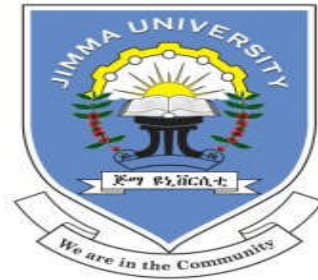


JIMMA UNIVERSITY
COLLEGE OF PUBLIC HEALTH AND MEDICAL SCIENCES
DEPARTMENT OF ENVIRONMENTAL HEALTH SCIENCE AND TECHNOLOGY



EXPERIMENTAL EVALUATION AND OPTIMIZATION OF SORPTIVE REMOVAL OF
FLUORIDE FROM WATER USING IRON ORE

BY: BEEKAM KEBEDE

THESIS SUBMITTED TO THE DEPARTMENT OF ENVIRONMENTAL HEALTH SCIENCE AND
TECHNOLOGY, COLLEGE OF PUBLIC HEALTH AND MEDICAL SCIENCES, JIMMA
UNIVERSITY; IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF
MASTER OF SCIENCE IN ENVIRONMENTAL HEALTH SCIENCE

JULY, 2013

JIMMA, ETHIOPIA

EXPERIMENTAL EVALUATION AND OPTIMIZATION OF SORPTIVE REMOVAL OF
FLUORIDE FROM WATER USING IRON ORE

BY: BEEKAM KEBEDE

ADVISORS: 1. ABEBE BEYENE (PhD, ASSIST. PROFESSOR)

2. FEKADU FUFA (MSc, PhD CANDIDATE)

DECLARATION

I, the undersigned, declare that this thesis is my original work and has not been presented in this or other university and all sources of materials used for this have been acknowledged.

Name: Beekam Kebede

Signature: _____

Name of institution: Jimma University

Date of submission: _____

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

Name of advisors	Signature	Date
1. Abebe Beyene (PhD, Assist. Prof.)	_____	_____
2. Fekadu Fufa (MSc, PhD Candidate)	_____	_____
Department Head:		
Tadesse Getahun (MSc, PhD candidate)	_____	_____

ACKNOWLEDGEMENTS

First of all I thank God for his unlimited blessings. ‘Thanks’ is a small word to Almighty God, for He who began this work and carried it to completion. Whatever I am today and whatever I achieved is with the help of Jesus Christ, as a reply of his love and affection towards me. Next, I am highly indebted to my research advisors, Dr. Abebe Beyene and Mr. Fekadu Fufa for their dedicated assistance, consistent guidance, invaluable comments, constant encouragements, indispensable support, constructive comments and constructive criticisms and sharing their rich experiences throughout this research work.

My thanks also go to the Office for Tiro Afeta District Mines, Water and Energy Resources for allowing me to collect the samples of IO and also Geoscience laboratory centre of Ethiopian Geological survey for characterizing chemical compositions of IO. In same way, I would like Jimma Institute of technology for permitting me to use the Construction Materials Laboratory for the analysis of particle size of the adsorbent. Department of Environmental Health Science and Technology is also acknowledged for giving me this golden and educating opportunity.

I would like as well to record deep respect to Mr. Siyum Derib for the technical assistance he gave me during my research work. My deepest thank also extend to my families for their support, encouragement and personal sacrifice showed me for the way of achieving my objective. Last, but not least, I would like to acknowledge all my dearest friends and well-wishers for their moral support and encouragement in all aspects.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	I
LIST OF TABLES	V
LIST OF FIGURES	VI
ABBREVIATIONS	VII
<i>ABSTRACT</i>	XI
CHAPTER ONE	1
INTRODUCTION	1
1.1. Background	1
1.2. Statement of the problem	3
1.3. Significance of the study	5
CHAPTER TWO	6
LITERATUREREVIEW	6
2.1. Source of fluoride.....	6
2.2. Behavior of fluoride with other ions	6
2.3. Mechanism of fluoride adsorption in human body	6
2.4. Health impacts of fluoride.....	7
2.4.1. <i>Dental fluorosis</i>	7
2.4.2. <i>Skeletal fluorosis</i>	8
2.4.3. <i>Other problems</i>	8
2.5. Solutions to the problems	8
2.6. Fluoride removal technologies	8
2.6.1. <i>Non-treatment and blending techniques</i>	9
2.6.2. <i>Precipitation/Coagulation</i>	9
2.6.3. <i>Membrane filtration process</i>	10
2.6.4. <i>Electrochemical technique</i>	10
2.6.5. <i>Distillation</i>	11
2.6.6. <i>Adsorption technique</i>	11
CHAPTER THREE	16
OBJECTIVES OF THE STUDY	16

3.1. General Objective.....	16
3.2. Specific objectives.....	16
CHAPTER FOUR.....	17
MATERIALS AND METHODS.....	17
4.1. Study area and period.....	17
4.2. Study design.....	17
4.3. Sample collection and analysis.....	17
4.4. Preparation and characterization of the adsorbent.....	17
4.1. Instrumentation.....	18
4.2. Reagent and standard solutions.....	18
4.3. Analysis of fluoride concentration.....	18
4.4. Batch adsorption experiment.....	19
4.5. Desorption experiment.....	20
4.6. Fluoride removal from natural groundwater.....	20
4.7. Data Analysis.....	20
4.8. Theories.....	21
4.8.1. <i>Adsorption kinetics</i>	21
4.8.2. <i>Adsorption isotherms</i>	22
4.9. Ethical consideration.....	24
4.10. Dissemination plan.....	24
4.11. Data quality management.....	24
CHAPTER FIVE.....	25
RESULTS.....	25
5.1. Adsorbent characterization.....	25
5.2. Effect of contact time.....	26
5.3. Adsorption kinetics.....	26
5.4. Effect of pH.....	28
5.5. Effect of agitation rate.....	29
5.6. Effect of particle size.....	30
5.7. Effect of adsorbent dose.....	31

5.8.	Effect of initial fluoride concentration	33
5.9.	Adsorption isotherm	34
5.10.	Effect of competing anions	37
5.11.	Desorption experiment	37
5.12.	Removal of fluoride from natural groundwater.....	38
CHAPTER SIX		40
DISCUSSIONS		40
CHAPTER SEVEN		46
7.	CONCLUSIONS AND RECOMMENDATIONS	46
7.1.	Conclusions	46
7.2.	Recommendations	46
REFERENCES		47
APPENDICES		XII

LIST OF TABLES

Table 1. Chemical compositions of IO.....	25
Table 2. The kinetics parameters for adsorption of fluoride onto IO.....	28
Table 3. Equilibrium isotherm parameters of fluoride adsorption onto IO.....	36
Table 4. Physico-chemical characteristics of natural groundwater.....	39

LIST OF FIGURES

Fig. 1. Fluoride removal as a function of contact time ($[F^-]_0$: 10 mg/L, particle size: < 0.075 mm, adsorbent dose: 5.0 g/L, pH: ~ 6.0 and agitation rate: 150 rpm).	26
Fig. 2. (a) Pseudo-first-order kinetic plot for fluoride removal (b) Pseudo-second-order kinetic plot for fluoride removal (c) Intra-particle ($[F^-]_0$: 10 mg/L, particle size: < 0.075 mm, adsorbent dose: 5.0 g/L, contact time: 120 min, agitation rate: 150 rpm and pH: ~ 6.0 and temperature 22 ± 2 °C).	27
Fig. 3. Fluoride removal as a function of solution pH ($[F^-]_0$: 10 mg/L, particle size: < 0.075 mm, adsorbent dose: 5.0 g/L, contact time: 120 min and agitation rate: 150 rpm).	29
Fig. 4. Fluoride removal as a function of agitation rate ($[F^-]_0$: 10 mg/L, particle size: < 0.075 mm, adsorbent dose: 5.0 g/L, contact time: 120 min and pH: ~ 6.0).....	30
Fig. 5. Fluoride removal as a function of particle size of the adsorbent ($[F^-]_0$: 10 mg/L, adsorbent dose: 5.0 g/L, contact time: 120 min, pH: ~ 6.0 and agitation rate: 150 rpm).....	31
Fig. 6. Fluoride removal as a function of adsorbent dose ($[F^-]_0$: 10 mg/L, particle size: < 0.075 mm, contact time: 120 min, agitation rate: 150 rpm and pH: ~ 6.0).	32
Fig. 7. The plot of K_d value as a function of adsorbent dose (pH ~ 6.0).	33
Fig. 8. Fluoride removal as a function of initial fluoride concentration (particle size: < 0.075 mm, adsorbent dose: 5.0 g/L, contact time: 120 min, agitation rate: 150 rpm and pH: ~ 6.0)	34
Fig. 9. Equilibrium isotherms of fluoride adsorption on IO ($[F^-]_0$: 10 mg/L, particle size: < 0.075 mm, adsorbent dose: 5.0 g/L, contact time: 120 min, agitation rate: 150 rpm and pH: ~ 6.0).	35
Fig. 10. D-Risotherm of fluoride adsorption on IO ($[F^-]_0$: 10 mg/L, particle size: < 0.075 mm, adsorbent dose: 5.0 g/L, contact time: 120 min, agitation rate: 150 rpm and pH: ~ 6. and temperature: 22 ± 2 °C).....	36
Fig. 11. Fluoride removal at different anion concentrations ($[F^-]_0$: 10 mg/L, particle size: < 0.075 mm, adsorbent dose: 5.0 g/L, contact time: 120 min, agitation rate: 150 rpm and pH: ~ 6.0).	37
Fig. 12. Percentage of fluoride desorbed as a function of NaOH concentration (particle size: < 0.075 mm, adsorbent dose: 5.0 g/L, contact time: 120 min and agitation rate: 150 rpm).	38

ABBREVIATIONS

ICOH	International Commission on Occupational Health
IGRAC	International Groundwater Resources Assessment Centre
NEERA	National Environmental Engineering Research Institute
MCL	Maximum Concentration Limit
NGO	Non-Governmental Organization
OMC	Orissa Mining Corporation
SNNPR	Southern Nation, Nationalities and People Region

