from 10^0 to 70^0 with scan step 0.02^0. This XRD analysis was performed in College of Natural Science, Department of Chemistry, AAU.

3.2.6.2. Fourier transformed infrared spectroscopy (FTIR)

To obtain qualitative group and complementary evidence for the intercalation of Fe^{3+} ions onto the bentonite minerals, FTIR spectra were performed in the region of 400-4,000 cm^{-1} using Spectrum 65 FT-IR (PerkinElmer), with samples prepared by the conventional KBr disc method. It shows the presence of quartz, alumina, haematite and different mineral matters. All the spectra were recorded and processed using IR solution software. This FTIR analysis was performed in College of Natural Science, Department of Chemistry, AAU.

3.2.6.3. Determination of Cation Exchange Capacity

Determination of cation exchange capacity of raw and modified bentonite was done by extracting the exchangeable cations using 1M ammonium acetate buffer at 7.4 pH. 0.5g samples of raw and modified bentonite clays were extracted using 25 ml aliquots of 1M ammonium acetate. Then the samples were equilibrated for 15 min using table shaker. After agitation, the samples were centrifuged at 3000 rpm for 15 min in order separate the adsorbent from the liquid. The mixture was decanted in a 100 ml bottle. This procedure was repeated four times for each sample. The cumulative extract was 100 ml. To remove the suspended solids, the cumulative extracts were filtered. Then the filtrate was acidified by adding three drops of nitric acid as a preservative and stored in a refrigerator until it was analyzed by AAS. The reason for the addition of nitric acid is explained in section 3.2.4.2. The samples were then analyzed for the availability of base cations like K^+, Na^+, Mg^{2+} and Ca^{2+}. The results in ppm were then converted to meq per 100g of sample.

3.2.6.4. Determination of point of zero charge

The surface chemistry of any material is determined by the acidic or basic character of their surface. Batch equilibrium experiments were used to estimate the point of zero charge. Forty-five milliliters of 0.1 M KCl solution were transferred to 6, 50 ml calibrated bottles and capped. The initial pH (pH_i) of the solutions was adjusted in the range of 2-10.0 by adding 0.1 M HCl and 0.1 M NaOH solutions. The total volume of the solution in each bottle was adjusted exactly to 50ml by adding the KCl solution of the same strength. 1g of dry bentonite clay was added to each bottle and the suspensions were then equilibrated for 24hr. After equilibration time, the solutions were filtered and the final pH value (pH_f) of the filtrate was measured. The difference between initial and final pH values ($\Delta pH = pH_i - pH_f$) was plotted against pH_i. The point of intersection of the resulting curve with abscissa (the coordinate that gives the distance along the horizontal axis), at which $\Delta pH=0$, was the indication of the point of zero charge. Same procedure was repeated twice but replacing the electrolyte with 0.01M and 0.001M KCl solution.

3.2.7. Testing the performance of prepared adsorbent for F^- removal

3.2.7.1. Effect of Contact Time

Effect of contact time on fluoride removal was studied using of 10 ppm F^- solution and 1g/50ml S/L ratio. After that samples were agitated for time of 5, 10, 30, 60 and 180 min at 250 rpm on a table shaker. Samples were then filtered through 45 µm pore cellulose membrane. pH, EC, TDS, and final F^- concentration were measured. Processes were carried out at room temperature (26±2). The analysis of F^- concentration was performed in Addis Ababa City Government, Environmental Protection Authority.

3.2.7.2. Effect of Adsorbate Concentration

Effect of adsorbate concentration on fluoride removal was studied at 30 min contact time and agitated at 250 rpm on a table shaker. 1g/50ml of S/L ratio was used; adsorbate concentration was varied as follows: 5, 10, 20, 30 and 40 ppm. Samples were then filtered through 45 µm pore cellulose membrane. pH, EC, TDS, and final F^- concentration were measured. Processes were carried out at room temperature (26±2). The analysis of F^- concentration was performed in Addis Ababa City Government, Environmental Protection Authority.

3.2.7.3. Effect of Adsorbent Dosage

Effect of adsorbent dosage on fluoride removal was studied using 10 ppm F^- solution. The adsorbent dosage was varied as follows: 0.1, 0.3, 0.5, 1 and 3g. Samples were then filtered through 45 µm pore cellulose membrane. pH, EC, TDS, and final F^- concentration were measured. Processes were carried out at room temperature (26±2). The analysis of F^- concentration was performed in Addis Ababa City Government, Environmental Protection Authority.

3.2.7.4. Effect of pH

Effect of pH on fluoride removal was studied at 10 ppm F^- concentration. Agitation was done for 30 min of contact time at 250 rpm on a table shaker and 1g/50ml of S/L ratio was employed. pH of the solution was varied as follows 2, 4, 6, 8 and 10. Samples were then filtered through 45 µm pore cellulose membrane. pH, EC, TDS, and final F^- concentration were measured. Processes were carried out at room temperature (26±2). The analysis of F^- concentration was performed in Addis Ababa City Government, Environmental Protection Authority.

3.2.8. De-fluoridation of surface water using the Raw and Fe^{3+} modified bentonite

Two liters of water for de-fluoridation experiment was collected from Lake Basaka, Metehara which is found in the Oromia region of central Ethiopia using tightly closed plastic container on March 28, 2018 and was kept at 4^0C until analysis. Lake Basaka is located in the Great Rift Valley about 200 kilometers south east of the capital Addis Ababa. The salt lake has grown significantly in the past 50 years, growing from 3 square kilometers in 1957 to 42.6 square kilometers in 2008. The lake has an average depth of 8m and surface elevation of 950m.

The de-fluoridation was done by conducting two sets of experiments; the first batch was done by using the water sample as collected at pH of 9.13 while the second batch was done by using water sample at pH of 6.14 (modified by adding 0.1ml of nitric acid). The de-fluoridation experiments were then carried out using both raw and Fe^{3+} modified bentonite.

The experiments involved 6 samples divided into two batches, the first three were mixed with raw bentonite and the other 3 were mixed with Fe^{3+} modified bentonite at masses of 0.1g, 0.4g and 1g Gitari (2013). All samples were agitated for 24 hours at the speed of 250 rpm and after agitation the samples were filtered. pH, EC, TDS, and initial & final F^- concentrations were measured. Processes were carried out at room temperature (26±2).

3.2.9. Experimental Design and Analysis

The experimental design for the de-fluoridation process was full factorial design resulting total of 32 runs with 5 center points per block. This study provided the application of response surface methodology (RSM); which consists 3-level factorial design for optimization of the removal of fluoride from aqueous solutions.

The experimental design and analysis of data such as, regression analysis and analysis of variance were carried out for fitting the model to the experimental data and to examine the statistical significance of the model which was done in the software package Design – Expert ®version 7.0.0. The model obtained was used to interpret the effect of various parameters on the response i.e. percentage removal of fluoride. The optimization process was aimed at finding the levels of three independent variables (adsorbent dosage, fluoride concentration and contact time) which would give maximum fluoride removal.

Table 3.3: Experimental factors and levels for testing fluoride removal efficiency

Factors	Levels		
	Low (-1)	Medium (0)	High (+1)
Adsorbent Dosage (g)	1	1.5	2
Fluoride Concentration (mg/l)	5	15	25
Contact Time (min)	15	30	45

3.3. Modelling Analysis

Percentage removal of fluoride from aqueous solution was computed using the following equation:

$$\% \text{ Removal} = ((Ci - Cf)/Ci) * 100 \quad \ldots\ldots (3.1)$$

Where C_i = initial fluoride concentration (mg L^{-1}) and C_f = equilibrium fluoride concentration (mg L^{-1}). This shows the amount of fluoride adsorbed by the composite from the aqueous solution.

The fluoride removal capacity of the adsorbent was computed using the following equation:

$$q = ((C_i - C_f) \times V)/m \quad \ldots\ldots (3.2)$$

Where C_i = initial fluoride concentration (mg L^{-1}) and C_f = equilibrium fluoride concentration (mg L^{-1}), V = volume of fluoride solution (L), and m = weight of bentonite clay (adsorbent) in grams (g). This shows the amount of fluoride adsorbed per gram of the composite.

3.3.1. Kinetic modelling

The kinetics of sorption describes the solute uptake rate, which in turn governs the residence time of sorption reaction. It is one of the important characteristics in defining the efficiency of sorption. In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the pseudo-first-order and pseudo-second order equations were applied to model the kinetics of fluoride adsorption onto modified bentonite clay.

3.3.1.1. Pseudo-First Order Kinetic Model

This model is also known as Largergren model, proposed in 1898. Linear equation of pseudo-first-order kinetics is as follows:

$\mathrm{Log}\,(q_e - q_t) = \mathrm{Log}\,q_e - (K_1/2.3)t$………………….....………………………………. (3.3)

Where q_e (mg g^{-1}) is adsorption capacity at equilibrium, q_t (mg g^{-1}) is the adsorption capacity at time t, and K_1 (min^{-1}) is the rate constant of pseudo first order. The values of log ($q_e - q_t$) were linearly correlated with t. The plot of log ($q_e - q_t$) versus t should give a linear relationship from which k_1 and qe can be determined from the slop and intercept of the plot, respectively.

3.3.1.2. Pseudo-second order kinetic model

Pseudo-second order kinetic assumes that chemisorption control the adsorption rate (B. Liu et. al., 2011). Linear equation of pseudo-second-order kinetics is as follows:

$t/q_t = 1/K_2q_e + (1/q_e)t$ ……………………..……………………………………….. (3.4)

This equation is applied to obtain K_2 (g/mg.min), the second-order rate from the plots t vs. t/q_t.

3.3.2. Adsorption Isotherm Models

Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. (Foo K. Y. & Hameed B. H., (2010).

$\mathrm{Adsorbate} + \mathrm{Adsorbent} \rightarrow \mathrm{Adsorption}$…………………………………...………… (3.5)

The adsorption isotherm is the most extensively employed method for representing the equilibrium states of an adsorption system. The purpose of an adsorption isotherm is to relate the adsorbate concentration in the bulk solution to the amount adsorbed at the solid/solution interface. The analysis of isotherm data is important in developing an equation which accurately represents the results and which can be used for design purposes (Y.Hanumantharao, Medikondu Kishore and K.Ravindhranath et. al., 2011). Adsorption isotherm helps in determining the feasibility of modified bentonite for treating fluoride ion in water.

The isotherm not only provides the general idea of the effectiveness of the adsorbent in removing fluorides, but also indicates the maximum amount of fluoride ions that was adsorbed by the adsorbent. The mechanisms and intensity of adsorption was described by the use of two common adsorption models: Langmuir and Freundlich adsorption isotherms; these models describe adsorption processes on a homogenous or heterogeneous surface, respectively to predict the behavior of fluoride adsorption onto the modified bentonite.

3.3.2.1. Langmuir Isotherm

Langmuir isotherm is valid for single-layer adsorption. The Langmuir model is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface. It is based on the assumption that all the adsorption sites have equal affinity for molecules of the adsorbate and there is no transmigration of adsorbate in the plane of the surface (A.R.Tembhurkar and Shilpa Dongre et. al., 2006).

Langmuir isotherm is based on the assumption that point of valence exists on the surface of the adsorbent and that each of these sites are capable of adsorbing one molecule. Thus, the adsorbed layer will be one molecule thick. Furthermore, it is assumed that all the adsorption sites have equal affinities for molecules of the adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site (A. V. Jamode, V. S. Sapkal and V. S. Jamode et. al., 2004).

It can be expressed in the following linear form:

$$\mathrm{Ce/Qe} = 1/\mathrm{Qmb} + \mathrm{Ce/Qm} \qquad (3.6)$$

Where Ce = equilibrium concentration (mg L^{-1}), Qe = amount adsorbed at equilibrium (mg g^{-1}), Qm = Langmuir constants related to adsorption capacity (mg g^{-1}) and b = Langmuir constants related to energy of adsorption (L mg^{-1}).

A plot of Ce vs. Ce/Qe should be linear, if the data are described by the Langmuir isotherm. The value of Qm is determined from the slope and the intercept of the plot. It is used to derive the maximum adsorption capacity and b is determined from the original equation and it represents the intensity of adsorption.

3.3.2.2. Freundlich Isotherm

The Freundlich isotherm is based on multilayer adsorption on the heterogeneous surface of the adsorbent containing an unequal amount of energies. It is not limited to a monolayer adsorption, but also it is applied for multilayer adsorption.

Linear equation of Freundlich isotherm is expressed as follows:

$$\mathrm{Log\,Qe} = 1/\mathrm{n}\,\mathrm{Log\,Ce} + \mathrm{Log\,Kf} \ldots\ldots (3.7)$$

Where Qe is the amount of F^- ions adsorbed per unit weight of adsorbents (mg/g) Ce is the equilibrium concentration in solution (mg/l) K_f and 1/n are the Freundlich constants. K_f and n are the indicators of the adsorption capacity and adsorption intensity, respectively.

The ability of Freundlich model to fit the experimental data was examined. For this case, the plot of log (C_e) Vs log (q_e) was employed to generate the intercept and the slope values to determine K_f and n respectively.

The magnitudes of K_f and n show easy separation of adsorbate ions from the aqueous solution and indicate favorable adsorption. The intercept K_f value is an indication of the adsorption capacity of the adsorbent; the slope 1/n indicates the effect of concentration on the adsorption capacity and n represents adsorption intensity.

The "n" should have values lying in the range of 1–10 for classification as favorable adsorption.

The intensity parameter, 1/n indicates the deviation of the adsorption isotherm from linearity. A smaller value of 1/n, points out a better adsorption mechanism and formation of relatively stronger bond between adsorbate and absorbent (A.R.Tembhurkar and Shilpa Dongre et. al., 2006). If $1/n < 1$, shows that the adsorption is favorable, new adsorption sites are available, adsorption capacity increases, and bond energies increases with surface density, if $1/n > 1$, indicates that the adsorption bonds are weak, adsorption capacity decreases, bond energy decreases with surface density and un-favorable. And if $1/n = 1$ all surface sites are equivalent and adsorption is linear with homogenous adsorption sites (A. V. Jamode, V. S. Sapkal and V. S. Jamode et. al., 2004). Values of R^2 were used to compare the isotherm model.

3.4. Reusability and regeneration of Fe^{3+}-modified bentonite

The cost of adsorption process primarily depends on the cost of an adsorbent and its reusability. Studies on the use of 1-8% solution of sodium hydroxide for regeneration of bentonite have been reported (Kanyora, A.K et. al., 2014). Based on that the regeneration studies of Fe^{3+}-modified bentonite were conducted using sodium hydroxide aqueous solution. The regeneration of exhausted modified bentonite was done by selecting the run which gave maximum percentage removal of fluoride from the design expert. The used modified bentonite was soaked in 15 ml of

0.5 M NaOH for 12 h and was washed with distilled water followed by drying in an oven at 50 ^{0}C. The regenerated adsorbent was reused in the next two adsorption experiments.

CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.1. Batch Adsorption tests for iron (III) loading

4.1.1. Effect of agitation time on iron (III) loading

The effect of the agitation time on iron (III) loading was tested by varying the agitation time. As shown in (Table 4.1), a decrease in both EC and TDS to a minimum is observed; which stabilizes with time with no significant changes. The EC change indicates a significant proportion of the attenuation kinetics happens within 10-30 min of agitation. No significant change in kinetics was observed after 30 min hence this time was chosen as the optimum for subsequent experiments.