ABSTRACT

Excessive fluoride in drinking water is a worldwide problem. Now a days, many millions of people rely on groundwater with fluoride concentrations above the World Health Organization (WHO) guideline value where Ethiopian people living in Rift Valley area are the case in point. Therefore, in this research, the capacity of locally available Iron ore (IO) to remove fluoride from synthetic and natural groundwater was investigated. Series of batch adsorption experiments were carried out to assess the effect of contact time, pH of the solution, agitation rate, particle size of the adsorbent, mass of the adsorbent, initial fluoride concentration and the presence of competing anions in the solution. The adsorption of fluoride in the first 120 min was fast and equilibrium time was achieved within 120 min. The adsorption kinetic was found to follow a pseudo-first-order rate equation. The equilibrium adsorption data were well described with the Freundlich ($R^2 = 0.993$) and Langmuir isotherm models ($R^2 = 0.983$), giving a sorption capacities of 1.465 and 4.433 mg/g, respectively. However, from the values of coefficient of determination and chi-square, the Freundlich isotherm equation best described the equilibrium adsorption of fluoride onto IO. The obtained mean free energy (10.206 kJ/mol) suggested that chemisorptions should be responsible for the adsorption of fluoride onto IO. The presence of carbonate, bicarbonate and phosphate significantly affected fluoride removal efficiency while chloride, sulfate and nitrate did not significantly affect fluoride removal efficiency within the concentration range tested (5.0-200 mg/L). The higher percentage of fluoride removal from laboratory prepared fluoride solution than from natural groundwater which could be due to the presence of other multiple factors that are not considered in this study. About 52% of fluoride was desorbed from the fluoride loaded IO indicating that strong bond formed between adsorbed fluoride and the adsorbent. The results of this study provided important information for the further evaluation of IO for the treatment of water contaminated with fluoride. Further investigation of IO for the treatment of fluoride from ground water should be considered to assess its practical application.

CHAPTER ONE

INTRODUCTION

1.1. Background

Fluoride is a ubiquitous element present in the Earth's crust and is also being added to the environment from anthropogenic sources. Fluorine is found in the soil, and the content of fluorine in the lithosphere varies between 100 and 1500 g/ton (Kloos and Tekle-Haimanot, 1999). Fluoride occurs mainly as sellaite (MgF_2), fluor spar (CaF_2), cryolite (Na_3AlF_6) and fluorapatite [$3Ca_3(PO_4)_2Ca(F, Cl_2)$]. As fluor spar, fluoride is found in sedimentary rocks, and as cryolite in igneous rocks. These fluoride minerals are nearly insoluble in water. Hence, fluorides will be present in groundwater only when conditions favour their dissolution or high fluoride containing effluents are discharged into the water bodies from industries (Ghorai and Pant, 2004).

Fluoride is well recognized as an element of public health concern (Ayoob and Gupta, 2006). Waters with high fluoride concentrations occur in large and extensive geographical belts associated with sediments of marine origin in mountainous areas, volcanic rocks and granitic and gneissic rocks. Excessive fluoride concentrations have been reported in ground waters of more than 20 developed and developing countries (Malakootian *et al.*, 2011). High fluoride concentrations in groundwater, up to more than 30 mg/L occur widely in many parts of the world, including Ethiopia, (Anand *et al.*, 2009). Approximately 200 million people worldwide rely on water sources contaminated with excessive fluoride. The probability of occurrence of high fluoride concentration in ground and surface water was detected in various countries such as India, China, Argentina, Mexico, and in several African countries (Abbaspour *et al.* 2008). In many parts of the East African Rift Valley elevated fluoride concentrations above the WHO guideline of 1.5 mg/L are found in groundwater. The East African Rift Valley which crosses through Ethiopia is geomorphologically still an active volcanic region. The volcanic rocks particularly in the young basalt contain high concentrations of fluoride and fluorapatite. In the Main Ethiopian Rift Valley (MER) about 14 million people rely on water sources with excessive

fluoride (Johnson *et al.*, 2011). According to the study conducted by Kloos and Tekle-Haimanot (1999) 100% of the hot springs, 75% of the lakes, 54 % of the shallow wells and 35% of the bore holes characterized in the MER contain above 5.0 mg/L fluoride. The study also revealed that the presence of fluoride above the guideline value in some high land part of Ethiopia. The lowest concentrations (< 1.5 mg/L) are found in springs and rivers. Low levels of fluoride, less than 1.0 mg/L is associated with high levels of dental decay (Kumar and Salim, 2011).The level of fluoride present in concentrations 1.5-2.0 mg/L in drinking water gives rise to mild dental fluorosis, while values exceeding 2.0 mg/L may have very high chances of dental and skeletal fluorosis (WHO, 1994). Because the intensity of fluorosis is not merely dependent on the fluoride content in water, but also on the fluoride from other sources, climatic condition, physical activity and dietary habits, there is no constant guideline for fluoride content in drinking water in all countries (Maheshwari, 2006). World Health Organization recommends that the fluoride content in drinking water should be in the range of 1.0-1.5 mg/L (WHO, 2011). The Ethiopian Ministry of Water Resources, on the bases of economical, practical and technical considerations proposed guideline for drinking water quality of fluoride at 3.0 mg/L (Ministry of Water Resources, Ethiopia, 2002). Therefore, treatment of all the water sources containing fluoride above the acceptable level is essential before they are decided for domestic use.

Some defluoridation techniques developed to control fluoride content in water are reverse osmosis, nalgonda technique, activated alumina process, ion exchange process, and adsorption process using sunflower plant dry powder, steam of phytomass, holly oke, neem bark powder, activated cotton jute carbon, bagasse ash, phosphate-treated saw dust, bone char, etc. as adsorbents (Rao, 2003). However, due to high cost or lower efficiency or non applicability on mass scale, these techniques are not much in use (Jamode and Sapka, 2004). However, it is widely recognized that adsorption is an ideal and appropriate technique compared to other techniques, for small community water source defluoridation (Chandravanshi *et al.*, 2007). Adsorption is frequently used as a robust technique to remove water soluble ions that are detrimental to human health from aqueous solutions, especially when these ions exist in low concentrations and an attractive method for the removal of fluoride in terms of low cost, simplicity of design, simplicity of operation and for the environmental protection purpose (Cirelli and Miretzky, 2011; Darchen *et al.*, 2010). However, the applicability of these low cost

adsorbents is limited either due to their low efficiency or lack of public acceptance. Therefore, it is important to identify materials with high rate of removal, economically, socially and technically feasible for practical application in rural communities (Chandravanshi *et al.*, 2007).

In the present study, Iron ore (IO) was selected since it is the mixture of different metal oxides responsible for the removal of fluoride under batch studies with optimization of various experimental conditions including the effects of contact time, pH of the solution, agitation rate, particle size of the adsorbent, dose of the adsorbent, initial fluoride concentration and presence of competing anions in the solution.

1.2. Statement of the problem

About 8 million people living in the MER is at risk of fluorosis. The population at risk lives spread over different regional states: Afar, Amhara, Oromia and SNNPR. Moreover, there is an influx of migrants into this potentially rich part of the country. In the absence of rivers in large part of MER area, communities largely depend either on rain-water harvesting ponds or increasingly on groundwater from public boreholes for their drinking water supply. The boreholes bring water that is relatively free from bacteriological contamination, but at the same time the use of borehole water increases the risk of fluorosis, as fluoride levels are high (Sidelil *et al.*, 2011).

In the MER dental mottling has been recognized in areas with fluoride concentrations in water as low as 2.0 mg/L fluoride. Higher levels, above 4.0 mg/L fluoride cause severe disfiguring dental fluorosis with enamel hyperplasia (Bushera *et al.*, 2009). A study by Sidelil *et al.* (2011) shows that the fluoride level of drinking water collected from deep wells of the MER ranged from 1.5 to 36 mg/L (in average 10 mg/L). Also the prevalence of dental fluorosis was found to be widespread among children, mainly in the age group of 10 to 14 years. Skeletal fluorosis invariably occurred in those that were consuming water with fluoride levels of more than 4.0 mg/L for over 10 years.

An earlier survey with data collected from 270 water resources in the Ethiopian Rift Valley established that 35 percent of all sources had fluoride levels in excess of 5 mg/L (Kloos and Tekle-Haimanot, 1999). A more recent extensive survey involving 1438 samples established that

50% of deep wells and 26% shallow wells of the Rift Valley yield fluoride levels above 1.5 mg/L and respectively 12% and 6% values above 7 mg/L. Outside the Rift only 4% and 5% of deep and shallow wells respectively have fluoride level above 1.5 mg/L. The main area with high fluoride levels outside the Rift Valley is the area around Jimma in the west of the country (Bjorvatn *et al.*, 2005)

At present there is no single policy to address the fluorosis problem in Ethiopia but under the Fluorosis Mitigation Project, coordinated by the federal Ministry of Water and Energy, several initiatives are on-going to address the issue: systematic mapping and looking at a range of mitigation measures. In public drinking water systems in cities in the Rift Valley, such as Ziway, the Nalgonda method (use of aluminium sulphate and lime) is practiced. In rural areas, where the majority of the population resides, defluoridation is tried at pilot scale, either as household or community level treatment-the main techniques used being Nalgonda and bone-char. In addition in some areas regional governments are opting for safe sourcing bringing relatively fluoride free water from often considerable distance (for some systems in access of 30 kilometers). There is as yet no attention for safe well development as implemented elsewhere (Cardona *et al.*, 2002).

Also, a mitigate project was implemented in rural Ethiopia in collaborative between Eawag, technical and social scientists at Addis Ababa University, Oromo Self-Help Organization (OSHO), the Catholic Diocese of Nakuru Water Quality Section (CDN WQ), and Swiss Interchurch Aid (HEKS) assessing technical performance, user acceptance and optimal institutional setting of bone char-based community and household filters for sustainable implementation. Two filters are being tested: the first contains bone char (BC), the second a mixture of BC and calcium-phosphate pellets (known as contact precipitation (CP) or the Nakuru Technique). Likewise, in April 2010, a CP community filter was built by OSHO in Wayo Gabriel, and 200 fluoride removal household filters (BC and CP) were distributed in three villages around Wayo Gabriel. While the fluoride content of the treated water at the community filter is still below 1.5 mg/L, household filters containing BC have already been replaced with CP (Johnson *et al.*, 2011).