Table 4.1: Variation of pH, EC, TDS and Temperature with agitation time (50ppm)

Agitation Time (min)	pH	EC (µs/cm)	TDS (mg/l)	Temperature (^{0}C)
0	2.80	36.7	23.121	20.4
1	2.76	29.4	18.522	19.9
3	2.82	28.7	18.081	19.2
5	2.97	28.0	17.64	18.5
10	3.84	27.6	17.388	18.3
30	3.86	27.2	17.136	18.2
60	3.92	28.9	18.207	18.0
180	3.99	27.4	17.262	17.5

4.1.2. Effect of Adsorbent Dose on iron (III) loading

The effect of the adsorbent dose on attachment of iron (III) was tested at the agitation time of 30 min by varying the adsorption dosage (Table 4.2). The pH was observed to increase gradually with increase in mass of adsorbent up to a dosage of 3 g, a drastic increase was thereafter observed as the dosage increased to 5 g. The increase in pH indicates a possible release of the hydroxyl as Fe^{3+} gets adsorbed on the surface of the adsorbent. The drastic increase of pH at high dosages could also be due to abstraction of H^+ from water molecules with subsequent release of hydroxyl groups as the negative surface charge increases with bentonite dosage.

Table 4.2: Variation of pH, EC, TDS and Temperature with adsorbent dosage (100ppm)

Adsorbent Dosage (g)	pH	EC (µs/cm)	TDS (mg/l)	Temperature (^{0}C)
0	2.86	36.4	22.932	21.6
0.2	2.93	32.8	20.664	21.1
0.3	3.09	31.7	20.288	20.7
0.5	3.18	30.8	19.404	20.3
0.8	3.22	30.0	18.9	20.1
1.0	3.29	35.3	22.239	21.4
3.0	3.54	36.1	22.743	22.3
5.0	4.72	37.4	23.562	22.5

A gradual decrease in EC and TDS was observed with increase in adsorbent dosage to a maximum at 0.8 g (Table 4.8). Adsorbent dosage of 0.8 g corresponded to the adsorption of Fe^{3+} (0.1 mg/l). Since EC, TDS and pH variables stabilized at 0.8g of dosage, it is chosen as the optimum for subsequent experiments. Subsequently the Fe^{3+}-modified bentonite for de-fluoridation experiments was synthesized at the obtained optimal conditions of 100ppm Fe^{3+} solution, 0.8 g bentonite and 30 min of agitation.

4.2. Characterization of raw and Fe^{3+}-Modified Bentonite

After modifying the raw bentonite using iron (III) sulphate solution at optimum conditions (0.358g of $Fe_2 (SO_4)_3.H_2O$ in 1L water and 8g raw bentonite). Then instrumental characterizations which are XRD, FTIR, CEC and pHpzc were done for raw and modified bentonite, of which results are discussed as follows.

4.2.1. X-ray diffraction

Mineral composition of raw and modified bentonite clay were determined by XRD studies. The occurrences of minerals in clay were identified by comparing 2 theta values.

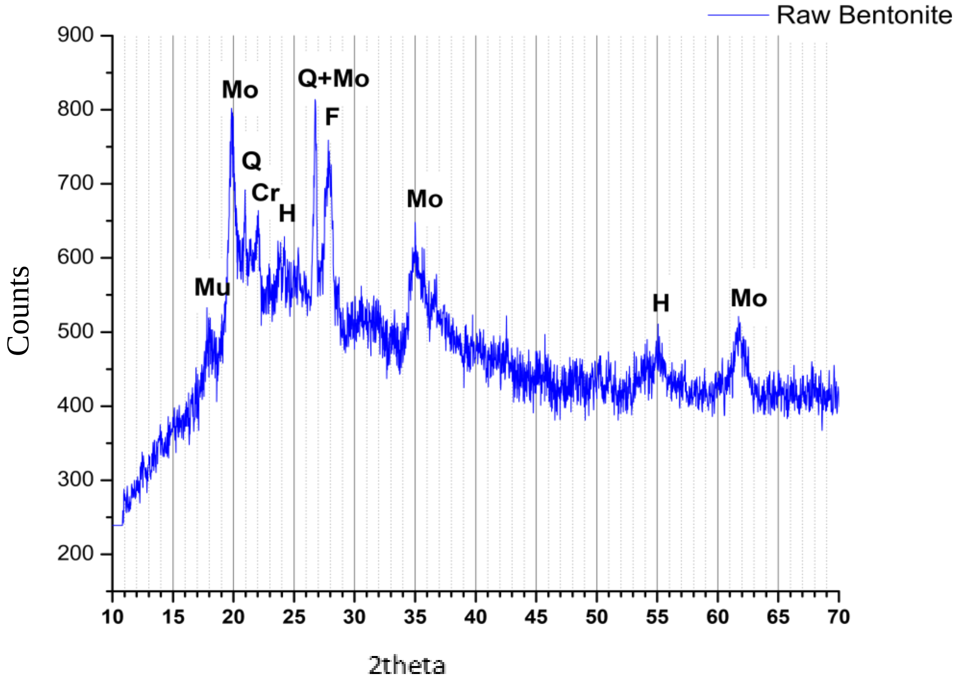


Figure 4.1: X-ray diffraction of raw bentonite

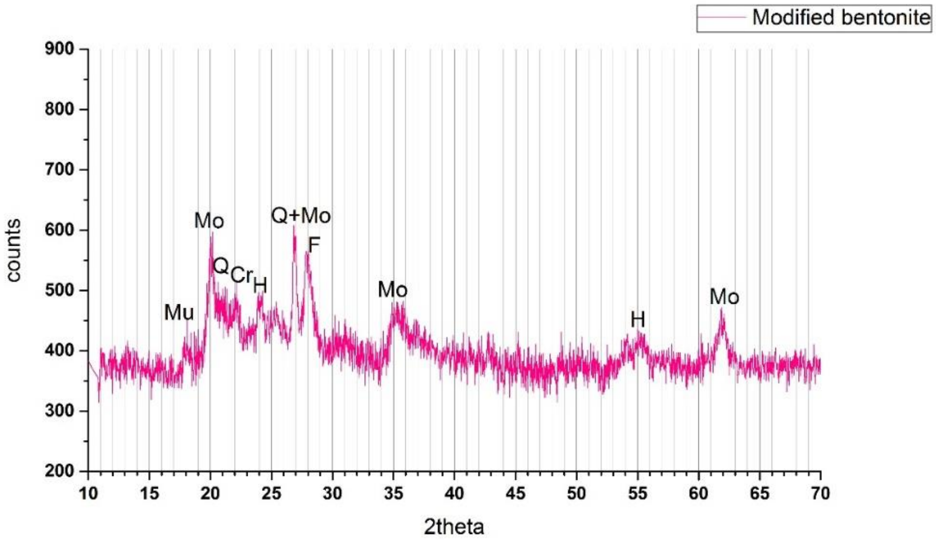


Figure 4.2: X-ray diffraction of modified bentonite

Characterization of XRD patterns for raw bentonite indicates the presence of Montmorillonite (Mo), Cristobalite (Cr), Quartz (Q), Muscovite (Mu), Hematite (H) and Feldspar (F) as the major phases (Table 4.3).

In comparison with the diffraction pattern of raw bentonite, the changes in the diffractogram of the modified bentonite, shows a decrease in the intensities of all reflections, indicating that they are all affected by F^{3+} treatment.

Table 4.3: Descriptions of the indicated minerals

Mineral name	Formula	Crystal system
Montmorillonite	$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$	Monoclinic
Quartz	SiO_2	Trigonal (hexagonal axes)
Hematite	Fe_2O_3	Hexagonal
Cristobalite	SiO_2	Tetragonal
Muscovite	$KAl_2(Si_3Al)O_{10}(OH)_2$	Monoclinic
Feldspar	$KAlSi_3O_8 – NaAlSi_3O_8 – CaAl_2Si_2O_8$	Triclinic

It can be seen that, the iron (III) ion treatment affected mainly the montmorillonite and quartz phases which gave intensity difference of 200 and 196, respectively Figure (4.1) and (4.2). This means that the process favors the production of amorphous phase by decomposing montmorillonite and quartz structures. On the other hand, since the montmorillonite peak is still present after the treatment, it can be assumed that the structure has been partially destroyed. Generally, this change is expected to have a positive impact on the adsorption efficiency of the modified bentonite clay.
The XRD results revealed that the bentonite clay contains 40% Montmorillonite, 20% Quartz, 10% Muscovite, 10% Cristobalite and 10% Feldspar. Which explains that the bentonite clay is mainly composed of SiO_2 and Al_2O_3 indicating that it is an aluminosilicate material.

4.2.2. Fourier transformed infrared spectroscopy (FTIR)

To recognize the functional group and identify characteristic bands of the raw and modified bentonite, the FTIR spectra were performed in the range from 4000 to 400cm^{-1} to investigate the effect of modification on the chemical composition of the bentonite. Published collections of spectra of clay minerals as those reported by palanivel and velrai (2002) are very useful for identification and characterization of the bentonite mineral. Figure (4.3) and (4.4) shows that there are three main absorption regions: 3000-3800cm^{-1}, 1300-1800cm^{-1}, and 500-1200cm^{-1}, and sharp differences could be found in each region of the bentonite samples.

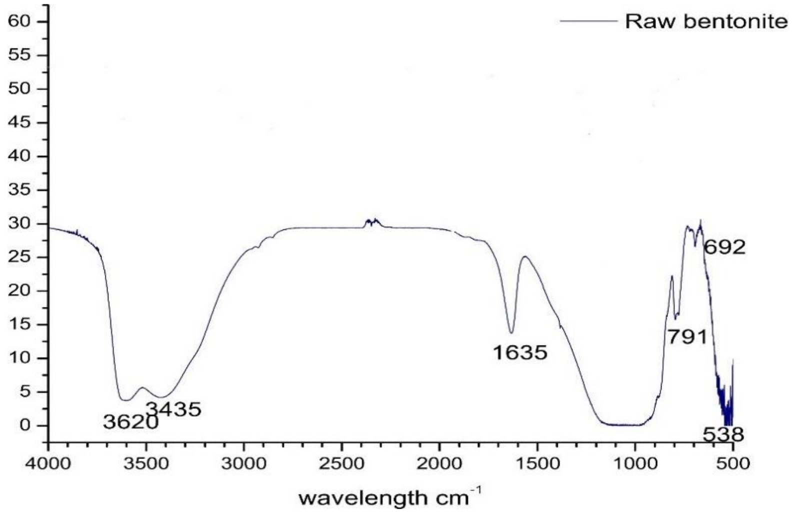


Figure 4.3: FTIR spectra of raw bentonite

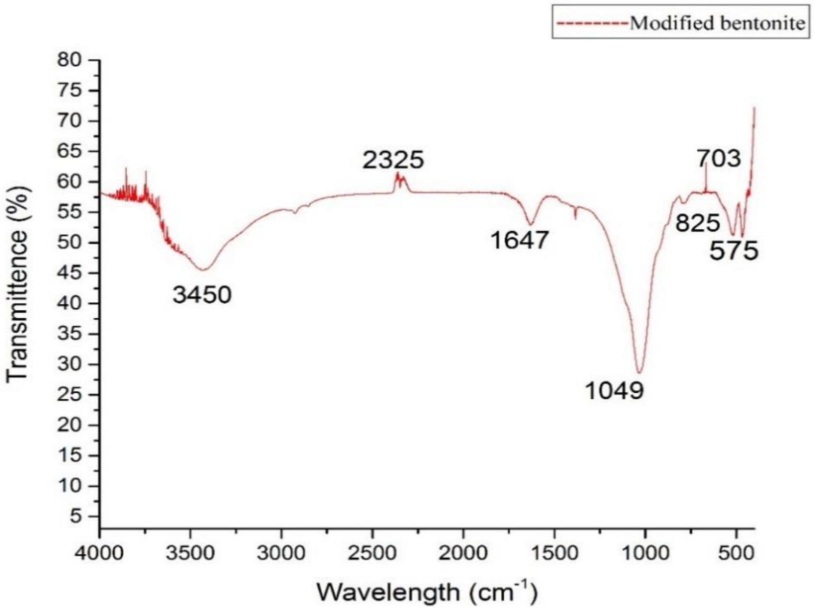


Figure 4.4: FTIR spectra of raw bentonite

The IR spectrum of raw bentonite indicates that montmorillonite is the dominant mineral phase in this bentonite. The KBr curve of raw bentonite was characteristic of montmorillonite with a broad band of 3450 cm^{-1} resulting vibrational stretching of structural hydroxyl groups and water. The absorption band at 1647 cm^{-1} was attributed to the OH deformation mode of water. The 703 cm^{-1} band corresponded to coupled Al–O and Si–O out-of-plane vibrations. Quartz was present as indicated by the bands at 825 cm^{-1} and 575 cm^{-1}, in agreement with XRD result.

FTIR is very sensitive to the structural changes which occur in the clay upon the impregnation of iron (III) (Breen et al., 1995) and the IR data recorded herein suggest that both the octahedral and tetrahedral sheets were susceptible to iron (III) ion attachment. The intensity of stretching bands observed at 3450 cm^{-1} (Al–OH–Al along with the Al–Mg–OH stretching vibrations) decreased after iron (III) ion modification. Modification with iron (III) ion has also resulted a decrease in the peaks of the bands associated with the adsorbed water at 2325 (H–O–H stretching) and 1647 cm^{-1} (H–O–H bending). It is due to the removal of octahedral cations, causing the loss of water and hydroxyl groups coordinated to them. The intensity of the band at 1049 cm^{-1} increases due to the formation of three–dimensional networks of amorphous Si–O–Si units. The intensity of band at 703 cm^{-1} (Al–OH–Si bending) almost disappeared with iron (III) ion modification, signifying the partial dissolution of aluminum ions present in the octahedral sheet of bentonite. The raw bentonite leads to the formation of amorphous silica, indicated by the increased intensity of the peak, which may provide more adsorption sites.

4.2.3. Cation exchange capacity

Determination of exchangeable cations by ammonium acetate method revealed that Mg^{2+}, Ca^{2+}, Na^{+}, and K^{+} are the exchangeable cations. The CEC results shown in (Table 4.4) reveals that the Ethiopian bentonite clay has a CEC of 59.89 meq/100 g, which decreased to 28.48 meq/100 g by the introduction of Fe^{3+} onto bentonite clay interlayers, indicating that the main mechanism of Fe^{3+} uptake is by ion exchange. This results also confirm that the main exchangeable cation is Ca^{2+}, hence assuring that the type of bentonite clay used in this study is Ca-bentonite clay.

Table 4.4: Cation exchange capacity of raw and iron (III) modified bentonite

	Exchangeable chemical species (mg/l)				CEC
	Na^{+}	K^{+}	Ca^{2+}	Mg^{2+}	(meq/100g)
Raw Bentonite	13.35	2.86	31.31	12.37	59.89
Fe^{3+}-modified Bentonite	4.60	1.35	14.43	8.10	28.48

4.2.4. Point of Zero Charge

PHpzc is the pH at which a surface has net a net charge of zero. If the measured pH of a colloid is lower than the PZC, the surface is positively charged; if the pH>PZC, the surface is net negatively charged (Spark 1997). As it is observed in Figure (4.5) and (4.6) there is an increase in the pH_{pzc} on the introduction of Fe^{3+} cations which resulted a slight difference in pH_{pzc} of Fe^{3+}-modified bentonite clay (9.2) as compared to raw bentonite (9.0). Both raw and Fe^{3+}-modified bentonite clay have high pH_{pzc} characteristic of clay minerals dominated by aluminosilicate materials and iron oxides. Modification of the raw bentonite clay with Fe^{3+} increases the pH_{pzc} and which extends the pH range for adsorption of anions meaning that the Fe^{3+}-modified bentonite clay will have high adsorption capacity for anions (in this case which is F^-) than that of raw bentonite clay. Dong-Su (2003) observed a pH_{pzc} of 8.0 for Korean bentonite clay. The result of Ethiopian bentonite clay showed greater pH_{pzc} than that of Korean clay.