Also, a mitigate project was implemented in rural Ethiopia in collaborative between Eawag, technical and social scientists at Addis Ababa University, Oromo Self-Help Organization (OSHO), the Catholic Diocese of Nakuru Water Quality Section (CDN WQ), and Swiss Interchurch Aid (HEKS) assessing technical performance, user acceptance and optimal institutional setting of bone char-based community and household filters for sustainable implementation. Two filters are being tested: the first contains bone char (BC), the second a mixture of BC and calcium-phosphate pellets (known as contact precipitation (CP) or the Nakuru Technique). Likewise, in April 2010, a CP community filter was built by OSHO in Wayo Gabriel, and 200 fluoride removal household filters (BC and CP) were distributed in three villages around Wayo Gabriel. While the fluoride content of the treated water at the community filter is still below 1.5 mg/L, household filters containing BC have already been replaced with CP (Johnson *et al.*, 2011).

1.3. Significance of the study

The results of the batch adsorption investigation of the present study could be used for further investigation of the adsorbent under continuous experiment and field trial for fluoride removal from water. At the same time, the Ministry of Health, the Ministry of Water, Mines and Energy Resources, Private sectors, NGOs and International organizations working on water and sanitation could use the results of this study for further investigation of IO for defluoridation. Thus, IO could be used for tackling the adverse human health impacts of fluoride by applying the principle of defluoridation technology.

CHAPTER TWO

LITERATURE REVIEW

2.1. Source of fluoride

Fluoride pollution in the environment can be caused either naturally due to breakdown of rocks or anthropogenically due to chemical fertilizers, sewage discharges in communities with fluoridated water supplies and liquid wastes from specific industrial activities (Felgenhauer and Perkovich, 2008). In addition, the use of fluoride containing pesticides in agriculture and fluoride in drinking water supplies also contribute to the release of fluoride into the environment (Green facts on fluoride, 2002).

2.2. Behavior of fluoride with other ions

The correlation studies provide an insight about the behavior of different ions with fluoride and which of these ions controls the fluoride concentration in groundwater. Fluoride shows a negative correlation with most of the ions (Ca^{2+} , Mg^{2+} , Na^+ and K^+). The ions having a negative correlation with fluoride are those which affect the fluoride in the water and vice versa are the ones with positive correlation. The groundwater where the fluoride concentration is high, bicarbonates and carbonates are predominant anions and the water is alkaline. Therefore, high fluoride waters are having more alkalinity, over hardness and are low calcium waters (Kumar and Salim, 2011).

2.3. Mechanism of fluoride adsorption in human body

When fluorides are ingested by humans, they are absorbed in the stomach and/or the intestine. Approximately 75-90% of ingested fluoride is absorbed. In an acidic stomach, fluoride is converted into hydrogen fluoride (HF) and up to about 40% of the ingested fluoride is absorbed from the stomach as HF. High stomach pH decreases gastric absorption by decreasing the concentration uptake of HF. Fluoride not absorbed in the stomach is absorbed in the intestine and is unaffected by pH at this site. Relative to the amount of fluoride ingested, high

concentrations of cations that form insoluble complexes with fluoride (e.g. calcium, magnesium and aluminium) can markedly decrease gastrointestinal fluoride absorption (Greenfacts, 2002).

Once absorbed into the blood, fluoride readily distributes throughout the body, with approximately 99% of the body burden of fluoride retained in calcium rich areas such as bone and teeth (dentine and enamel) where it is incorporated into the crystal lattice. In infants about 80 to 90% of the absorbed fluoride is retained but in adults this level falls to about 60%. Fluoride crosses the placenta and is found in mother's milk at low levels essentially equal to those in blood. Under certain conditions, plasma fluoride levels provide an indication of the level of fluoride in the drinking-water consumed. Levels of fluoride that are found in the bone vary with the part of the bone examined and with the age and sex of the individual. Bone fluoride is considered to be a reflection of long-term exposure to fluoride (IPCS, 2002).

2.4. Health impacts of fluoride

Fluoride in drinking water is known for both beneficial and detrimental effects on health (Rao, 2003). Fluorosis problem ranges from mild dental fluorosis to crippling skeletal fluorosis as the level and period of exposure increases (Bailey, 2006). Children drinking fluoridated water are expected to have up to 35% less tooth decay than those drinking non-fluoridated water (Felgenhauer and Perkovich, 2008).

2.4.1. Dental fluorosis

The degree of dental fluorosis depends on the amount of fluoride exposure up to the age of 8.0-10 years (Maheshwari, 2006). Small amount of fluoride, 1.0-1.5 mg/L, strengthens the enamel. But exposures to concentrations in the range of 1.5-4.0 mg/L result in dental fluorosis. White and yellow glistening patches on the teeth are seen which may eventually turn brown. The yellow and white, patches when turned brown as horizontal streaks. The brown streaks may turn black and affect the whole tooth and may get pitted, perforated and chipped off at the final stage. Dental fluorosis not only poses cosmetic problems but has serious social problems too, in terms of matrimonial problems of the children (Anand *et al.*, 2009; Rao, 2003).

2.4.2. Skeletal fluorosis

Prolonged exposure at higher fluoride concentrations (4.0-10 mg/L) progresses from dental fluorosis to skeletal fluorosis (Anand *et al.*, 2009). Skeletal fluorosis affects young and old alike. It can also damage the fetus if the mother consumes water and food with a high concentration of fluoride during pregnancy/breast feeding, infant mortality due to calcification of blood vessels can also occur (Rao, 2003).

2.4.3. Other problems

Besides skeletal and dental fluorosis, excessive consumption of fluoride may lead to muscle fiber degeneration, low hemoglobin levels, deformities in RBCs (Red blood cells), neurological manifestations, muscular manifestations, gastrointestinal problems as well as alterations in the functional mechanisms of liver, kidney, digestive system, respiratory system, excretory system, central nervous system and reproductive system, destruction of about 60 enzymes (Maheshwari, 2006; Rao, 2003).

2.5. Solutions to the problems

A community with excessive fluoride in its water supply may meet the local MCL in one or more of several ways. Fluoride poisoning can be prevented or minimized by using alternate water sources, by improving the nutritional status of the population at risk or by defluoridation technology (Maheshwari, 2006).

2.6. Fluoride removal technologies

A scientific alternative to improve the quality of water with high fluoride concentration is defluoridation of drinking water (Rujanawisan, 1999). Any particular defluoridation technology, which is suitable at a particular region, may not meet the requirements at some other place. Therefore, any defluoridation technology/treatment process should be site specific as per local needs and prevailing conditions as each technology has some limitations and no one process can serve the purpose in diverse conditions (Maheshwari, 2006).

2.6.1. Non-treatment and blending techniques

In areas where several water sources are available, installation of multiple wells may provide an opportunity for obtaining water with low fluoride levels without necessarily treating the water. One disadvantage of this method is that the MCL can only be achieved if the quality of the source waters is good (Darchen *et al.*, 2010).

2.6.2. Precipitation/Coagulation

In the 1970s, a co-precipitation technique, the so called “Nalgonda technique”, was introduced to the Indian population for fluoride removal from drinking water and also has been tested at a pilot scale level in developing countries such as Kenya, Senegal and Tanzania. The method involves the addition of alum and lime into water followed by rapid mixing. After some time, the stirring intensity is reduced and this induces floc formation that is subsequently removed by simple settling. Although precipitation is an economical and a robust technique in the removal of fluoride from water, it has not been very attractive to many end users, especially in developing countries, due to excessive sludge generation and dewatering. Therefore, the technique is only suited to centralized water treatment system (Darchen *et al.*, 2010). Also due to use of aluminum sulfate as coagulant, the sulfate concentration increases tremendously and in a few cases, it crosses the MCL of 400 mg/L, which causes a cathartic effect in human beings. Regular analysis of feed and treated water is required to calculate the correct dose of chemicals to be added, maintenance cost of the plant is high and the process is not automatic. It requires a regular attendant for addition of chemicals and looking after treatment process, a large space is required for the drying of the sludge, and silicates have an adverse effect on the efficiency of the method. Temperature also affects the defluoridation capacity of the process (Maheshwari and Meenakshi, 2006). Chang and Liu (2007) summarized that precipitation of fluoride from wastewater with CaCl_2 , and the removal of CaF_2 through coagulation flocculation can be that precipitation of fluoride was expedient, and residual fluoride concentration did not vary much in the pH range from 6.5 to 8.5.

2.6.3. Membrane filtration process

Reverse osmosis and electrodialysis are two membrane filtration processes which can be used for removal of fluoride (Feenstra *et al.*, 2007). The process is highly effective for fluoride removal. The membrane filtration processes also provide an effective barrier to suspended solids, all inorganic pollutants, organic micro pollutants, pesticides and microorganisms. The process permits the treatment and disinfection of water in one step, ensures constant water quality, no chemicals are required and very little maintenance is needed. The life of the membrane is sufficiently long, so problem of regeneration or replacement is encountered less frequently. It works under wide pH range, no interference by other ions is observed and the process works in a simple, reliable automated operating regime with minimal manpower using a compact modular model (Maheshwari and Meenakshi, 2006). Although membrane use has received universal acceptance, some of the limitations have showed its use in developing countries include high investment cost, requires high technology for operation and maintenance, brine discharge from the reverse osmosis plant is highly concentrated and requires treatment, fouling arising from feed water characteristics and high quantity of water rejection typically between 35% and 65%, then not suitable for regions where water is scarce (Darchen *et al.*, 2010). In addition, this technique removes all the ions present in water though some minerals are essential for proper growth, demineralization is required after treatment and the water becomes acidic and needs pH correction (Maheshwari and Meenakshi, 2006).

2.6.4. Electrochemical technique

Electrochemical technique is a simple and efficient method for the treatment of potable water. But the limitation of this technique is the hydrogen gas produced prevents the flocs from settling properly on leaving the electrolyzer (Darchen *et al.*, 2010). Hoshyaripour *et al.* (2010) investigated performance of a parallel-plate electro coagulation process with aluminum electrodes for the removal of fluoride from treated industrial wastewater originated from the steel industry.

2.6.5. Distillation

There are commercially available distillation filters that can be purchased to remove fluoride from water (Kumar and Salim, 2011).

2.6.6. Adsorption technique

The different adsorbents used for fluoride removal include activated alumina, carbon, bone charcoal and synthetic ion exchange resins (Feenstra *et al.*, 2007). Some substances adsorb fluoride by its surface, and it can exchange its negative ions such as hydroxyl group for fluoride. Here are some materials used in the adsorption and ion exchange method: activated alumina (Al_2O_3), fluidized activated alumina, activated bauxite (hydrate of $\text{Al}(\text{OH})_3$), zeolite ($\text{NaO}_2 \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_3 \cdot x\text{H}_2\text{O}$), tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), super phosphate ($\text{CaHPO}_4 + \text{CaSO}_4$), magnesite (MgCO_3), activated bone char ($\text{Ca}_{10}(\text{PO}_4)_8 \cdot \text{OH}_2$), activated carbon, plant carbon, charcoal, clay and bricks (Rujanawisan, 1999). Different natural materials attempted for removal of fluoride revealing that red soil has good fluoride removal capacity followed by brick, fly-ash, serpentine and charcoal (Chidambaram *et al.*, 2003). Iron containing lateritic ores and chromite overburden demonstrated as effective adsorbents for fluoride removal from aqueous solutions (Anand *et al.*, 2009). Adsorption can remove fluoride up to 90% and cost-effective technique. On the contrary, the process is highly dependent on pH and works best only in a narrow pH range (5.0-6.0). The presence of sulfate, phosphate or carbonate results in ionic competition. Another limitation of adsorption technique is effectiveness of adsorbent for fluoride removal reduces after each regeneration and disposal of fluoride laden sludge and concentrated regenerant is also a problem (Maheshwari and Meenakshi, 2006).

According to the study conducted by Anand and Sujana (2011) bauxite was investigated for fluoride removal from synthetic as well as groundwater samples and then as the solution pH increased the fluoride adsorption efficiency also increased achieving maximum at pH 6.4. The rate of adsorption was rapid and followed pseudo-first-order kinetics as the rate determining step. Since bauxite is an abundantly available mineral in many parts of the world, it can provide a simple, effective and yet low cost method for removing fluoride from contaminated water. A study by Chandravanshi *et al.* (2007) showed that 85% fluoride removal efficiency was obtained within 60 min contact time at an optimum adsorbent dose of 16 g/L for initial fluoride

concentration of 10 mg/L by using waste residue from alum manufacturing process as an adsorbent. The percentage of fluoride removal remains nearly constant within the pH range of 3.0-8.0. Also the study showed that the presence of bicarbonate at higher concentrations (100–500 mg/L) significantly affected fluoride removal efficiency while other anions (chloride, sulphate, phosphate and nitrate) did not significantly affect fluoride removal efficiency within the concentration range tested for the concentration tested. Heibati *et al.* (2012) demonstrated that the maximum sorption capacity of pumice was found to be 13.51 mg/g at an optimum pH 3.0. The sorption data fitted well to pseudo-second-order kinetic and Freundlich isotherm model. The study showed that pumice can be used as cheap, effective and efficient adsorbent for fluoride removal from aqueous solutions. A study by Banerjee *et al.* (2012) showed that both activated silica gel and activated rice husk ash showed the removal of fluoride increased with increase in contact time and then attained equilibrium after 100 min. Both adsorbents showed that the rate of adsorption followed pseudo-second-order kinetics. Langmuir and Freundlich isotherm models were found to represent the measured adsorption data well for both adsorbents with adsorption capacity of 0.244 mg/g and 0.402 mg/g respectively.

According to Gao *et al.* (2009) kinetic data using activated alumina attained equilibrium within 10 min with maximum adsorption between pH range of 5.5 and 7.5. A study by Chen *et al.* (2011) showed that porous granular ceramic adsorbents containing dispersed aluminum and iron oxides achieved maximum fluoride adsorption capacity of 1.79 mg/g at optimum pH 6.0. Both the Langmuir and Freundlich isotherm models were found to represent the measured adsorption data well. The experimental data were well explained with pseudo-second-order kinetic model. Bardsen *et al.* (1997) investigated fluoride removal using five soil samples, collected from the highland areas around Addis Ababa, and then showed that fluoride content of the water reduced from ~15 to 1.0 mg/L dosage levels of ~ 100 g/L. Also stirring speeded up the process, but it did not influence the finally obtained removal capacity. Equilibrium isothermal sorption experiments showed that dosages of 6.0 g/L rice husk and 1000 mg/L acid extract of natural polyelectrolyte *Moringa Oleifera* seed accomplished a removal of 83% and 88% fluoride, respectively (Karthikeyan and Vivek, 2011). Maximum removal of fluoride from water was attained after ~ 120 min at pH 5.0-8.0 using Kanuma mud as an adsorbent. Adsorption data fitted well to Freundlich isotherm model and followed the pseudo-second-order kinetic model. Also it was found that adsorbed fluoride could be easily desorbed by washing the adsorbent with a solution

of pH 12 indicating that the adsorbent could be easily recycled (Chen, 2010). *Phyllanthus emblica* showed 82.1% removal of fluoride was attained at equilibrium time of 75 min and adsorption of fluoride decreased from 87.95 to 47.22% as initial fluoride concentration increased from 2.0 to 10 mg/L. Higher fluoride adsorption achieved at 0.75 g/L of the adsorbent at smaller particle size. Chloride and nitrate did not significantly interfere with fluoride removal even at a concentration of 500 mg/L, while sulfate began to show some adverse effects when its concentration increased to 500 mg/L. However, bicarbonate showed significant effect on fluoride adsorption by decreasing quickly from 82.1 to 51.9% as its concentration increased to 500 mg/L (Alagumuthu and Veeraputhiran, 2011).

A study by Gao *et al.* (2009) showed that higher fluoride adsorption efficiency was achieved with smaller particle sized synthetic hydroxyapatites (HAPs). On the contrary, bulk synthetic HAPs, sample with the largest particle size, presented the lower adsorption efficiency. Freundlich isotherm was the best model to describe the adsorption behaviors of nanosized synthetic HAPs. However, the adsorption pattern of the bulk sample fitted to both Langmuir and Freundlich isotherm models. Borah and Dey (2009) showed that fluoride removal efficiency decreased with increasing particle size of the low grade coal. According to study by Kaseva (2006) the maximum fluoride adsorption efficiency and maximum adsorption capacity of 70.64% and 0.75 mg/g were achieved respectively for a sample with bone char material. Anand *et al.* (2009) showed that the rate of fluoride adsorption on amorphous iron and aluminum mixed hydroxides was fast and equilibrium was attained within 120 min. The adsorption followed pseudo-first-order kinetics as the rate determining step. The experimental data fitted well to both Freundlich and Langmuir adsorption isotherm models. Fluoride removal efficiency of synthetic iron (III)-aluminum (III)-chromium (III) ternary mixed oxide showed that equilibrium was attained at 90 min at optimum pH range between 4.0 and 7.0. The kinetic data were well described by pseudo-second-order and equilibrium data were well described by Langmuir isotherm equation. Regeneration of fluoride adsorbed material could be possible up to 90% with 0.5 M NaOH (Biswas *et al.*, 2010).

The application of *Cynodondactylon*-based thermally activated carbon for fluoride removal indicated that the adsorbent surface sites are heterogeneous in nature and that fits into a heterogeneous site-binding model. The time to reach equilibrium condition appears to be 105

min for the maximum defluoridation of the sorbent. The efficiency of fluoride adsorption decreased from 84 to 51% as fluoride concentration increased from 2.0 to 10.0 mg/L. The effect of coexisting anions examined showed that chloride and nitrate did not significantly affect fluoride removal even at a concentration of 500 mg/L, while sulfate began to show adverse effects when the sulfate concentration increased. However, bicarbonate significantly affected fluoride removal decreasing its adsorption efficiency from 83.7 to 51.5% with the increase of its concentration 0-300 mg/L (Alagumuthu, 2010). It was found that the presences of carbonate and bicarbonate showed significant effect on the adsorption of fluoride using lanthanum impregnated chitosan flakes. The adsorption of fluoride is high at optimum pH 5.0. It was observed that fluoride removal from field water samples was increased from 10 to 90% with increase in adsorbent dose from 0.05 g/50 mL to 1.0 g/50 mL. The experimental data fitted well to Freundlich isotherm and follows pseudo-second-order kinetic model (Das *et al.*, 2011).

According to a study by Cai *et al.* (2010) aluminum oxide embedded with Fe₃O₄ nanoparticles was found to remove excessive fluoride from aqueous solution attaining equilibrium time within 60 min at an optimum pH 6.5. The adsorption capacity fitted well to pseudo-second-order kinetic model. Dey *et al.* (2012) tested removal of fluoride using Zirconium (IV)-ethylenediamine hybrid material as an adsorbent and then fluoride adsorption equilibrium was attained within 14 min with removal efficiency of 99%. The amount of fluoride adsorbed increased as the pH of the solution increased from 2.0 to 7.0. Beyond pH 7.0, adsorption of fluoride dramatically decreased and reduced to almost zero when pH 12. The adsorption followed a pseudo-second-order kinetic model. The adsorbed fluoride easily desorbed from the material by using 0.1 M NaOH solution. Devotta *et al.* (2008) showed that fluoride removal efficiency increased from 47.46 to 92.37% with increase in dose of hydrated cement from 2.0 to 20 g/L. But no significant change was observed on fluoride removal efficiency after a dosage of 10 g/L. In addition, it was noticed that with increase in initial fluoride concentration, the removal efficiency of fluoride decreased. The presence of carbonate and bicarbonate showed negative effect while chloride, nitrate, and sulfate did not significantly affect fluoride removal. The experimental data were fitted well into the linearly transformed Freundlich and Langmuir isotherm models. Similarly a study by Devotta *et al.* (2009) showed that maximum removal of fluoride from aqueous solution using bleaching powder was attained within 60 min. Equilibrium adsorption data were fitted well into linearly transformed Langmuir isotherm model. Carbonate and bicarbonate significantly affected removal

capacity of the adsorbent. However, the presence of sulphate, nitrate and chloride did not significantly affect fluoride removal.