Table 4.5: Variation of pH_i and ΔpH at different KCl concentrations (a) raw bentonite (b) modified bentonite

(a)

	ΔpH (pH_i-pH_f)		
pH_i	0.1M KCl	0.01M KCl	0.001M KCl
2	-0.15	-0.05	-0.09
4	-0.24	-0.48	-0.73
6	-1.05	-1.1	-1.15
7	-0.08	-0.26	-0.8
8	-0.82	-1.3	-1.47
10	1.03	1.44	1.62

(b)

	ΔpH (pH_i-pH_f)		
pH_i	0.1M KCl	0.01M KCl	0.001M KCl
2	-0.07	-0.17	-0.23
4	-0.35	-0.42	-0.79
6	-1.09	-1.11	-1.13
7	-0.17	-0.22	-0.34
8	-1.28	-0.56	-1.54
10	1.08	0.47	1.18

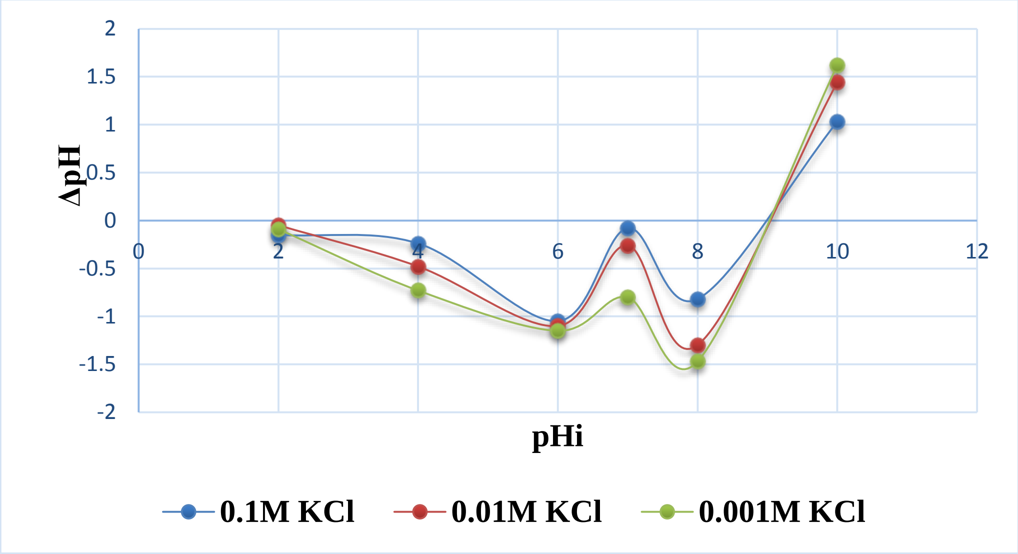


Figure 4.5: pH of zero point of charge of raw bentonite

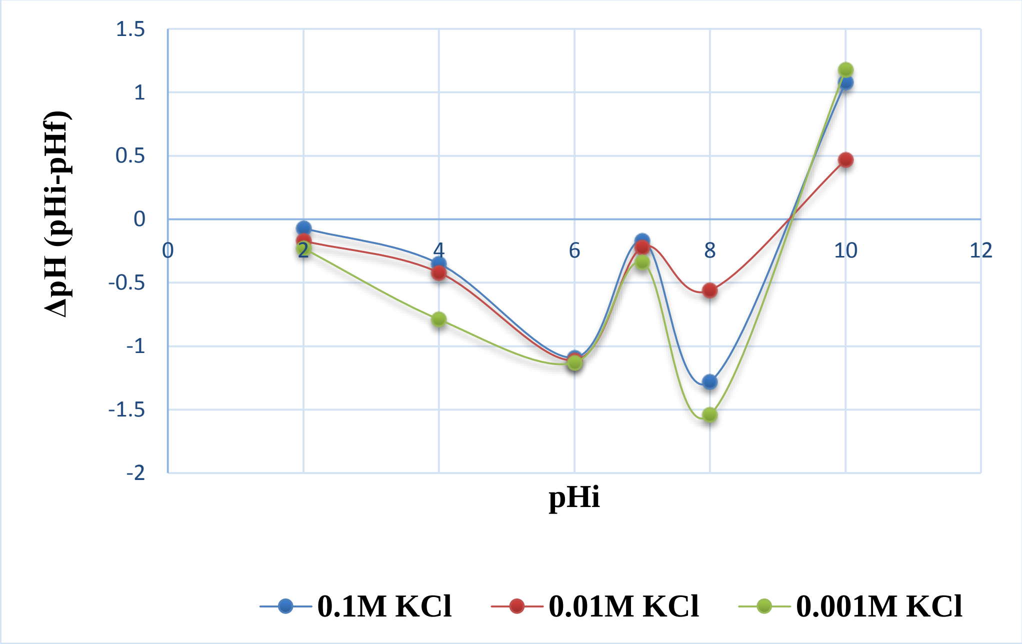
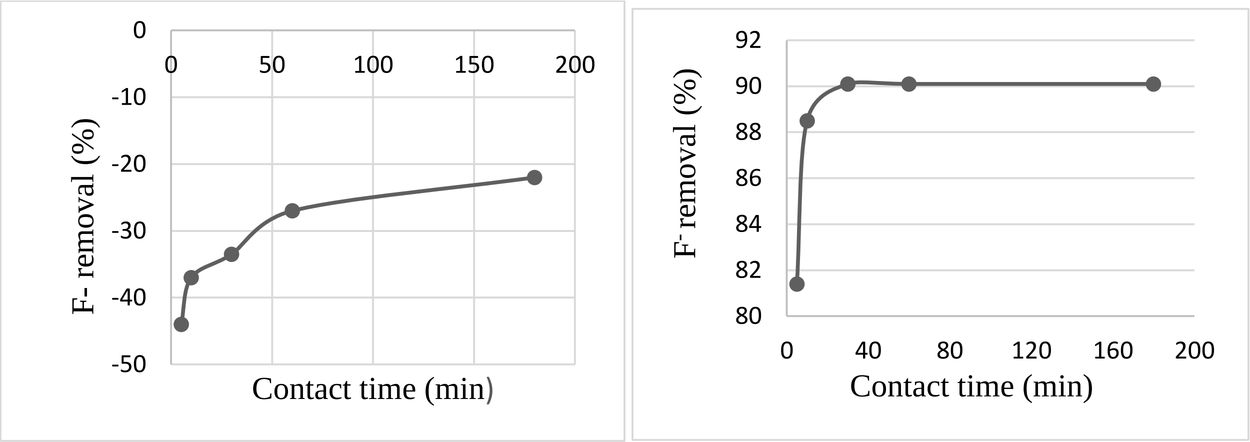


Figure 4.6: pH of zero point of charge of modified bentonite

4.3. Effect of adsorption process variables on fluoride removal

4.3.1. Effect of contact time

As shown in Figure 4.7 (b) the adsorption of fluoride ions onto modified bentonite clay increased rapidly with an increase in contact time from 5 to 30 min, with equilibrium being reached at 30 min. Further increase in time had no effect on the adsorption of fluoride ions, hence depicting that the reaction had reached equilibrium.



(a) (b)

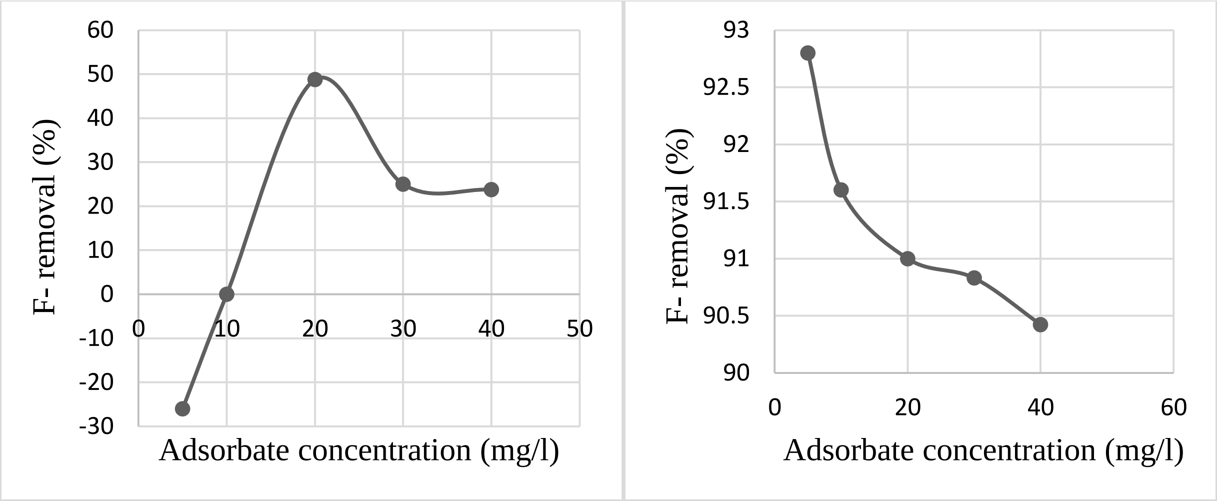
Figure 4.7 Percentage removal as a function of contact time (a) raw bentonite and (b) Fe^{3+}-modified bentonite.

High adsorption affinity may be due to an increase in density of sorption sites as a result of the introduced Fe^{3+} ion, which has high charge density. The maximum contact time of 30 min was therefore considered as the optimum time for subsequent optimization experiments. Fe^{3+}-modified bentonite reduced F^- concentration below 1.5 ppm within 10 min. This clearly indicates the changes in the physicochemical and surface properties of the bentonite clay on the introduction of Fe^{3+} ions. Thereafter, F^- concentration stabilized at values less than 1ppm, while pH stabilized at 3.65 at 30 min of contact time as shown in Appendix B (Table B2).

The TDS and EC increased with contact time for raw bentonite as shown in Appendix B (Table B1) indicating possible release of soluble chemical species in solution. The raw bentonite seems to increase the pH of solution through possible dissolution of alkaline metal oxides, in addition raw bentonite seems to release F^- into solution.

4.3.2. Effect of adsorbate concentration

As shown in Figure 4.8 (b) an increase in adsorbate concentration results an increase in adsorption capacity, hence depicting strong affinity between fluoride species and Fe^{3+}-modified bentonite clay. However, an increase in adsorbate concentration reduces adsorption sites, since more ions are introduced into the system, therefore, with time the system will approach a saturation phase.



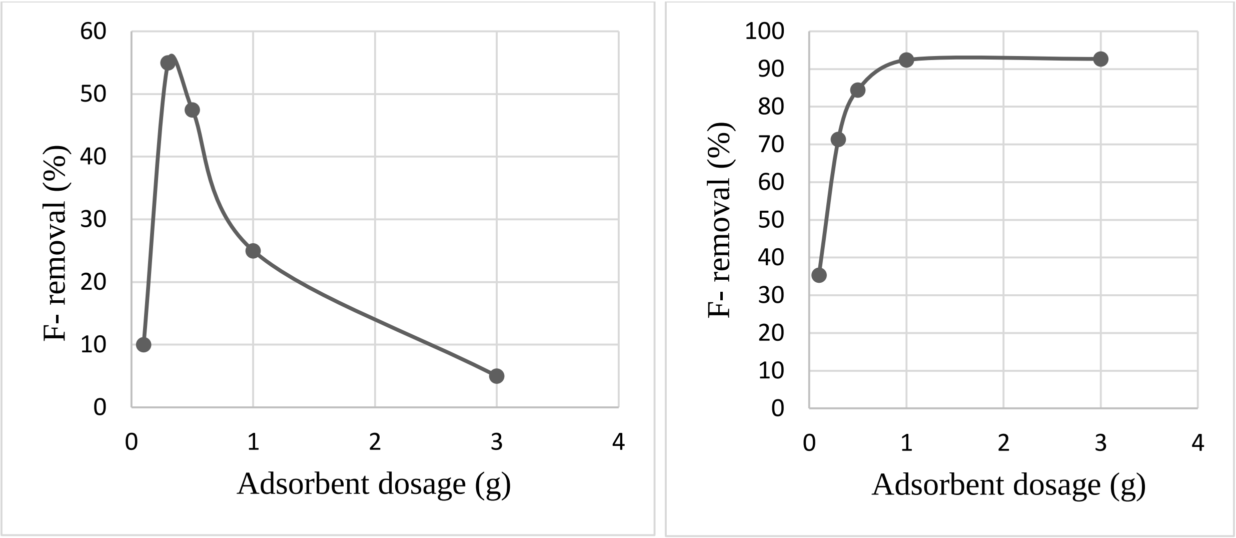
(a) (b)

Figure 4.8: Percentage removal as a function of adsorbate concentration (a) raw bentonite and (b) Fe^{3+}-modified bentonite.

At low concentration, more adsorption sites are available and adsorption is high, but as the concentration increases, the adsorption sites become limiting factor hence resulting in lower adsorption. This study shows good adsorption capacity at elevated concentrations as compared to conventional fluoride removal technologies as shown in Appendix B (Table B4).

Raw bentonite was observed to release F^- in the reaction mixture. As it can be seen in Appendix B (Table B3). Fe^{3+}-modified bentonite shows efficient adsorption, removing >90% of F^- even as the adsorbate concentration increases to 40ppm.

4.3.3. Effect of adsorbent dosage



(a) (b)

Figure 4.9: Percentage removal as a function of adsorbent dosage (a) raw bentonite and (b) Fe^{3+}-modified bentonite.

The minimum dosage required to remove fluoride to prescribed standards of 1.5mg/l and as stipulated by WHO (2011) was determined by varying the dosages of Fe^{3+}-modified bentonite. As shown in Figure 4.9 (b), there was a drastic increase in the adsorption of fluoride ions from aqueous solution onto bentonite clay as the adsorbent dosage increased. The adsorption system revealed that greater than 1g of Fe^{3+}-modified clay is capable of scavenging fluoride from the solution.

An increase in adsorption with an increase in dosage is attributed to an increase in adsorption surfaces. As such, 1g was selected as the optimum dosage for subsequent experiments. At low dosage, finite surfaces are provided for adsorption hence leading to limited removal efficiencies but as the dosage increase, more surfaces which are suitable for adsorption are presented hence enhancing the adsorption efficiency of Fe^{3+}-modified bentonite. Thakrea et al. (2010) have reported that 3g is suitable to reclaim water to a potable standard by removing fluoride to below 1.5mg/l as recommended by WHO. The required dosages are observed to be very high as compared to the results obtained from this study.

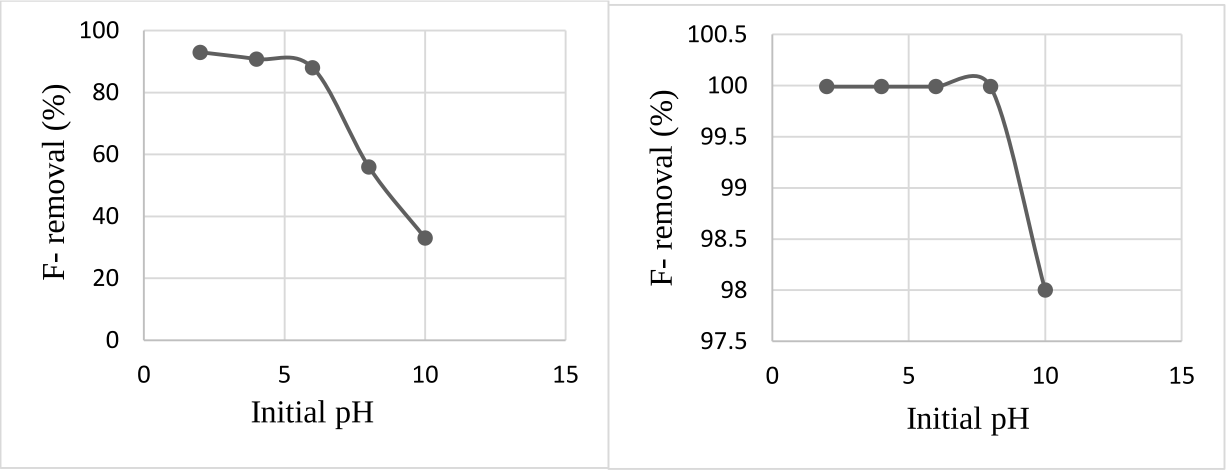
An observation of Figure 4.9 (a) shows that raw bentonite actually releases F^- into solution; this was observed to increase with adsorbent dosage. pH also increases with adsorbent dosage confirming release of OH^- in solution through possible dissolution of alkaline metal oxides. But when it comes to Fe^{3+}-modified bentonite the pH decreases with an increase of adsorbent dosage.

The modified bentonite could be releasing H^+ to compensate for the adsorbed F^- ions, hence lowering pH or the hydrolysis of hydrated $[Fe\ (H_2O)_6]^{3+}$ in the bentonite interlayers.

$$[\mathrm{Fe}\ (\mathrm{H_2O})_6]^{3+} \rightarrow [\mathrm{Fe}\ (\mathrm{H_2O})_5\ \mathrm{OH}]^{2+} + \mathrm{H}^{+} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.1)$$

4.3.4. Effect of initial pH

Raw bentonite shows lower adsorption of F^- at pH ≥ 8. However, Fe^{3+}-modified bentonite clay shows strong adsorption of F^- at pH range of 2-10 for 10-15ppm F^- concentrations. As it can be seen in Appendix B (Table B8), it can be concluded that pH doesn't affect the adsorption of F^- onto Fe^{3+} modified bentonite clay if F^- concentration is lower than 15ppm. But as the F- concentration increases pH greatly affects the adsorption process. This shows the strong interaction of pH and concentration.



(a) (b)

Figure 4.10: Percentage removal as a function of initial pH (a) raw bentonite and (b) Fe^{3+}-modified bentonite.

As shown in Appendix B (Table B9) the F^-concentration increases above 15ppm Fe^{3+}-modified bentonite clay shows strong adsorption at pH range of 2-10. A slight decrease was observed at pH 6-10, this is attributed to the change in surface charge as the pH of the solution approaches pH_{pzc} (9.2) for Fe^{3+}-modified bentonite clay. At pH< $pH_{pzc,}$ the modified clay surfaces are positively charged, whereas at pH> $pH_{pzc,}$ the modified surfaces are negatively charged. The low adsorption at high alkaline pH could be due to the competition of adsorption sites with OH^- and due to the fact that the surface of the clay is becoming negatively charged and there is an increased electrostatic repulsion of the anionic fluoride as the pH> pH_{pzc} for Fe^{3+}-modified bentonite clay by diminishing the positively charged sites of Fe^{3+}-modified bentonites. Similar results were also observed on the adsorption of F^- with Mg-bentonite clay (Thakrea et al. 2010).

The mechanism of F^- adsorption by Fe^{3+}-modified bentonite seems to involve largely the interaction of the F^- ion with the hydrated Fe^{3+} ion in the bentonite interlayers.

$$[\mathrm{Fe}\ (\mathrm{H_2O})_6]^{3+} \rightarrow [\mathrm{Fe}\ (\mathrm{H_2O})_3\ (\mathrm{OH})_3] + 3\mathrm{H}^+] \ldots\ldots \quad (4.2)$$

$$[\mathrm{Fe}\ (\mathrm{H_2O})_3\ (\mathrm{OH})_3] + \mathrm{F}^- \rightarrow [\mathrm{Fe}\ (\mathrm{H_2O})_3\ (\mathrm{OH})_2\ (\mathrm{F})] + \mathrm{OH}^- \ldots\ldots \quad (4.3)$$

$$[\mathrm{Fe}\ (\mathrm{H_2O})_3\ (\mathrm{OH})_2\ (\mathrm{F})] + \mathrm{F}^- \rightarrow [\mathrm{Fe}(\mathrm{H_2O})(\mathrm{OH})(\mathrm{F_2})] + \mathrm{OH}^- \ldots\ldots \quad (4.4)$$

At pH 2 the surface of the clay is positively charged and F^- would be electrostatically attracted to the clay surface which explains the high F^- adsorption. However, as pH increases to 4 there was an increase of OH^- ions that compete with F^- for the adsorption sites. This explains the slight decrease in F^- adsorption over the pH range of 4-10.

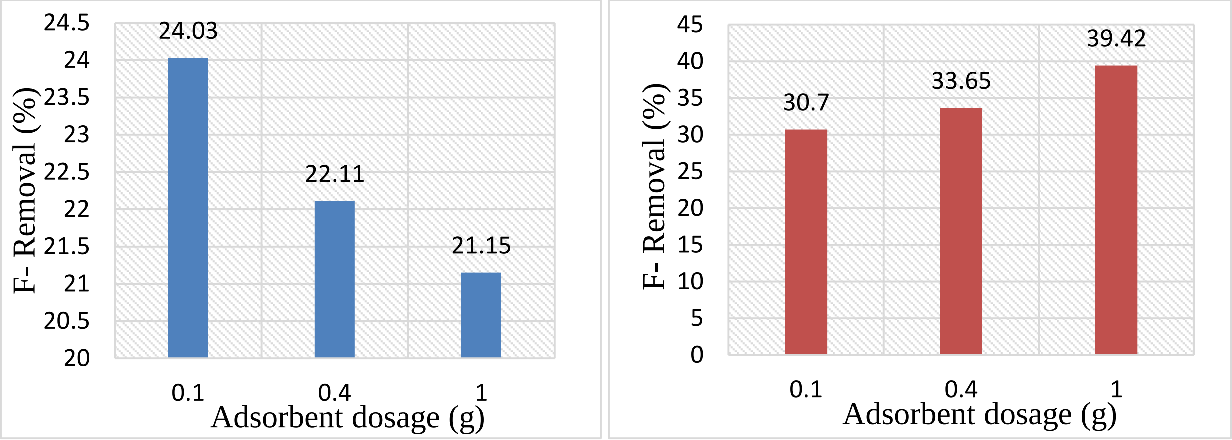
As the pH increased the adsorption of F^- onto the raw bentonite decreased; which resulted an increase in EC and TDS. This is due to the presence of OH^- ions, the greater their concentrations, the greater the conductivity (which is a function of mobility and velocity).

4.4. De-fluoridation of Surface Water

Table 4.6: Physicochemical Parameters of the Basaka Lake

pH	EC (µs/cm)	TDS (mg/l)	F^- (mg/l)	Cl^- (mg/l)	$SO4^{2-}$ (mg/l)
9.13	52.8	33.264	26	192.187	65.628

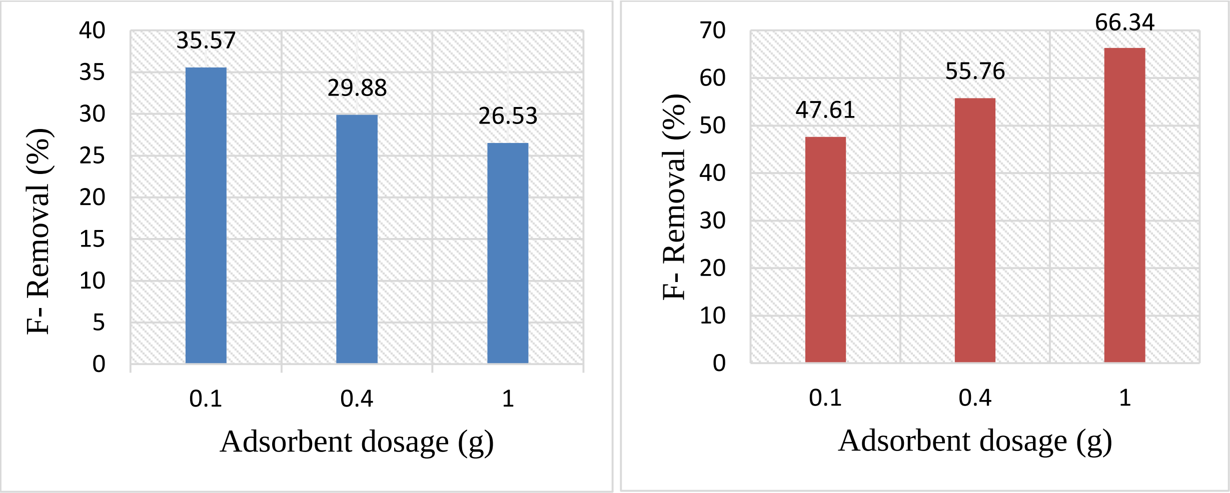
A slight increase in the F^- concentration was observed as the amount of adsorbent increased for the raw bentonite as shown in Figure 4.11 (a); with a maximum being observed at 1g/100ml S/L ratio. These observations indicate that the raw bentonite can be a source of F^- and will need further investigation to ascertain its F^- leaching potential at various pH. As for Fe^{3+}-modified bentonite a decrease in F^- concentration was observed as the adsorbent increased with maximum adsorption being observed at 1g/100ml S/L ratio. Poor adsorption of F^- at normal pH (9.13) of the surface water could be attributed to the competition for adsorption sites between F^-, OH^-, Cl^-, and SO_4^{2-} ions (Table 4.6).



(a) (b)

Figure 4.11: Effect of (a) raw and (b) modified bentonite dosage of on percentage removal of fluoride for water obtained from Lake Basaka at 9.13 pH

When it comes to surface water de-fluoridation at pH 6.14, a gradual increase in pH of supernatant was observed as the adsorbent dosage increased.



(a) (b)

Figure 4.12: Effect of raw bentonite dosage of on percentage removal of fluoride for water obtained from Lake Basaka at 6.14 pH

As shown in Figure 4.12 (a) there was negative absorption of F^- as the adsorbent dosage increased meaning that the raw bentonite was leaching F^- ions into the supernatant. The pH of the filtrate was observed to decrease with increase in adsorbent dosage Figure 4.12 (b). The decrease in pH is an indication that the F^- removal by the Fe^{3+}-modified bentonite was accompanied by the release of hydroxyl ions that reacted with H^+ ions in solution. A drastic decrease in F^- concentration was observed with increasing adsorbent dosage with a minimum concentration observed at 1g dosage.

4.5. Performance of Fe^{3+}-Modified Bentonite for F^- Removal from synthetic water Solution of fluoride

Optimization for the Fe^{3+}-modified bentonite was carried out using full factorial design with three factors (Adsorbent Dosage, Adsorbate Concentration and Contact Time) and one response (% F^- Removal). Statistical analysis was carried out to determine correlation coefficients of the model as a function of responses.

4.5.1. Analysis of model adequacy and response surface methodology

Design-Expert Software 7.0.0 is a statistical software package from Stat-Ease Inc. that is specifically dedicated to performing design of experiments (DOE). Statistical significance of factors was established with Analysis of Variance (ANOVA).

The experimental design selected for this study was Response Surface Methodology (RSM) and the response variable measured was percentage fluoride removal. RSM provides an estimate for the value of responses for every possible combination of the factors by varying the values of all factors in parallel, making it possible to comprehend a multi-dimensional surface with non-linear shapes (Jerry Fireman et. al., 2011).

RSM may involve the main effects and interactions or they may also have quadratic and possibly cubic terms to account for curvature. RSM designs are formed by combining 3^K factorial where K was three for three factors (independent variables) used in the analysis. A total of 27 runs and 5 center points were conducted in the optimization study. The RSM 3-Level factorial design conditions and their respective responses are given in Appendix E (Table E1).

The adequacy of the model was further checked with analysis of variance (ANOVA) as shown in (Table 4.7), based on a 95% confidence level, F-value is a test for comparing model variance with residual (error) variance. If the variables are close to the same, the ratio will be close to one and it is likely that any of the factors have significant effect on the response with the P-value less than 0.05. It is calculated by the model mean square divided by residual mean square.

Table 4.7: Analysis of variance (ANOVA) of the fitted quadratic model

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Model	4309.94	9	478.88	22.43	< 0.0001	Significant
A-Adsorbent Dosage	581.45	1	581.45	27.23	< 0.0001	
B-Fluoride Concentration	1092.30	1	1092.30	51.16	< 0.0001	
C-Contact Time	142.27	1	142.27	6.66	0.0170	
AB	165.53	1	165.53	7.75	0.0108	
AC	96.06	1	96.06	4.50	0.0454	
BC	209.88	1	209.88	9.83	0.0048	
A^2	47.59	1	47.59	2.23	0.1497	
B^2	1688.41	1	1688.41	79.07	< 0.0001	
C^2	2.52	1	2.52	0.12	0.7346	
Residual	469.75	22	21.35			
Lack of Fit	424.31	17	24.96	2.75	0.1340	not significant
Pure Error	45.45	5	9.09			
Cor Total	4779.70	31				

The Model F-value of 22.43 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise (personal error or disturbance). Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC, BC, B^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

The "Lack of Fit F-value" of 2.75 implies the Lack of Fit is not significant relative to the pure error. There is a 13.40% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good so that the model could fit.

This shows that the adsrobent dosage, fluoride concentration, contact time, interaction between adsorbent dosage and fluoride concentration, interaction between adsorbent dosage and contact time, fluoride concentration and contact time affects the percentage removal significantly.

The model was tested for adequacy by analysis of variance. The regression model was found to be highly significant with the correlation coefficients of determination of R-Squared, Adjusted R-Squared and Predicted R-Squared having values of 0.9017, 0.8615 and 0.7829 respectively.

The quality of the model developed could be evaluated from their coefficients of correlation. The value of R-Squared for the developed correlation was 0.9017. It implies that 90.17% of the total variation in the percentage removal of fluoride was attributed to the experimental variables studied. The Predicted R-Squared of 0.7829 is in reasonable agreement with the Adjusted R-Squared of 0.8615. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. In this case, ratio of 18.611 indicates an adequate signal. This model can be used to navigate the design space.

The graph of the predicted values obtained using the developed correlation predicted versus actual values is shown in Figure (4.13). The results in Figure (4.13) demonstrate that the regression model equation provided an acceptable description of the experimental data, in which most of the points are close to the line of perfect fit. This indicates that it was successful in capturing the correlation between the three de-fluoridation process variables to the percentage removal of fluoride.

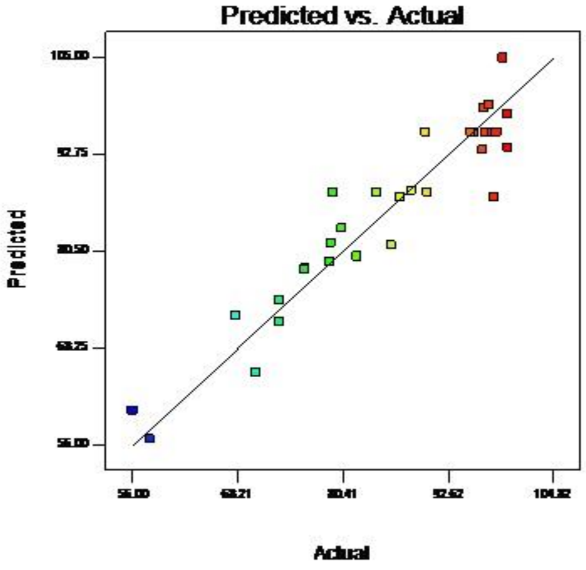


Figure 4.13: predicted versus actual percentage removal of F^- in aqueous solutions

The statistical software program is used to generate the model equation, interaction effects of the independent variables and surface plots using the fitted equation obtained from the regression analysis. The actual % removal of fluoride from aqueous solution obtained at different process parameters were evaluated in Addis Ababa City Environmental Protection Authority.