A study by Cengeloglu *et al.* (2011) indicated that equilibrium for fluoride adsorption using red mud was reached after 120 min at optimum pH 5.5. The result of study illustrated that adsorption capacity values increased with increase in initial fluoride concentration. The experimental data were fitted to both Freundlich and Langmuir isotherm equations. According to a study by Tor (2006) maximum removal of fluoride from an aqueous solution by using montmorillonite was achieved within 180 min at an optimum pH 6.0. Freundlich isotherm model was the best fitting adsorption isotherm. A study by Cheng *et al.* (2011) indicated that fluoride adsorption of natural stilbite zeolite modified with Fe (III) adsorbent attained equilibrium within 120 min at which maximum adsorption efficiency and maximum adsorption capacity of ~ 92% and ~ 0.54 mg/g were achieved respectively at optimum pH 6.94. However, adsorption capacity slightly decreased to 0.45 mg/g increase in pH to 8.05 and then after that, the adsorption capacity dramatically decreased and the adsorbent exhibits negligible adsorption of 0.11 mg/g at pH 11.2. Experimental data were well described by the Langmuir adsorption model and pseudo-first-order kinetic model. Chen *et al.* (2010) showed that maximum removal of fluoride using granular ceramic as adsorbent was obtained at pH 5.0-8.0 indicating that no harmful metal ions, Al^{3+} , Fe^{2+} or Fe^{3+} , were leached into the treated water when the pH of initial solutions was ranked from 5.0 to 10. The adsorption process followed both the Langmuir and the Freundlich isotherm equations. However, Freundlich isotherm equation gives a more satisfactory fit than Langmuir isotherm equation. The adsorption process was observed to follow a pseudo-second-order kinetic model. Duana *et al.* (2006) found that maximum removal of fluoride from aqueous solutions, reaching 88%, was obtained within 300 min at pH 6.0 with initial fluoride concentration of 50 mg/L using calcined Mg-Al- CO_3 layered double hydroxides as adsorbent. The fluoride removal efficiency increased with increasing dosage of adsorbent and largest percentage removal of 90% was exhibited at 4.0 g calcined Mg-Al- CO_3 layered double hydroxides per 1.8 L. The adsorption data were described by Freundlich and Langmuir isotherm equations. The adsorption process was observed to follow a pseudo-second-order kinetic model.

CHAPTER THREE

OBJECTIVES OF THE STUDY

3.1. General Objective

- To study and optimize the removal of fluoride by iron ore

3.2. Specific objectives

- to characterize the adsorbent (IO)
- to investigate the effect of various experimental conditions (contact time, solution pH, agitation rate, particle size of the adsorbent, adsorbent dose, initial fluoride concentration and competing anions) on the removal of fluoride
- to analyze the equilibrium adsorption capacity using isotherm models
- to analyze the regenerative property of the fluoride loaded IO
- to evaluate the fluoride removal efficiency of IO using natural groundwater

CHAPTER FOUR

MATERIALS AND METHODS

4.1. Study area and period

The sample of IO was collected from Akko locality, Tiro Afeta District, Jimma Zone, Oromia Regional National State, Ethiopia. Tiro Afeta district is one of the seventeen districts, which are located in Jimma zone, Southwestern of Ethiopia. The largest town in this district is Dimtu. Dimtu town is located at about 56 kilometers away from Jimma town. The study was conducted from July to September 2012.

4.2. Study design

Laboratory based experimental study was conducted.

4.3. Sample collection and analysis

Three samples of IO were collected from Akko locality, Tiro Afeta District, Jimma Zone, Oromia Regional National State, Ethiopia. The sample of real natural ground water was collected from drilled well found in Jimma University campus.

4.4. Preparation and characterization of the adsorbent

The three samples of IO collected were crushed and afterwards a composite sample was prepared mixing the three samples on equal proportion. The thoroughly mixed composite sample was dried in the laboratory at room temperature (22 ± 2 °C) for 7 days. Then, the dried sample was ground with hand using a mortar. The ground sample was sieved using a stack of sieves of 0.075, 0.425, 2.0 and 4.75 mm openings according to the American Society for Testing and Materials (ASTM D 422) and soil textural classification system (Liu and Evett, 2003). And the sieved particles of different size were stored in air tight plastic bottles for further study. Then, the chemical compositions of composite sample of IO were analyzed by X-Ray Fluorescence (XRF) spectrometry at Ethiopian Geoscience laboratory center of Ethiopian Geological survey. And

also, some of the physical characteristics (pH, bulk density, particle density and porosity) of the particle of size < 0.075 mm of the adsorbent were determined according to soil characterization protocol in Environmental graduate and staff research laboratory of Jimma University.

4.1. Instrumentation

A Spectrophotometer (DR-5000 UV/VIS Spectrophotometer) was employed for the measurement of fluoride ion concentration. The Multiparameter probe (HACH HQd) was used to measure pH, conductivity, electrical conductivity, dissolved oxygen, and turbidity. Thermometer was to measure the room temperature of laboratory during conducting the experiments and also to measure the temperature of the natural ground water used in the study. The equipments (cylinders, beakers, etc) used in experiments were of polyethylene coatings.

4.2. Reagent and standard solutions

All reagents and chemicals used were of analytical grade. Stock solution of fluoride was prepared by dissolving 0.221 g anhydrous NaF (99.0% NaF) in 1000 mL distilled water. A stock solution was then appropriately diluted to get the desired solution for the practical use. Solution pH was maintained using 0.1 M NaOH and/or HCl. Alizarin red and Zirconyl acid reagent were used as colored agents for fluoride analysis. Zirconyl chloride octahydrate and Hydrochloric acid were used to prepare zirconyl acid reagent. Sodium arsenite was used to control chlorine interference. NaCl, KNO₃, K₂SO₄, KH₂PO₄, CaCO₃ and NaHCO₃ were used for the preparation of chloride, nitrate, sulfate, phosphate, carbonate and bicarbonate anions concentration respectively. Two percent HNO₃ was used to wash laboratory wares.

4.3. Analysis of fluoride concentration

One hundred mL of clear and colorless supernatant samples of fluoride solution were added into graduated cylinders. One drop (0.05 mL) of sodium arsenite solution was added into each sample for the removal of each 0.1 mg of residual chlorine present in the samples. Then the samples were mixed by inverting each cylinder four to six times and allowed coming to the same temperature, because the color development depends critically on temperature. With a volumetric pipette, 5.0 mL Alizarin red reagent and 5.0 mL Zirconyl acid reagent were added to

each of the sample which was completed within 5.0 minutes and the contents were mixed by inverting each cylinder four to six times. The samples were allowed to stand for at least 1 h \pm 5 minutes and analyzed for their fluoride concentration using Alizarin red photometric method on Spectrophotometer (DR-5000 UV/VIS Spectrophotometer) at 570 nm wavelength. A calibration curve was obtained using NaF standard solutions with different fluoride concentrations from 0 to 1.0 mg/L. The results were plotted as fluoride concentration (mg/L) versus absorbance.

4.4. Batch adsorption experiment

The fluoride adsorption experiments were carried out by a batch method at room temperature (22 \pm 2 °C). The pH of the fluoride solution in the experiment was adjusted to \sim 6.0 (except in the analysis of the effect of pH of the solution) using 0.1 M NaOH and/or HCl. Two hundred mL of fluoride solution containing 10 mg/L fluoride and 5.0 g/L IO were loaded in plastic bottle and agitated at a rate of 150 rpm on an orbital shaker (Typ SM 30A). Blank and control experiments were conducted at every set of the experiments. All experiments were performed in duplicate and mean value was reported.

The effect of contact time was investigated using 10 mg/L fluoride and 5 g/L IO at pH \sim 6.0. The solution samples were agitated at a rate of 150 rpm and the supernatant solution samples were collected at different contact time (5.0-240min). The effect of solution pH was carried out using 10 mg/L fluoride and 5 g/L IO varying solution pH (3.0-11) at agitation rate of 150 rpm for 120 min. The effect of agitation rate was carried out using 10 mg/L fluoride and 5.0 g/L IO at pH \sim 6.0 varying agitation rate (50-250 rpm) for 120 min. The effect of particle size of the adsorbent was carried out using 10 mg/L fluoride and 5.0 g/L IO varying particle size of an adsorbent (>4.75, 4.75 to 2.0, 2.0 to 0.425, 0.425 to 0.075 and < 0.075 mm) at pH \sim 6.0, agitation rate of 150 rpm and contact time of 120 min. The effect of adsorbent dose was investigated using 10 mg/L fluoride varying the dose (1.0-25 g/L) at pH \sim 6.0, agitation rate of 150 rpm for 120 min. The effect of initial fluoride concentration was carried out using 5 g/L IO varying fluoride concentration (2.0-29 mg/L) at pH \sim 6.0, agitation rate of 150 rpm for 120 min. The effect of the presence of competing anions (CO_3^{2-} , HCO_3^- , PO_4^{3-} , Cl^- , NO_3^- and SO_4^{2-}) in the solution on the efficiency of fluoride adsorption was studied using 10 mg/L fluoride and 5.0 g/L IO varying the

concentration of anions (5.0-200 mg/L) at solution pH ~ 6.0, agitation rate of 150 rpm for 120 min.

4.5. Desorption experiment

Desorption study was investigated using 5.0 g/L IO used for the adsorption of 10 mg/L fluoride solution. The adsorbent was separated from the solution by filtration using Whatman filter paper and washed gently with distilled water to remove unadsorbed fluoride and dried in an oven. Fluoride loaded adsorbent was shaken with different concentration of NaOH (0.01-0.5M).

4.6. Fluoride removal from natural groundwater

A sample of fluoride contaminated groundwater was collected from Jimma University Main campus. The physico-chemical analysis of the sample was carried out and it was found that the concentration of fluoride in the groundwater was 14.22 mg/L. Different dose of IO (5-20 g/L) with particle size < 0.075 mm were allowed to adsorb the fluoride of the sample of groundwater without adjusting the pH of the water.