4.5.2. Effect of de-fluoridation process variables

Based on the analysis of variance, effects of each individual process variables and their interaction effects on the target response of percentage removal of fluoride was determined. RSM provided a good information on the experimental data analysis in capturing individual process variables that significantly affect the defluoridation process which include adsorbent dosage, fluoride concentration and contact time. In addition to individual effects, significant interaction effects were considered for analysis.

4.5.2.1. Effect of individual process parameters

As shown in Figure (4.14) the percentage fluoride removal was significantly affected by adsorbent dosage. An increase in percentage removal with an increase in adsorbent dosage was attributed to an increase in adsorption surfaces. At low dosage, finite surfaces are provided for adsorption hence leading to limited removal efficiencies but as the dosage increase, more surfaces which are suitable for adsorption are presented.

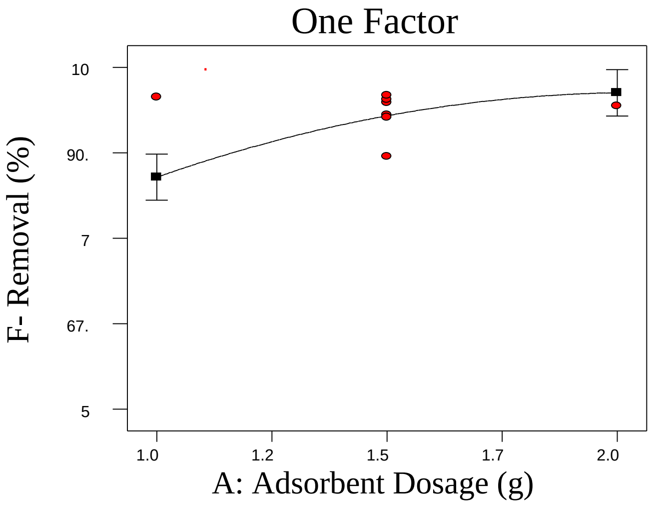


Figure 4.14: Effect of adsorbent dosage on percentage removal of fluoride

As shown in Figure (4.15) the percentage fluoride removal was significantly affected by initial fluoride concentration. Increasing fluoride concentration (until 18ppm) would result in increament of the percentage removal of fluoride, hence depicting strong affinity between fluoride and species and Fe^{3+}-modified bentonite clay. The percentage removal of fluoride then starts to drop as the fluoride concentration tends to increase above 18ppm. Such behaviour could be attributed to; An increase in adsorbate concentration reduces adsorption sites which were available on the modified bentonite clay. Since more ions were introduced into the system, with time the system will approach a saturation phase. At low fluoride concentrations, more adsorption sites were available and adsorption was high, but as the concentration increases, the adsorption sites become limiting factor hence resulting in lower adsorption.

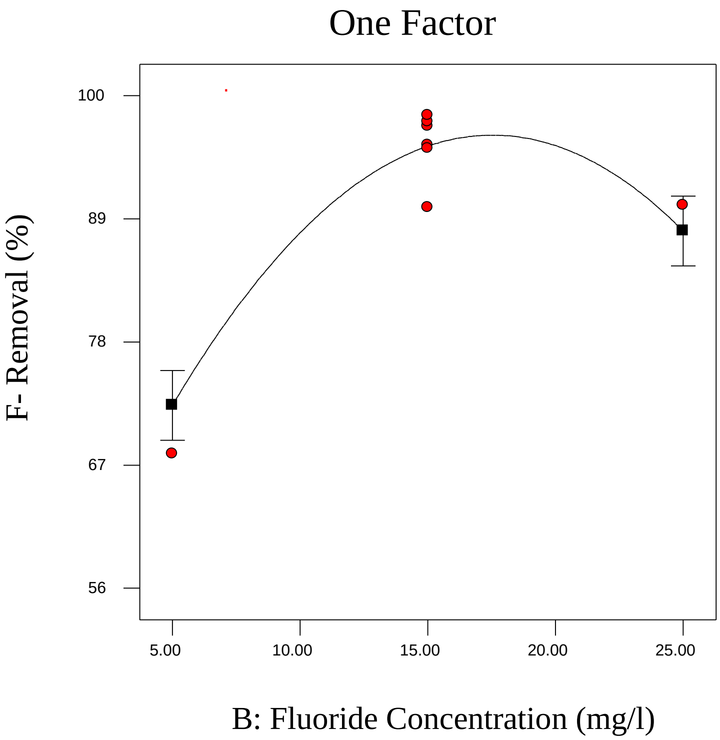


Figure 4.15: Effect of initial fluoride concentration on percentage removal of fluoride

As shown in Figure (4.16) increasing contact time resulted an increase in percentage removal of fluoride depicting that as time increases the F^- ions were attached at the surface of the modified bentonite more thoroughly.

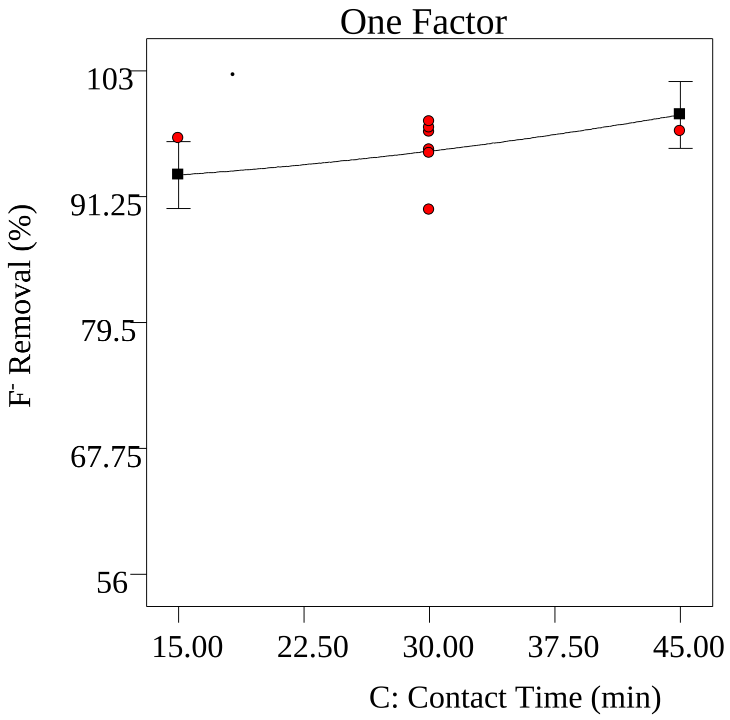


Figure 4.16: Effect of contact time on percentage removal of fluoride

4.5.2.2. Effect of Interaction between Process Variables

The most common way to summarize the results of response surface methodology (3-level full factorial) design experiment is in the form of three dimensional response surface plot and via response contour plot. The process variables were found to have high significant interaction effects, relatively less interaction effect is observed between adsorbent dosage and contact time. Meanwhile, higher interaction effect is observed between adsorbate concentration and contact time.

Figure (4.17, 4.19 and 4.21) shows the interaction effect of adsorbent dosage with fluoride concentration, the interaction effect of adsorbent dosage with contact time and the interaction effect of fluoride concentration with contact time, respectively. As shown in Figure (4.17) the maximum F^- removal is achieved at higher adsorbent dosage and medium fluoride concentration. Also it can be seen in Figure (4.19) that the maximum F- removal is achieved at higher adsorbent dosage and high contact time. Figure (4.21) also shows at higher range of time, fluoride concentration at center point and adsorbent dosage at intermediate will result maximum F^- removal.

From the three interaction effects shown in the figures and contours at higher range of adsorbent dosage, fluoride concentration at center point and contact time at intermediate, always resulted in higher fluoride removal than when using lower or higher contact time.

The above observations can easily be explained as higher adsorbent dosage and medium contact time will result in higher F^- removal, while medium F^- concentration will favor high contact time with increased adsorbent dosage and also higher contact time & medium F^- concentration at medium adsorbent dosage will ensure the F^- removal goes to maximum value.

The observations showed that using a combination of higher F^- concentration, lower contact time and lower adsorbent dosage is not beneficial in increasing the percentage removal of F^-. This is because at this process conditions, lower amount of F^- concentration is sufficient to push the F^- removal efficiency forward. This phenomenon is further supported by the fact that the F^- concentration is the most significant process variable that affect the percentage removal of F^- as indicated by the highest F-value in the ANOVA as shown in Appendix B.

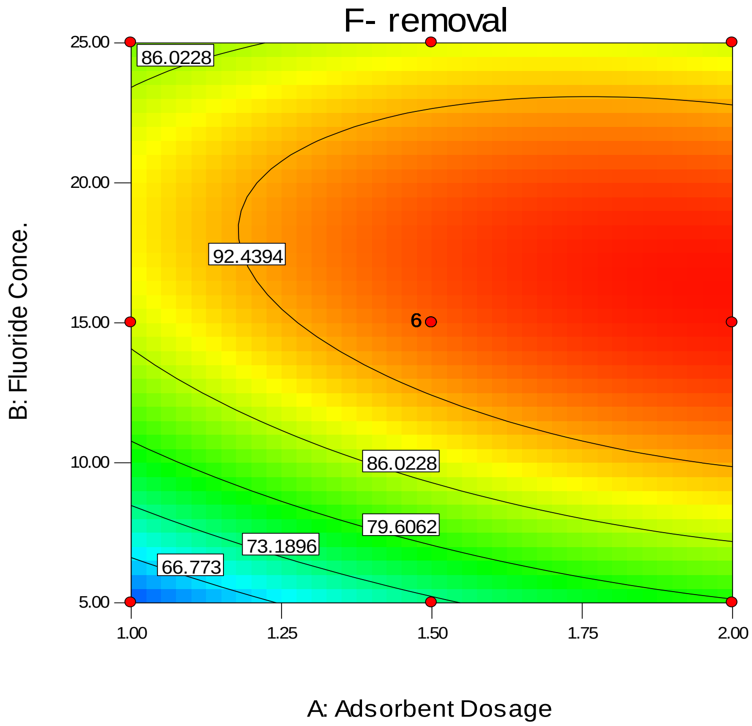


Figure 4.17: Contour plot of the interaction effect of adsorbent dosage and fluoride concentration versus F^- removal when the contact time is 30 min.

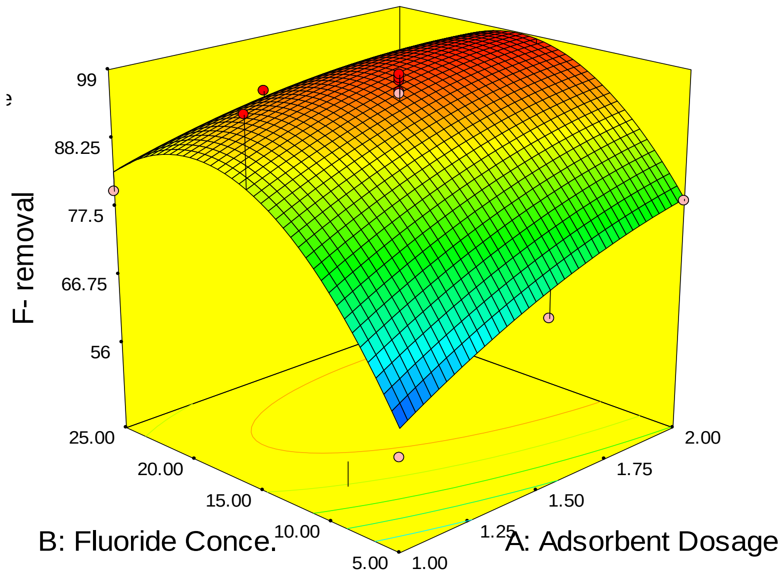


Figure 4.18: 3D-surface plot of the interaction effect of adsorbent dosage and fluoride concentration versus F^- removal when the contact time is 30 min.

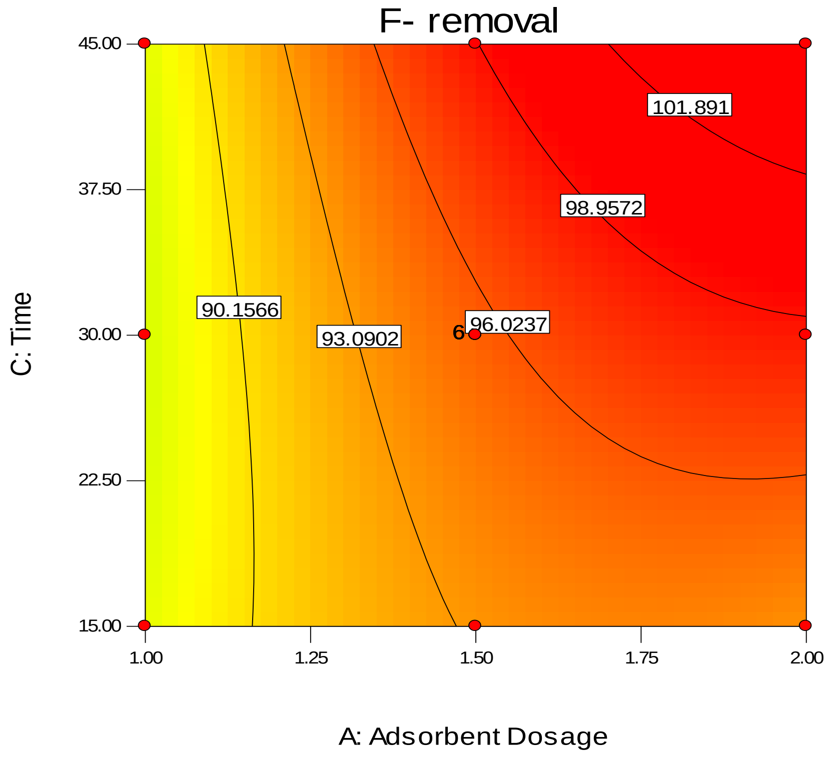


Figure 4.19: Contour plot of the interaction effect of adsorbent dosage and time versus F^- removal when the fluoride concentration is 15.00 ppm

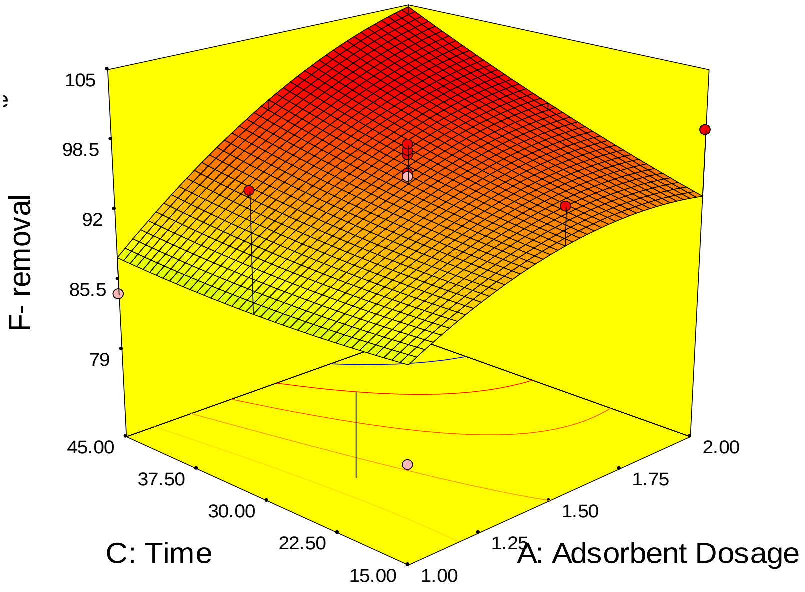


Figure 4.20: 3D-surface of the interaction effect of adsorbent dosage and time versus F^- removal when the fluoride concentration is 15.00 ppm

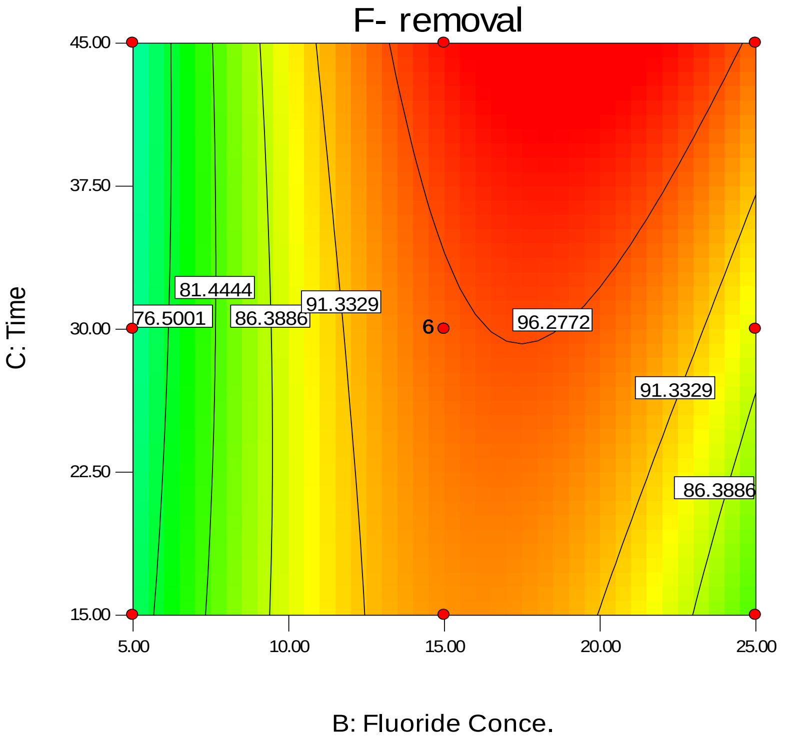


Figure 4.21: Contour plot of the interaction effect of fluoride concentration and time versus F^- removal when the adsorbent dosage is 1.5 g

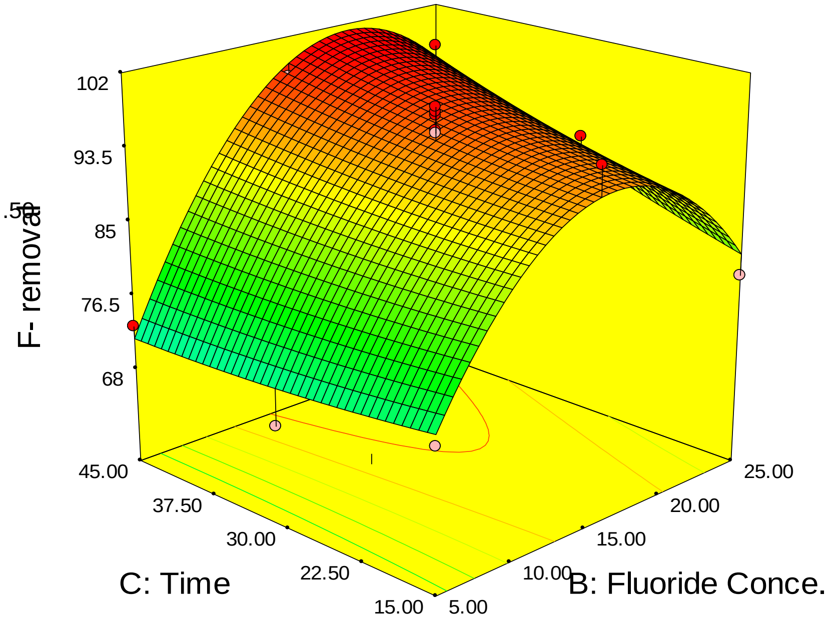


Figure 4.22: 3D-surface plot of the interaction effect of fluoride concentration and time versus F^- removal when the adsorbent dosage is 1.5 g

4.5.3. Development of Regression Model Equation

Experimental values were fitted to a second-order polynomial model Equation (4.5) and the model equation that correlates the response (% removal of F^-) to the de-fluoridation process variables in terms of actual value after excluding the insignificant terms is given below. The predicted model for percentage removal of fluoride in terms of the coded factors is given in Equation (4.5).

Kumar et al. (2008) stated that when regression coefficient has a positive sign, the increase of the associated factor causes an increase in response and a negative sign would cause a decrease in the optimization parameter.

$$\text{Percentage removal} = +95.49 + 5.68 * A + 7.79 * B + 2.81 * C - 3.71 * A * B + 2.83 * A * C + 4.18 * B * C - 2.58 * A^2 - 15.36 * B^2 + 0.59 * C^2 \ldots\ldots\ldots\ldots\ldots\ldots (4.5)$$

Where A= Adsorbent Dosage B= Fluoride concentration C= Contact Time

4.5.4. Optimization of process variables

The results above have shown that the de-fluoridation process variables and the interaction among the variables in order to obtain the highest percentage removal of fluoride using the model regression developed. Therefore, in order to obtain the maximum percentage removal of fluoride, the predicted combination of parameters was as follows: adsorbent dosage of 1.52g, fluoride concentration of 18.37 ppm and time of 39.90 minutes. Under this conditions, the model predicted fluoride removal of 99.6118% with a desirability value of 1.

To validate the optimum conditions predicted by the model using desirability ramp, triplicate experiments were conducted using the optimized de-fluoridation process conditions and mean percentage conversion value of 98.5213% (98.214%, 99.457% and 97.893%) was obtained and results are closely related with the data obtained from optimization analysis using desirability functions. Therefore, this study shows that modification of raw bentonite with Fe^{3+} can definitely enhance fluoride removal from aqueous solutions.

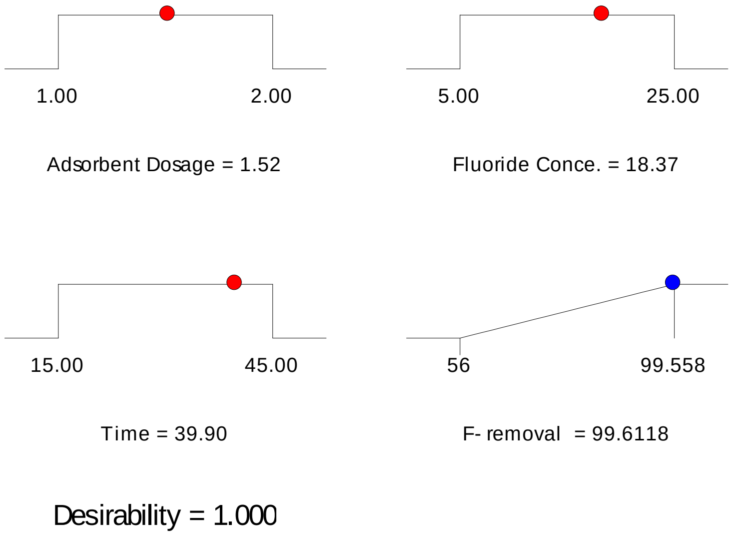


Figure 4.23: Optimum condition of de-fluoridation

4.6. Adsorption kinetics

Kinetic studies were carried out to see the effect of initial fluoride concentration on the fluoride removal rate. The effect of time factor was studied starting from 1 min to 180 min at different initial fluoride concentration (5-25 mg/L). It has also been observed that the removal of fluoride is very rapid in the first 10 min and then reaches maximum at time of 30 min. This nature is due to the high surface area of the small particles which leads to high affinity towards adsorption of fluoride. For the adsorbent dose of 1 g, the amount of fluoride ion adsorbed at each concentration increased rapidly in the beginning and slowly at the end. The equilibrium was reached within 30-60 min.

The fluoride adsorption on Fe^{3+}-modified bentonite was found to be very fast, almost 90.1% of the total adsorption was completed within 30 minutes. The change in the rate of removal might be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient is high requiring longer contact time to be dispersed and get attached to the active site of the adsorbent in this case the fluoride ions compete to get attached to Fe^{3+}-modified bentonite which has high magnetic property.

In order to elucidate the adsorption kinetic process, the data in Appendix D was applied for the two most widely used models (i.e. pseudo- first order rate and pseudo-second order rate models). Based on the calculations done and summarized in (Table 4.8) the linear regression of pseudo first and second order kinetic models are shown in Figure (4.24) and Figure (4.25).

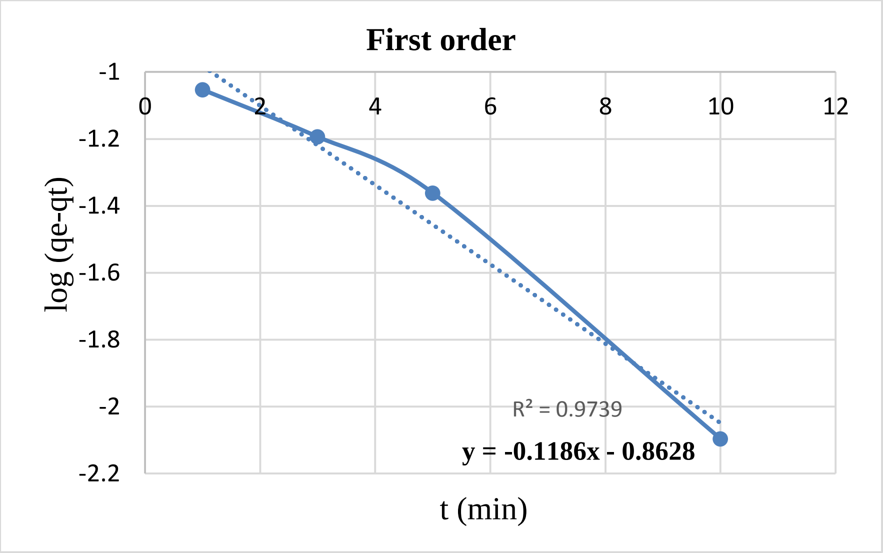


Figure 4.24: Linear regression of the pseudo-first order kinetic model

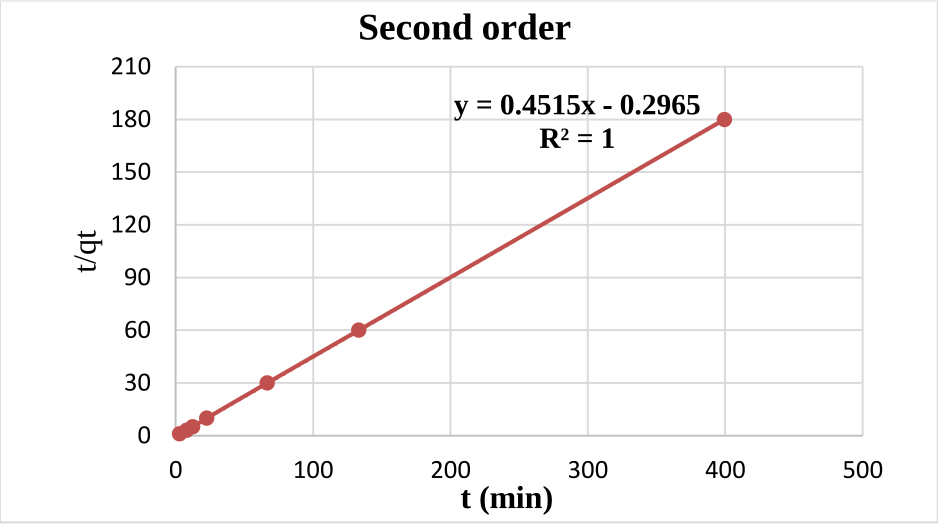


Figure 4.25: Linear regression of the pseudo-second order kinetic model

Table 4.8: Parameters for Pseudo-first order and Pseudo-second order kinetic model

Order	Parameter			
	Equation	R^2	q_e	**K-value**
First order kinetics	y = -0.1186x - 0.8628	0.9739	0.137151	K_1=0.27278
Second order kinetics	y = 0.4515x - 0.2965	1	2.21	K_2=-0.133869

4.7. Adsorption isotherm

The experimental data obtained for different initial fluoride concentrations (5 to 25 mg/L with an interval of 10) at constant temperature and pH were plotted in a linearized form of Langmuir and Freundlich adsorption isotherms. Experimental data were fitted to Langmuir and Freundlich isotherms. The maximum adsorption capacity for fluoride ions onto Fe^{3+}-modified bentonite was 1.77mg/g.

Figure (4.26) and (4.27) Shows that the Freundlich isotherm is a better model than the Langmuir isotherm on the basis of correlation coefficients (R^2=0.9289 for Freundlich, R^2= 0.8359 for Langmuir). The best fit Freundlich parameters are K_f = 0.0.506057, n = 1.36277, 1/n= 0.7338. The 1/n value in the range of 0.1-1 indicates a favorable adsorption process. The Langmuir parameters fit are Qm=3.37 mg/g b= 0.17812 L/mg.

The removal of fluoride by different adsorbents has been studied in recent years and some of these reports provide Qm values. Although these values were obtained under different range of conditions, they can be useful criterion of the adsorbent capacity. The Qm value obtained in these study is greater than those of reported on (Table 4.10).

The adsorption data of fluoride fitted to both Langmuir and Freundlich isotherm models as shown in Figure (4.26) and (4.27). The calculated isotherm parameters along with correlation coefficients are given in (Table 4.9). The ‘n” value indicates the bond strength between adsorbate and adsorbent and heterogeneous nature of the surface.