4.7. Data Analysis

The percentage of fluoride removed and the amount of fluoride adsorbed were computed applying Eq. (1) and Eq. (2) respectively (Cheng *et al.*, 2011):

$$A\% = \frac{(C_o - C_t) \times 100}{C_o} \quad (1)$$

$$q_t = \frac{(C_o - C_t) \times V}{M} \quad (2)$$

Where C_o is initial fluoride concentration (mg/L), C_t is fluoride concentration at time t (mg/L), q_t is the amount of fluoride adsorbed at time t (mg/g), V is volume of the solution (L) and M is mass of the adsorbent used (g).

A distribution coefficient (K_d) which reflects the binding ability of the surface for fluoride mainly depends on pH and type of adsorbent surface. A distribution coefficient (K_d) value for

fluoride of the adsorbent at pH ~ 6.0 was calculated according to the following equation (Alagumuthu and Veeraputhiran, 2011):

$$K_d = \frac{q_t}{C_t} (L/g) \quad (3)$$

Where q_t is the concentration of fluoride in the solid particles (mg/g) and C_t is the concentration of fluoride in water (mg/L).

4.8. Theories

4.8.1. Adsorption kinetics

To determine an appropriate contact time between the IO and solution containing fluoride, fluoride removal capacities were measured as a function of time. The kinetic data of fluoride adsorption were evaluated using the pseudo-first-order and pseudo-second-order kinetic models (Fan *et al.*, 2003). The pseudo-first-order can be expressed as (Bulut *et al.*, 2009):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (4)$$

Where q_t and q_e are the amount of fluoride adsorbed (mg/g) at time t and at equilibrium time, respectively. k_1 ($g\ mg^{-1}\ min^{-1}$) is pseudo-first-order rate constant for adsorption. The adsorption rate constant k_1 was determined from the slope of the linear plot of $\log(q_e - q_t)$ versus t .

The mathematical equation of the pseudo-second-order reaction is expressed as (Duran *et al.*, 2009):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

Where k_2 ($g\ mg^{-1}\ min^{-1}$) is the equilibrium rate constant of pseudo-second-order reaction. k_2 was obtained by plotting of t/q_t versus t .

Besides adsorption at the outer surface of the adsorbent, the fluoride may also diffuse into the interior of the adsorbent (Bulut *et al.*, 2009). Intraparticle diffusion model based on the theory

proposed by Weber and Morris was tested to determine if the particles diffusion is the rate-limiting step for the fluoride adsorption onto IO (Benghalem *et al.*, 2010). According to this theory (Anand *et al.*, 2009):

$$q_t = k_p t^{0.5} \quad (6)$$

Where q_t is the amount of fluoride adsorbed (mg/g) at a given time t (min) and k_p ($\text{mg g}^{-1} \text{min}^{-1/2}$) is the intraparticle diffusion rate constant. The k_p value was obtained from plotting of q_t versus $t^{0.5}$.

4.8.2. Adsorption isotherms

The distribution of fluoride ion between the liquid and solid phase is a measure of the position of equilibrium in the adsorption process which can be expressed by the Freundlich and Langmuir isotherm models. Freundlich adsorption isotherm model, the multilayer adsorption, commonly used to describe adsorption characteristics for heterogeneous surface. It can be described by Eq. (7) (Attar *et al.*, 2009):

$$q_e = k_f C_e^{\frac{1}{n}} \quad (7)$$

Where C_e is the equilibrium concentration (mg/L), q_e is equilibrium adsorption capacity (mg/g), k_f and $1/n$ are the Freundlich constants, related to minimum adsorption capacity and energy or adsorption intensity, respectively. The values of k_f and $1/n$ were obtained from the slope and intercept of the linear Freundlich plot of $\log q_e$ versus $\log C_e$.

The Langmuir adsorption isotherm model, the monolayer adsorption, used to describe adsorption characteristics for homogeneous surface. It is based on the assumption that the point of valance exists on the surface of the adsorbent and that each of these site is capable of adsorbing one molecule. It is assumed that the adsorption sites have equal affinities for molecules of adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site. The Langmuir isotherm mathematical equation is written as (Chen *et al.*, 2011):

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (8)$$

Where C_e is the equilibrium concentration (mg/L), q_e is the equilibrium adsorption capacity (mg/g), q_{\max} and b are the Langmuir constants, related to maximum adsorption capacity (mg/g) and adsorption intensity (L mg⁻¹), respectively. The values of q_{\max} and b were obtained from the slope and intercept of the linear Langmuir plot of $1/q_e$ versus $1/C_e$.

In order to evaluate the feasibility of the process, the Langmuir isotherm can be described in terms of the dimensionless constant called separation factor or equilibrium parameter (R_L):

$$R_L = \frac{1}{1 + bC_o} \quad (9)$$

Where, C_o is the initial concentration of fluoride (mg/L) and b is a rate constant related to energy or intensity of adsorption. There are four probabilities for the R_L value: for favorable adsorption $0 < R_L < 1$, for unfavorable adsorption $R_L > 1$, for linear adsorption $R_L = 1$ and for irreversible adsorption $R_L = 0$.

Another equation used in the analysis of isotherms was the Dubinin and Radushkevich (D-R) isotherm to determine the adsorption type (physical or chemical). The linear form of this model is expressed by Eq. (10) (Chen *et al.*, 2007):

$$\ln q_e = \ln q_s - \beta E^2 \quad (10)$$

Where q_e is the amount of fluoride adsorbed (mol/g), q_s is monolayer sorption capacity (mol/g), C_e is the equilibrium fluoride concentration (mol/L), and β is the activity coefficient related to mean sorption energy (mol²/kJ²). The mean sorption energy, E (kJ/mol), can be calculated by Eq. (11) (Chandravanshi *et al.*, 2007). ε is the Polanyi potential described as:

$$\varepsilon = RT \left(1 + \frac{1}{c_e} \right) \quad (11)$$

The mean sorption energy, E (kJ/mol), can be calculated by Eq. (11) (Chandravanshi *et al.*, 2007).

$$E = \frac{1}{\sqrt{-2\beta}} \quad (12)$$

4.9. Ethical consideration

Ethical clearance was obtained from ethical committee of Jimma University, College of Public Health & Medicinal sciences for the permission of iron ore sample collection obtained from Akko locality, Tiro Afeta, Oromia national regional state as well as for Geoscience laboratory of Ethiopian Geological survey for analyzing chemical compositions of the IO.

4.10. Dissemination plan

Final result of this study will be submitted to Jimma University, College of Public Health & Medicinal sciences, Department of Environmental Health science and Technology. Also publication on national and international journals will be tried.

4.11. Data quality management

Data quality was maintained by conducting duplicate experiments and reporting the average values of the duplicate measurements. Analytical equipment was calibrated at each set of analysis using freshly prepared standard solution. Blank and control experiments were conducted. Laboratory wares were washed with 2% HNO₃ followed by repeated wash and rinsing with distilled water to prevent contamination.

CHAPTER FIVE

RESULTS

5.1. Adsorbent characterization

The chemical compositions and physical characteristics of IO are given in Table 1. The adsorbent contained relatively higher iron and silicon oxides as compared to the other oxides. The sum total of the content of the ionic metal oxides of the adsorbent was negligible as compared with the other oxides. The pH of the adsorbent determined in water was 5.4 that could be due to the low content of ionic metal oxides of the adsorbent. The bulk and particle densities of IO of particle size < 0.075 mm were 0.53 and 0.71 g/cm^3 respectively. The porosity of the adsorbent determined from the bulk and particle densities was 25%.

Table 1. Chemical compositions of IO

Oxides	Value (wt %)
SiO ₂	28.98
Al ₂ O ₃	7.71
Fe ₂ O ₃	38.50
CaO	1.52
MgO	0.42
Na ₂ O	0.24
K ₂ O	0.60
MnO	1.76
P ₂ O ₅	0.15
TiO ₂	0.43
H ₂ O	6.22
LOI ^a	12.10

^aLoss on ignition.

5.2. Effect of contact time

The percentage of fluoride adsorbed from aqueous solution with time is presented in Figure 1. As shown in Figure 1, it was observed that fluoride adsorption increased with increasing in contact time and the equilibrium was attained within 120 min at which maximum adsorption efficiency (~ 86%) and maximum adsorption capacity (~ 0.095 mg/g) were achieved. Therefore, 120 min contact time was fixed for further experiments in this study.

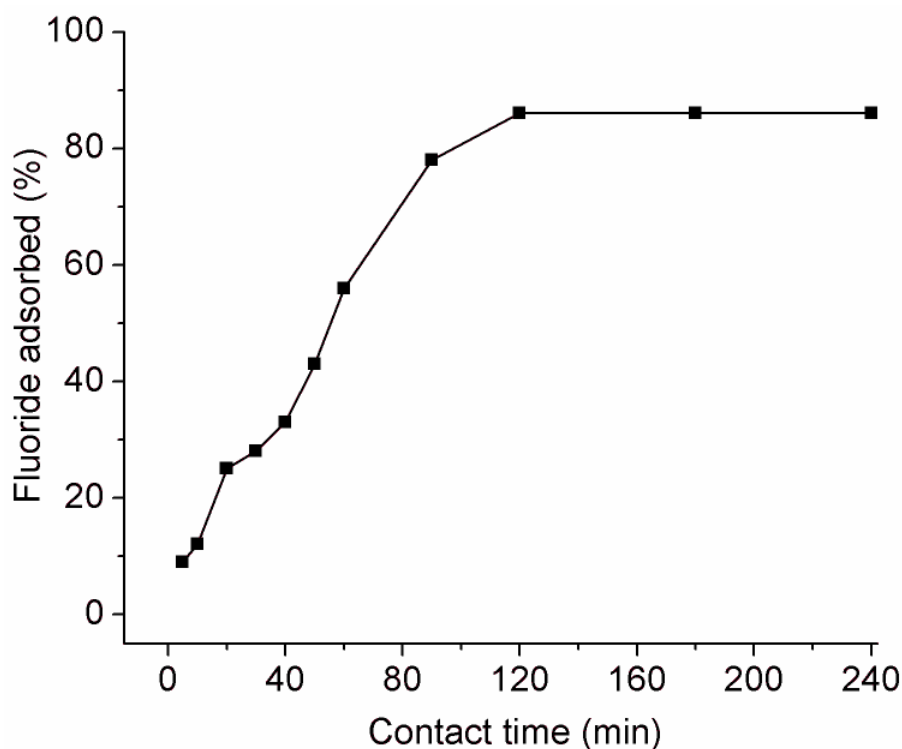


Fig. 1. Fluoride removal as a function of contact time ($[F]_0$: 10 mg/L, particle size: <0.075 mm, adsorbent dose: 5.0 g/L, pH: ~ 6.0 and agitation rate: 150 rpm).