Table 4.9: Parameters for Langmuir and Freundlich adsorption isotherm model

Order	Parameter			
	Equation	R^2	Q_m	
Freundlich	y = 0.7338x - 0.2958	$R^2 = 0.9289$	-	n= 1.36277, K_f = 0.506057
Langmuir	y = 0.296x + 1.6618	$R^2 = 0.8359$	3.37 mg/g	b= 0.17812 mg/g

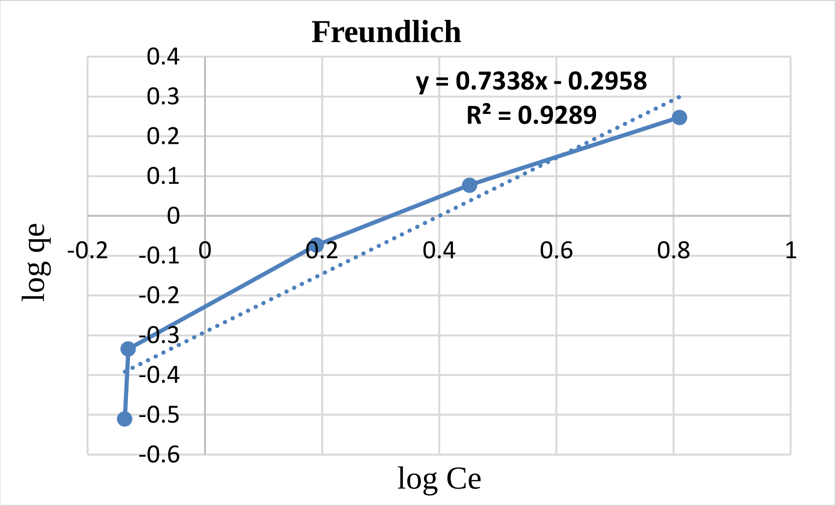


Figure 4.26: Plot of Freundlich isotherm

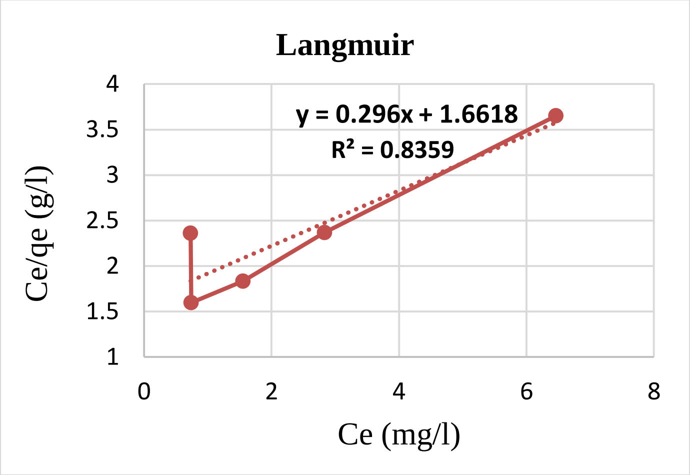
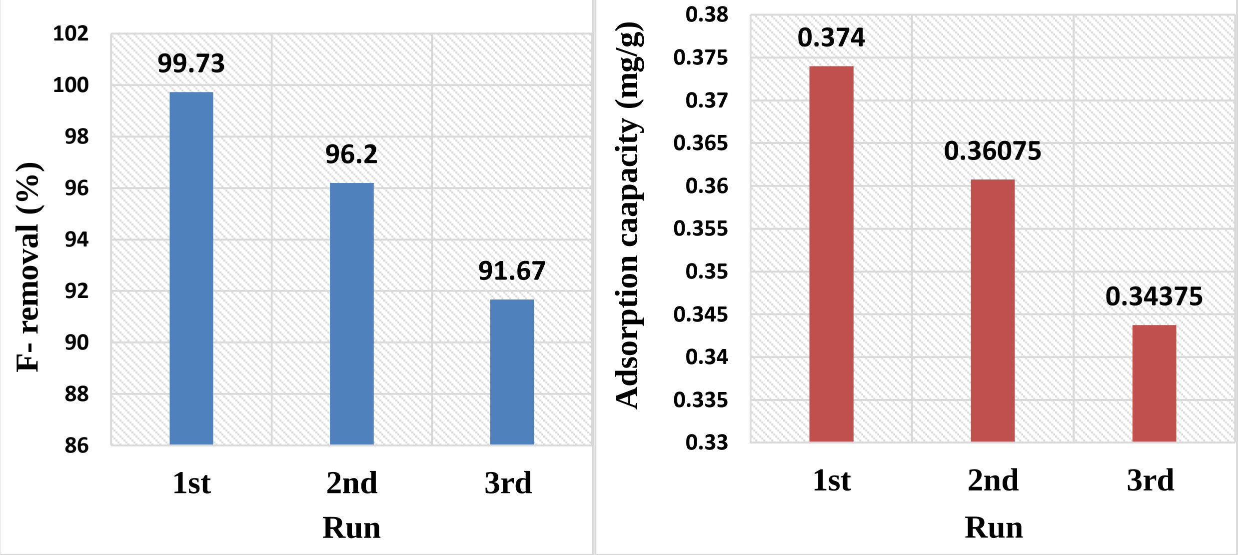


Figure 4.27: Plot of Langmuir isotherm

4.8. Reusability and regeneration of Fe^{3+}-modified bentonite

The regeneration of exhausted modified bentonite was done by selecting the run which gave maximum percentage removal of fluoride (99.558%) from the design expert using 15 ml of 0.5 M NaOH. The variables that resulted maximum percentage removal were adsorbent dosage of 2 g, initial fluoride concentration of 15 ppm and contact time of 15 min (Table E1). The regenerated adsorbent was reused in the next two adsorption experiments.



(a) (b)

Figure 4.28: Variation of (a) percentage removal of F^- (b) adsorption capacity for reused modified bentonite

As shown in Figure 4.28 (a) the reused bentonite also showed a decrease in percentage removal which was about 3.5% and 4.53% between the first & second runs and between second and third runs, respectively. The adsorption capacity has decreased with the amount of 0.01325 mg/g between the runs. This is due to the fact that most of the active sites are already occupied by the fluoride ions resulting a reduction in adsorption.

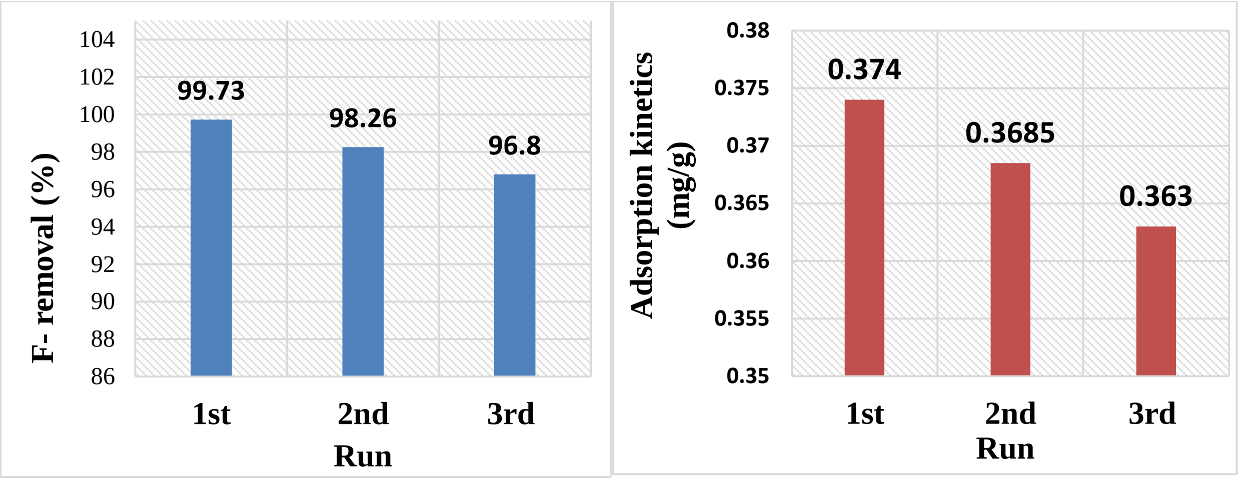


Figure 4.29: Variation of (a) percentage F^- removal (b) adsorption capacity for regenerated modified bentonite

As shown in Figure 4.29 (a) the regenerated modified bentonite also resulted a decrease in percentage removal of F- between the first & second run and between the second & third run which was only about 1.433% and 1.467%, respectively. The adsorption capacity has decreased with the amount of 0.0055 mg/g between the runs. This is due to the fact that the regenerated modified bentonite has free active sites since the fluoride ions are removed by reacting with Na forming NaF resulting more active sites available on the surface of the adsorbent (modified bentonite) for adsorption of another fluoride ions. This confirms that the regeneration of modified bentonite was successful.

Comparing the percentage removal of fluoride and adsorption capacity between the regenerated and the reused modified bentonite it can be concluded that regeneration is more favored. This also has a positive impact on environmental protection since it reduces the amount of sludge (modified bentonite) disposed to the environment.

4.9. Comparison of Fe^{3+}-modified bentonite clay and other adsorbents

As shown in (Table 4.10), it is clear that Fe^{3+}-modified bentonite clay has higher adsorption capacity as compared to other conventional adsorbents. Therefore, Fe^{3+}-modified bentonite clay can be effectively applied for removal of fluoride from aqueous solution because of its ability to adsorb fluoride to greater extent as compared with other adsorbents.

Table 4.10: Comparison of adsorption capacity of Fe^{3+}-modified bentonite clay and other different adsorbents used for de-fluoridation

Adsorbent	Adsorption capacity (mg/g)	Reference
Acid activated kaolinite clay	0.1	Gogoi and Baruah (2008)
Kaolinite	0.7	Srimurali, Pragathi, and Karthikeyan (1998)
Montmorillonite clay	1.5	Karthikeyan, Pius, and Alagumuthu (2005)
Activated aluminsa	1.1	Maliyekkal, Sharma, and Philip (2006)
Al-impregnated activated carbon	1.1	Ramos, Ovalle-Turrubiartes, and Sanchez-Castillo (1999)
Bentonite	1.2	Srimurali, Pragathi, and Karthikeyan (1998)
Fe^{3+}-modified bentonite clay	3.37	This study

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

High concentrations of fluoride in drinking water is a public health concern globally and of critical importance in the Rift Valley region, Ethiopia. Under this study, as a low-cost water treatment option, the de-fluoridation capacity of locally available bentonite clay adsorbent media was investigated by introducing high cationic density species Fe^{3+} ion.

Optimum conditions for the modification of bentonite clay with Fe^{3+} are 30 min of agitation time, 4 g of adsorbent dosage, and 500 ml iron (III) solution at (26±2) ^{0}C temperature. The objective of this research was to prepare high surface area, increased magnetic property and mechanically stable adsorbent that results high percentage removal of fluoride from aqueous solution. The Fe^{3+}-modified bentonite was physically and chemically characterized using XRD, FTIR, CEC, and pHpzc. Structural study through XRD showed a decrease in the intensities of all reflections mainly the montmorillonite and quartz phases, indicating that they are affected by Fe^{3+} treatment. This concludes that the process favors the production of amorphous phase by decomposing montmorillonite and quartz structures. The XRD results also showed that the bentonite clay is mainly composed of montmorillonite and quartz, indicating that the bentonite clay used for this study is an alumino silicate material. On the other hand FTIR results suggested that both the octahedral and tetrahedral sheets were susiptable to Fe^{3+} impregnation. The modification resulted a decrease in the intensities of stretching bands and peaks of the bands associated with the adsorbed water. The CEC results showed that the Ethiopian bentonite clay has a CEC of 59.89 meq/100g, which decreased to 28.48 meq/100g by the introduction of Fe^{3+} onto bentonite clay interlayers, indicating the main mechanism of Fe^{3+} uptake is by ion exchange. This results also confirm that the main exchangeable cation is Ca^{2+}, hence assuring that the type of bentonite used in this study is Ca-Bentonite clay. The pHpzc showed a slight increment on the introduction of Fe^{3+}-modified bentonite (9.2) as compared to raw bentonite (9.0) meaning that Fe^{3+}-modified bentonite will have high adsorption capacity for anions than that of raw bentonite.

The adsorption of fluoride on to the Fe^{3+}-modified bentonite clay increased with an increase of contact time and adsorbent dosage. The adsorption system revealed that greater than 1 g of Fe^{3+}-modified bentonite was capable of removing fluoride from aqueous solution. Fe^{3+}-modified bentonite shows efficient adsorption, removing > 90% of fluoride up to 40 ppm. Raw bentonite shows lower adsorption of F^- at pH ≥ 8. However, Fe^{3+}-modified bentonite clay showed strong adsorption of F^- at pH range of 2-10 for 10-15ppm F^- concentrations. As it can be seen from the results, it can be concluded that pH doesn't affect the adsorption of F^- onto Fe^{3+} modified bentonite clay if F^- concentration is lower than 15ppm. But as the F^- concentration increases then pH greatly affects the adsorption process. This shows the strong interaction of pH and concentration.

Fe^{3+}-modified bentonite resulted a decrease in F^- concentration of the surface water as the adsorbent dosage increased with maximum adsorption being observed at 1g/100ml S/L ratio and removal efficiency of > 66% at initial fluoride concentration of 26 mg/l. Poor adsorption of F^- at normal and optimized pH of surface water, is attributed to the competition for adsorption sites between F^-, OH^-, Cl^-, and SO_4^{2-} ions.

The output of the experiment conducted have been analyzed by employing Design-Expert 7.0.0, response surface methodology, three-level-full-factorial. Based on the analysis of the experimental results, it is found that the three process variables exhibited significant interaction effect on the percentage removal of fluoride ion. This shows the capability of the design of experimental analysis in successfully capturing the effects. An adsorbent dosage of 2 g, adsorbate concentration of 15 ppm and contact time of 15 min resulted an optimum value of 99.56 % fluoride removal. Kinetic studies revealed that fluoride adsorption fitted well to pseudo-second-order model and Freundlich adsorption isotherm, hence confirming multilayer adsorption. Comparing the percentage fluoride removal of the regenerated and reused modified bentonite it can be concluded that regeneration is more favorable.

As such, it can be concluded that Fe^{3+}-modified bentonite with high percentage removal of fluoride was successfully prepared and regenerated. Fe^{3+}-modified bentonite is a potential adsorbent which can be applied in rural areas of Ethiopia and other developing countries. This study proves that Fe^{3+}-modified bentonite is promising adsorbent with good adsorption capacity of fluoride and can be a candidate for conventional de-fluoridation methods.

5.2. Recommendation

- It is recommended to perform BET tests in order to analyze the surface area and volume of the pores produced.
- It is suggested to perform preliminary design, economic feasibility study and establish economic scale for bentonite modification manufacturing unit.
- An investigation of the potability of the treated water must be carried out in order to avoid the health effect.
- Since effect of other parameters such as agitation speed and temperature were not studied in the modification studies, it is recommended that these parameters get studied even though their effects as compared to the others is less as observed in literature reviews.
- Further study on the leaching properties of raw bentonite is required.
- Regeneration studies have to be further studied at different process variables such as; concentration, volume and contact time.
- The scale up of batch adsorption process of fluoride on modified bentonite to a continuous process is vitally important for its practicality on the commercial and industrial scale.

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Appendix-A: PHpzc data for raw Bentonite

Table A1: pHpzc determination at 0.1 KCl

Number	pH initial	pH final	ΔpH (pH_i-pH_f)
1.	2	2.15	-0.15
2.	4	4.24	-0.24
3.	6	7.05	-1.05
4.	7	7.08	-0.08
5.	8	8.82	-0.82
6.	10	8.97	1.03

Table A2: pHpzc determination at 0.01 KCl

Number	pH initial	pH final	ΔpH (pH_i-pH_f)
1.	2	2.05	-0.05
2.	4	4.48	-0.48
3.	6	7.10	-1.1
4.	7	7.26	-0.26
5.	8	9.30	-1.3
6.	10	8.56	1.44

Table A3: pHpzc determination at 0.001 KCl

Number	pH initial	pH final	ΔpH (pH_i-pH_f)
1.	2	2.09	-0.09
2.	4	4.73	-0.73
3.	6	7.15	-1.15
4.	7	7.80	-0.8
5.	8	9.47	-1.47
6.	10	8.38	1.62

PHpzc data for modified Bentonite

Table A4: pHpzc determination at 0.1 KCl

Number	pH initial	pH final	ΔpH (pH_i-pH_f)
1.	2	2.07	-0.07
2.	4	4.35	-0.35
3.	6	7.09	-1.09
4.	7	7.17	-0.17
5.	8	9.28	-1.28
6.	10	8.92	1.08

Table A5: pHpzc determination at 0.01 KCl

Number	pH initial	pH final	ΔpH (pH_i-pH_f)
1.	2	2.17	-0.17
2.	4	4.42	-0.42
3.	6	7.11	-1.11
4.	7	7.22	-0.22
5.	8	8.56	-0.56
6.	10	9.53	0.47

Table A6: pHpzc determination at 0.001 KCl

Number	pH initial	pH final	ΔpH (pH_i-pH_f)
1.	2	2.13	-0.23
2.	4	4.79	-0.79
3.	6	7.13	-1.13
4.	7	7.34	-0.34
5.	8	9.54	-1.54
6.	10	8.82	1.18

Remark: the negative sign shows direction (decrement).

Appendix-B: Effect of adsorption process variables

Table B1: Variation of F^-, pH, EC, and TDS with contact time for raw bentonite

Time (min)	pH	EC (μs/cm)	TDS (mg/l)	Final F^- concentration (mg/l)	F^- removal (%)
5	6.08	3.1	1.953	14.4	-44
10	7.5	3.4	2.142	13.7	-37
30	7.75	3.6	2.268	13.35	-33.5
60	7.94	4.0	2.52	12.7	-27
180	8.03	4.5	2.835	7.8	-22

Table B2: Variation of F^-, pH, EC, and TDS with contact time for modified bentonite

Time (min)	pH	EC (μs/cm)	TDS (mg/l)	Final F^- concentration (mg/l)	F^- removal (%)
5	7.75	4.8	3.024	1.86	81.4
10	7.63	5.1	3.213	1.15	88.5
30	7.65	5.0	3.15	0.99	90.1
60	7.64	5.0	3.15	0.99	90.1
180	7.62	5.1	3.213	0.99	90.1

Table B3: Variation of F^-, pH, EC, and TDS with adsorbate concentration for raw bentonite

Adsorbate Concentration (mg/l)	pH	EC (μs/cm)	TDS (mg/l)	Final F^- concentration (mg/l)	F^- removal (%)	Adsorption capacity (mg/g)
5	7.95	2.7	1.701	6.3	-26	-0.065
10	7.89	3.3	2.079	10	0	0
20	7.81	3.9	2.457	10.25	48.75	0.4875
30	7.45	4.1	2.583	22.5	25	0.375

40	7.17	4.8	3.024	27.5	23.75	0.475

Table B4: Variation of F^-, pH, EC, and TDS with adsorbate concentration for modified bentonite

Adsorbate Concentration (mg/l)	pH	EC (µs/cm)	TDS (mg/l)	Final F^- concentration (mg/l)	F^- removal (%)	Adsorption capacity (mg/g)
5	7.56	6.1	3.843	0.36	92.8	0.232
10	7.64	5.3	3.339	0.84	91.6	0.458
20	7.81	4.4	2.772	1.8	91	0.91
30	7.90	4.1	2.583	2.75	90.83	1.3625
40	8.14	3.5	2.205	3.83	90.423	1.8085

Table B5: Variation of F^-, pH, EC, and TDS with adsorbent dosage for raw Bentonite

Adsorbent Dosage (g)	pH	EC (µs/cm)	TDS (mg/l)	Final F^- concentration (mg/l)	F^- removal (%)
0.1	7.83	1.3	0.819	9.0	10
0.3	7.89	1.6	1.008	4.5	55
0.5	7.96	2.1	1.323	5.25	47.5
1	8.08	3.1	1.953	7.5	25
3	8.22	8.2	5.166	9.5	5

Table B6: Variation of F^-, pH, EC, and TDS with adsorbent dosage for modified bentonite

Adsorbent Dosage (g)	pH	EC (µs/cm)	TDS (mg/l)	Final F^- concentration (mg/l)	F^- removal (%)
0.1	7.63	1.1	0.693	6.462	35.38
0.3	7.42	1.9	1.197	2.83	71.7
0.5	7.35	2.2	1.386	1.55	84.5
1	7.16	5.7	3.591	0.74	92.4

3	7.04	12.4	7.812	0.73	92.7

Table B7: Variation of F$^-$, pH, EC, and TDS with initial pH (10ppm) for raw bentonite

Initial pH	Final pH	EC (µs/cm)	TDS (mg/l)	Final F$^-$ concentration (mg/l)	F$^-$ removal (%)
2	2.11	3.2	2.016	0.7	93
4	4.48	4.3	2.709	0.92	90.8
6	7.1	5.6	3.528	1.2	88
8	9.2	6.2	3.906	4.4	56
10	8.67	5.9	3.717	6.7	33

Table B8: Variation of F$^-$, pH, EC, and TDS with initial pH (10ppm) for modified bentonite

Initial pH	Final pH	EC (µs/cm)	TDS (mg/l)	Final F$^-$ concentration (mg/l)	F$^-$ removal (%)
2	2.08	3.3	2.079	<0.0001	99.99
4	4.35	4.1	2.583	<0.0001	99.99
6	7.07	5.2	3.276	<0.0001	99.99
8	9.17	6.0	3.78	<0.0001	99.99
10	8.62	5.6	3.528	0.2	98

Table B9: Variation of F$^-$ with initial pH (20ppm) for Raw and Modified Bentonite

pH	Raw Bentonite F$^-$ concentration	Modified Bentonite F$^-$ concentration
2	2.5	1.3
4	4.3	1.9
6	5.2	2.2
8	7.1	2.35
10	13.3	2.8

Table B10: Effect of raw bentonite dosage of on percentage removal of fluoride for water obtained from Lake Basaka at 9.13 pH

Dosage (g)	pH	EC (µs/cm)	TDS (mg/l)	Temperature (^0C)	Final F^- concentration (mg/l)	F^-Removal (%)
0.1	8.74	50.1	31.563	18.9	19.75	24.03
0.4	8.87	50.5	31.815	19.4	20.25	22.11
1	9.03	47.8	30.114	19.9	20.5	21.15

Table B11: Effect of modified bentonite dosage of on percentage removal of fluoride for water obtained from Lake Basaka at 9.13 pH

Dosage (g)	pH	EC (µs/cm)	TDS (mg/l)	Temperature (^0C)	Final F^- concentration (mg/l)	F^- Removal (%)
0.1	9.00	50.0	31.5	19.9	18	30.7
0.4	8.85	47.4	29.862	19.9	17.25	33.65
1	8.51	46.3	29.169	20.5	15.75	39.42

Table B12: Effect of raw bentonite dosage of on percentage removal of fluoride for water obtained from Lake Basaka at 6.14 pH

Dosage (g)	pH	EC (µs/cm)	TDS (mg/l)	Temperature (^0C)	Final F^- concentration (mg/l)	F^- Removal (%)
0.1	4.53	58.9	37.107	20.2	16.75	35.57
0.4	5.75	59.6	37.548	20.7	18.23	29.88
1	5.97	61.9	38.997	21.1	19.1	26.53

Table B13: Effect of modified bentonite dosage of on percentage removal of fluoride for water obtained from Lake Basaka at 6.14 PH

Dosage (g)	**pH**	**EC (µs/cm)**	**TDS (mg/l)**	**Temperature (^{0}C)**	**Final F$^-$ concentration (mg/l)**	**F$^-$ Removal (%)**
0.1	8.02	56.7	35.721	19.2	13.62	47.61
0.4	7.83	56.1	35.343	19.5	11.5	55.76
1	7.76	55.7	35.091	19.9	8.75	66.34

Appendix-C: Reusability and regeneration data

Table C1: Variation on percentage F^- removal and adsorption capacity of reused modified bentonite

Run	Initial F^- concentration (ppm)	Final F^- concentration (ppm)	F^- removal (%)	Adsorption capacity (mg/g)
1st	15	0.04	99.73	0.37400
2nd	15	0.57	96.2	0.36075
3rd	15	1.25	91.67	0.34375

Table C2: Variation on percentage F^- removal and adsorption capacity of regenerated modified bentonite

Run	Initial F^- concentration (ppm)	Final F^- concentration (ppm)	F^- removal (%)	Adsorption capacity (mg/g)
1st	15	0.04	99.73	0.37400
2nd	15	0.26	98.26	0.36850
3rd	15	0.48	96.8	0.363

Appendix-D: Kinetic modelling and adsorption isotherm data

Table D1: Kinetic data

Adsorbent dosage (g)	Time (min)	Initial F^- conc. (mg/l)	Ce (mg/l)	qt (mg/g)	qe (mg/g)	qe-qt (mg/g)	Log (qe-qt)	t/qt
1	1	10	2.76	0.362	0.4505	0.0885	-1.053056	2.762431
1	3	10	2.27	0.3865	0.4505	0.064	-1.19382	7.761966
1	5	10	1.86	0.407	0.4505	0.435	-1.365151	12.285
1	10	10	1.15	0.4425	0.4505	0.008	-2.0961	22.59887
1	30	10	0.99	0.4505	0.4505	0	-	66.59267
1	60	10	0.99	0.4505	0.4505	0	-	133.18537
1	180	10	0.99	0.4505	0.4505	0	-	399.556

Table D2: Adsorption isotherm data

Adsorbent dosage (g)	Time (min)	Initial F^- conc. (mg/l)	Ce (mg/l)	qe (mg/g)	Ce/qe (g/l)	Log Ce	Log qe
0.1	30	10	6.462	1.769	3.6529112	0.810367	0.247727
0.3	30	10	2.83	1.195	2.3682008	0.451786	0.077367
0.5	30	10	1.55	0.845	1.8343195	0.190331	-0.07314
0.8	30	10	1.184	0.551	2.1488203	0.073351	-0.25884
1	30	10	0.74	0.463	1.5982721	-0.130768	-0.33441
1.5	30	10	0.73	0.309	2.3624595	-0.136677	-0.51004

Appendix-E: Design expert run data

Table E1: Experimental and Predicted Values

Std	A:Adosrbent Dosage (g)	B:Fluoride Concentration (ppm)	C:Contact Time (min)	Experimental removal of F^- (%)	Predicted removal of F^- (%)	Residual
1	1.00	5.00	15.00	70.333	65.15	5.18
2	1.50	5.00	15.00	73	74.30	-1.30
3	2.00	5.00	15.00	76	78.29	-2.29
4	1.00	15.00	15.00	79.2	87.83	-8.63
5	1.50	15.00	15.00	96.6667	93.27	3.40
6	2.00	15.00	15.00	99.558	93.54	6.02
7	1.00	25.00	15.00	82	79.79	2.21
8	1.50	25.00	15.00	79	81.51	-2.51
9	2.00	25.00	15.00	76	78.07	-2.07
10	1.00	5.00	30.00	56	60.36	-4.36
11	1.50	5.00	30.00	68	72.33	-4.33
12	2.00	5.00	30.00	78.8	79.15	-0.35
13	1.00	15.00	30.00	97.998	87.22	10.77
14	1.50	15.00	30.00	97.2667	95.49	1.78
15	2.00	15.00	30.00	96.8	98.59	-1.79
16	1.00	25.00	30.00	80.3	83.36	-3.06
17	1.50	25.00	30.00	90.2	87.91	2.29
18	2.00	25.00	30.00	87	87.30	-0.30
19	1.00	5.00	45.00	57.96	56.75	1.21
20	1.50	5.00	45.00	73	71.56	1.44
21	2.00	5.00	45.00	85.99	81.20	4.79
22	1.00	15.00	45.00	84.28	87.80	-3.52
23	1.50	15.00	45.00	97.3333	98.89	-1.56
24	2.00	15.00	45.00	98.998	104.82	-5.83

25	1.00	25.00	45.00	88.32	88.12	0.20
26	1.50	25.00	45.00	96.9333	95.50	1.43
27	2.00	25.00	45.00	99.5488	97.72	1.83
28	1.50	15.00	30.00	95.6	95.49	0.11
29	1.50	15.00	30.00	95.28	95.49	-0.21
30	1.50	15.00	30.00	90	95.49	-5.49
31	1.50	15.00	30.00	97.6667	95.49	2.18
32	1.50	15.00	30.00	98.24	95.49	2.75

Table E2: Sequential model sum of squares analysis

Source	Sum of Squares	df	Mean Square	F-value	p-value Prob > F	
Mean vs Total	2.352E+005	1	2.352E+005			
Linear vs Mean	1816.02	3	605.34	5.72	0.0035	
2FI vs Linear	471.47	3	157.16	1.58	0.2200	
Quadratic vs 2FI	2022.46	3	674.15	31.57	< 0.0001	Suggested
Cubic vs Quadratic	69.70	7	9.96	0.37	0.9039	Aliased
Residual	400.06	15	26.67			
Total	2.400E+005	32	7498.53			

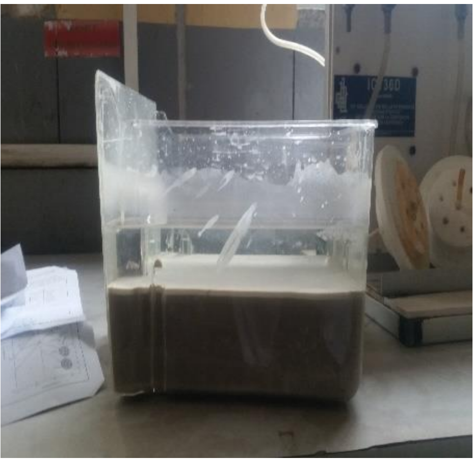
Appendix-F: Pictures of laboratory equipment and process


Raw bentonite


1st size reduction


3rd size reduction


Sieving


Washing

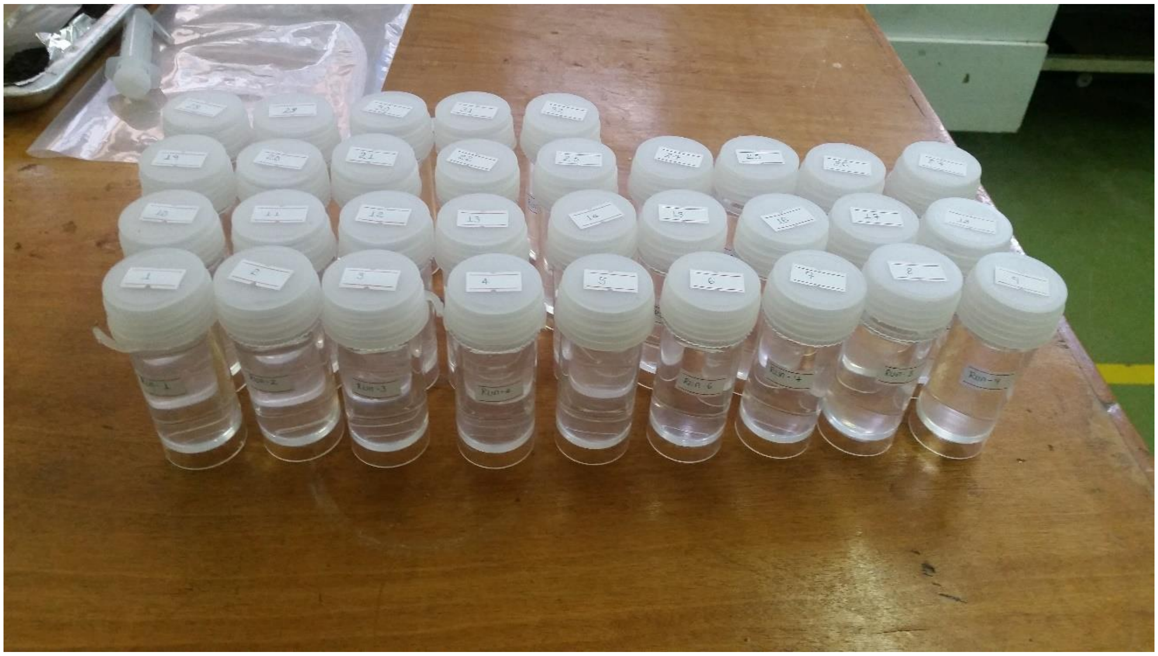

Vacuum filter


Before drying


After drying

Iron solution preparation

Incubator shaker



32-Experimental Runs