5.3. Adsorption kinetics

The plots of the kinetics of fluoride adsorption onto IO are given in Figure 2. The values of the calculated parameters of the kinetics of fluoride adsorption are presented in Table 2. The fluoride adsorption kinetic data were fitted to the pseudo-first-order kinetic model with the higher coefficient of determination ($R^2 = 0.882$) value as compared to the pseudo-second-order ($R^2 = 0.694$). The rate constant of the pseudo-first-order equation was $0.024 \text{ g mg}^{-1} \text{ min}^{-1}$. The

intraparticle diffusion rate constant (k_p) value obtained from the slope of plot of q_t versus square root of time was found to be $0.0103 \text{ mg g}^{-1} \text{ min}^{-1/2}$ for the initial fluoride concentration of 10 mg/L .

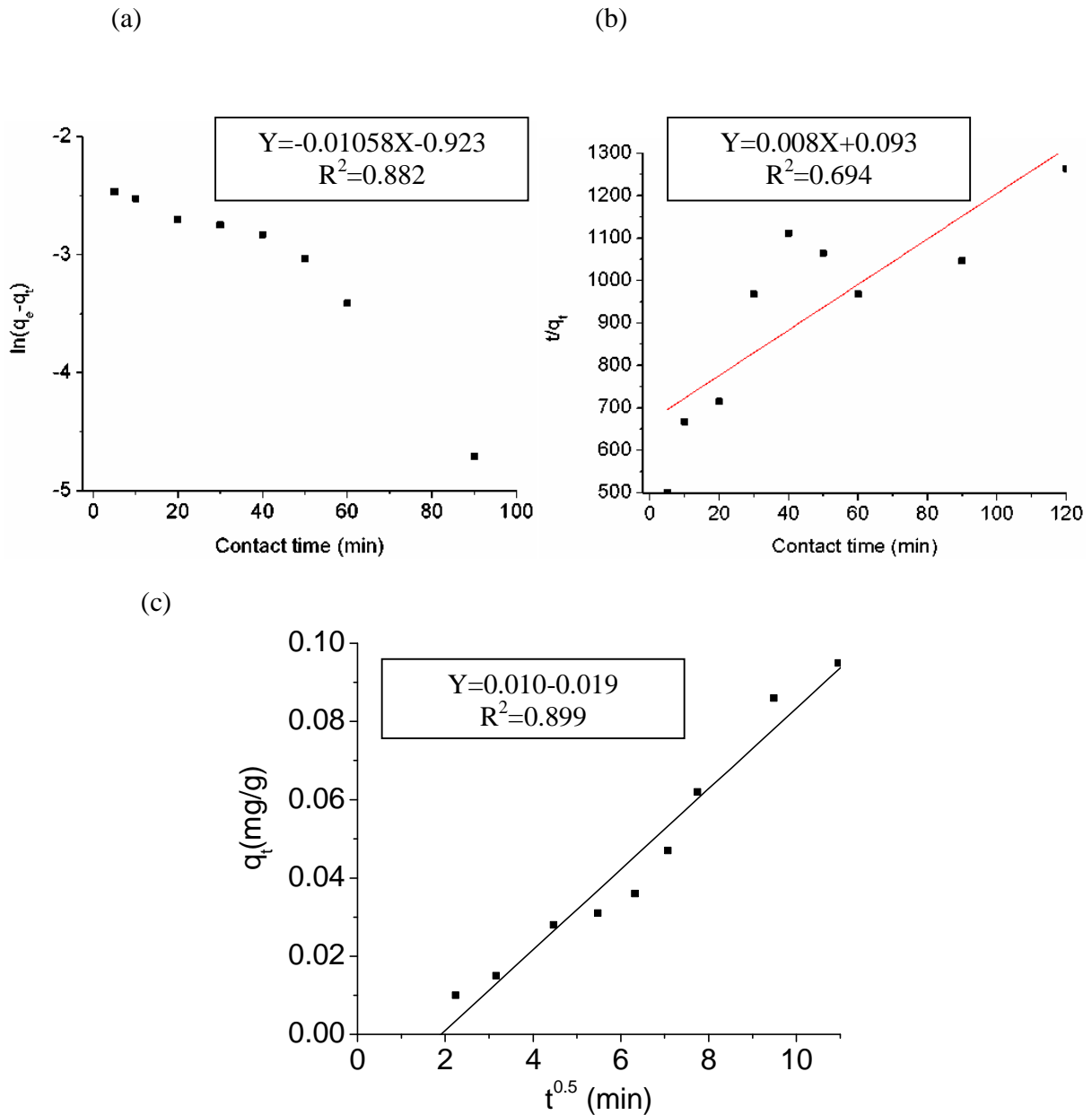


Fig. 2. (a) Pseudo-first-order kinetic plot for fluoride removal (b) Pseudo-second-order kinetic plot for fluoride removal (c) Intra-particle ($[F]_0$: 10 mg/L , particle size: $< 0.075 \text{ mm}$, adsorbent dose: 5.0 g/L , contact time: 120 min , agitation rate: 150 rpm and pH : ~ 6.0 and temperature $22 \pm 2 \text{ }^\circ\text{C}$).

Table 2. The kinetics parameters for adsorption of fluoride onto IO.

Pseudo-first-order		Pseudo-second-order		Intraparticle diffusion	
Parameters	Value	Parameter	Value	Parameter	Value
$q_{e \text{ exp.}}(\text{mg/g})$	0.095	$q_{e \text{ exp.}}(\text{mg/g})$	0.095	R^2	0.960
$q_{e \text{ calc.}}(\text{mg/g})$	0.119	$q_{e \text{ calc.}}(\text{L/mg})$	0.187	$K_p(\text{mgg}^{-1}\text{min}^{-1/2})$	0.0103
R^2	0.882	R^2	0.694		
$K_1(\text{g}^{-1}\text{mg}^{-1}\text{min})$	0.024	$K_2(\text{g}^{-1}\text{mg}^{-1}\text{min})$	0.166		

5.4. Effect of pH

The percentage of fluoride adsorbed and fluoride adsorption capacity progressively increased from 62 to ~ 86% and 0.07 to ~ 0.095 mg/g as the pH of the solution increased from 3.0 to ~ 6.0 respectively (Fig. 3). However, adsorption efficiency and adsorption capacity slightly decreased to 83% and 0.093 mg/g respectively at pH 7.0. With the increase in pH above neutral to pH 11, the adsorption efficiency and adsorption capacity dramatically decreased to 14% and 0.018 mg/g respectively. Therefore, pH ~ 6.0 was fixed as an optimal value for the next experiments.

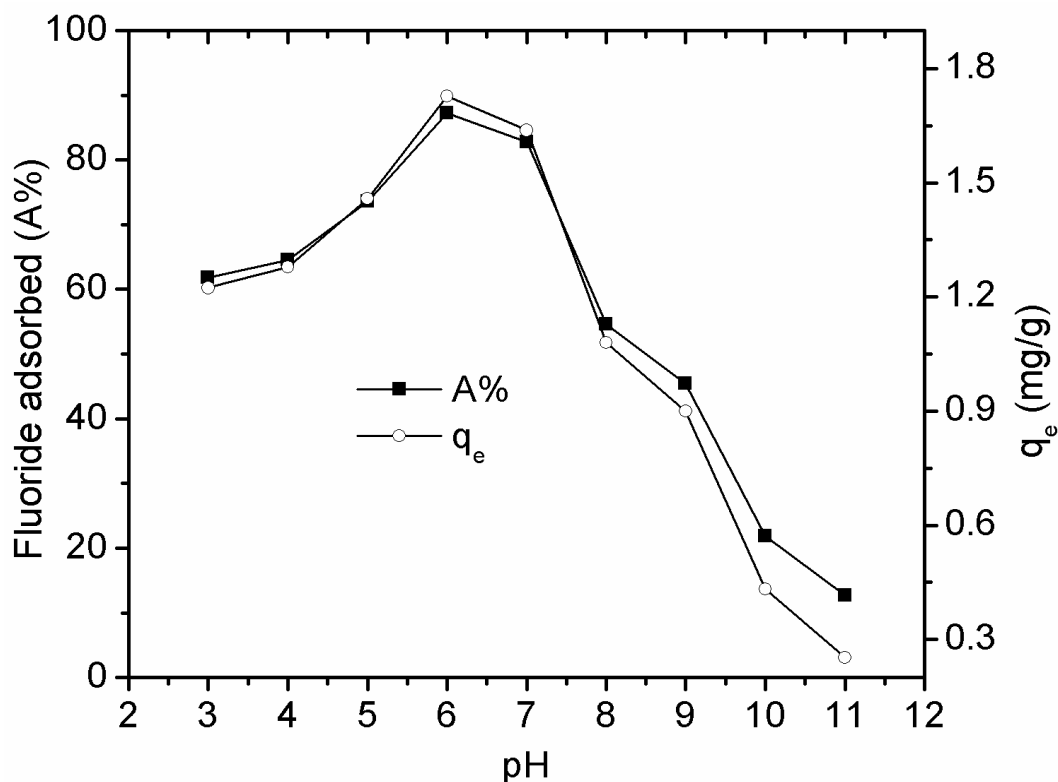


Fig. 3. Fluoride removal as a function of solution pH ($[F]_0$: 10 mg/L, particle size: < 0.075 mm, adsorbent dose: 5.0 g/L, contact time: 120 min and agitation rate: 150 rpm).

5.5. Effect of agitation rate

Figure 4 shows that fluoride adsorption efficiency and fluoride adsorption capacity increased from 49 to ~ 86% and 0.054 to ~ 0.095 mg/g as agitation rate increased from 50 to 150 rpm respectively. However, after agitation rate of 150 rpm fluoride adsorption efficiency and fluoride adsorption capacity slightly decreased. Therefore, 150 rpm was chosen as the optimal agitation rate for the other experiments in this study.

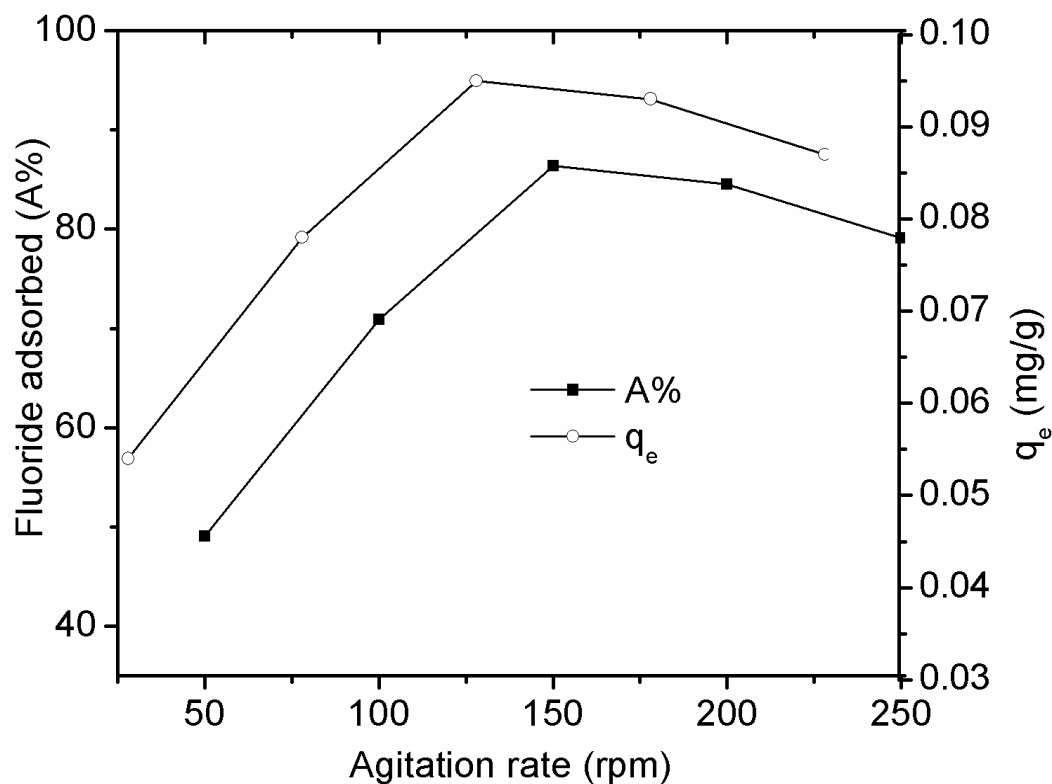


Fig. 4. Fluoride removal as a function of agitation rate ($[F]_0$: 10 mg/L, particle size: < 0.075 mm, adsorbent dose: 5.0 g/L, contact time: 120 min and pH: ~ 6.0).

5.6. Effect of particle size

The influence of particle size of the adsorbent on fluoride adsorption efficiency is illustrated in Figure 5. The fluoride adsorption efficiency increased from 13 to ~ 86% as particle size of the adsorbent decreased from > 4.75 to < 0.075mm. Therefore, adsorbent with particle size of < 0.075mm was used throughout the study.

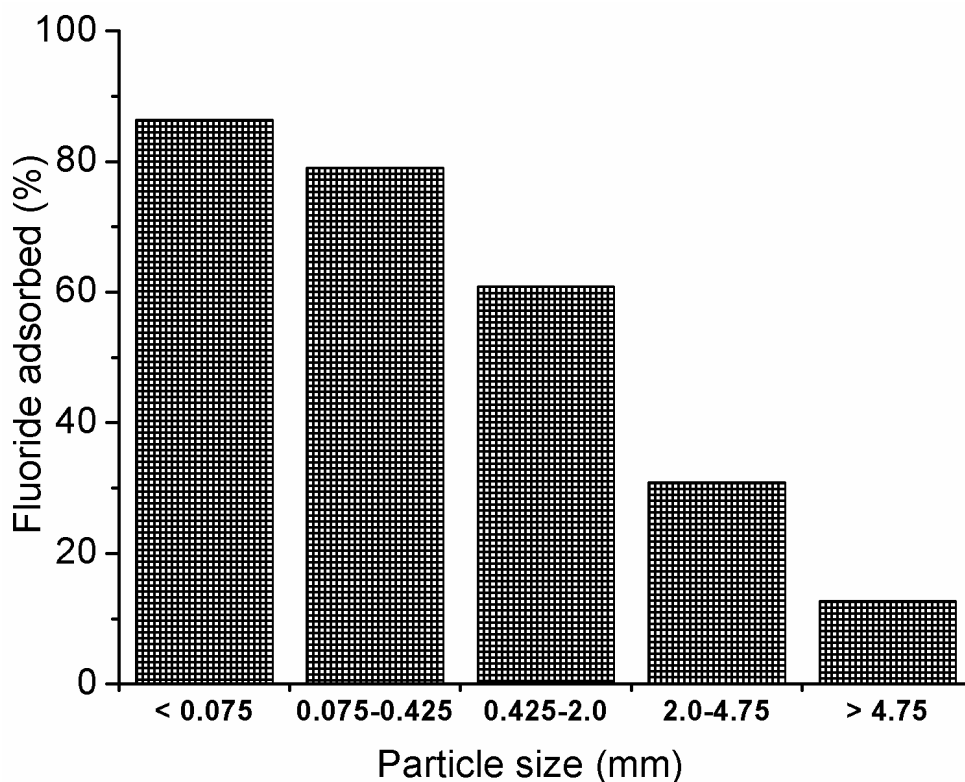


Fig. 5. Fluoride removal as a function of particle size of the adsorbent ($[F]_0$: 10 mg/L, adsorbent dose: 5.0 g/L, contact time: 120 min, pH: ~ 6.0 and agitation rate: 150 rpm).

5.7. Effect of adsorbent dose

It was observed that fluoride adsorption efficiency increased from 25 to ~ 86% as dose of the adsorbent increased from 1.0 to 5.0 g/L as given in Figure 6. However, after a dose of 5.0 g/L, there was no significant change in fluoride adsorption efficiency. It was observed that 5.0 g/L IO of particle size < 0.075 mm reduced 10 mg/L fluoride to below the level of the maximum permissible limit (1.5 mg/L) for fluoride in drinking water. Therefore, 5.0 g/L IO was used for considered as a minimum dose for maximum adsorption of fluoride in the further study. On the contrary, it was observed that fluoride adsorption capacity decreased from 0.205 to 0.0204 mg/g as dose of the adsorbent increased from 1.0 to 25 g/L.

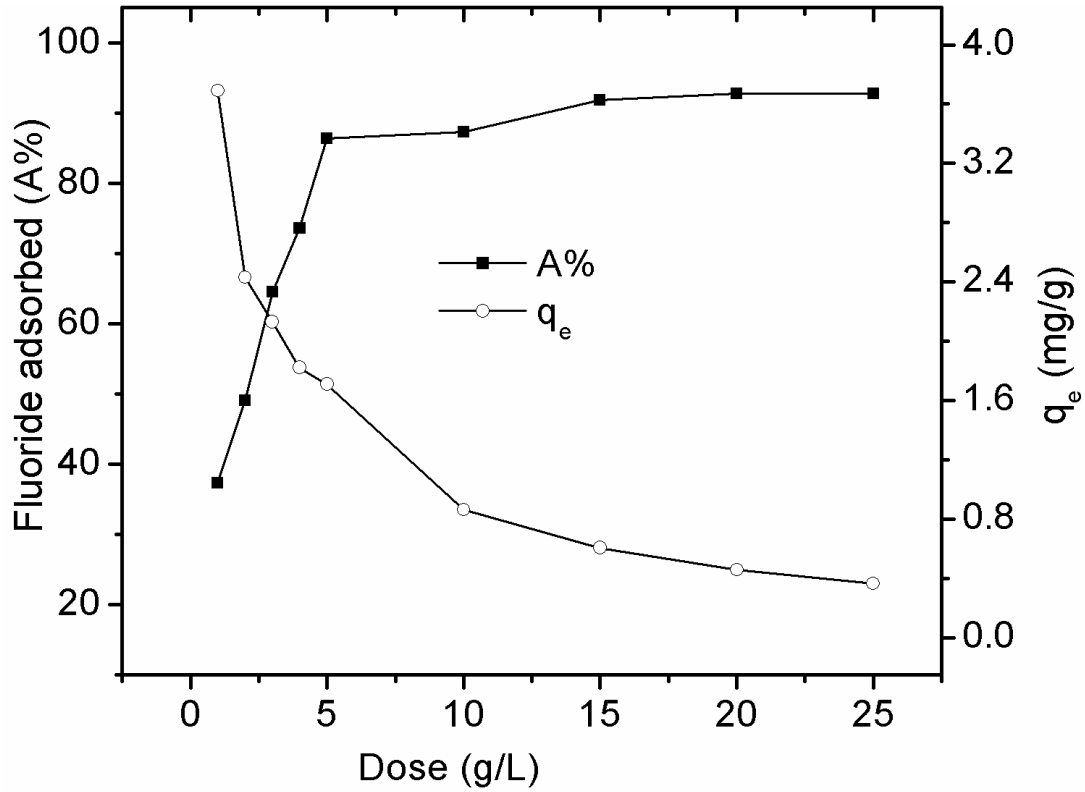


Fig. 6. Fluoride removal as a function of adsorbent dose ($[F]_0$: 10mg/L, particle size: < 0.075 mm, contact time: 120 min, pH: ~ 6 and agitation rate: 150 rpm).

The distribution coefficient (K_d) value for fluoride adsorption on the adsorbent was calculated using Eq.(12) (Chen *et al.*, 2011).

$$K_d = \frac{q_t}{C_t} (L/g) \quad \text{Eq. (13)}$$

The plot of K_d values versus dose of the adsorbent is given in Figure 7. It was observed that the value of the K_d progressively increased along with the increase in the dose the adsorbent.

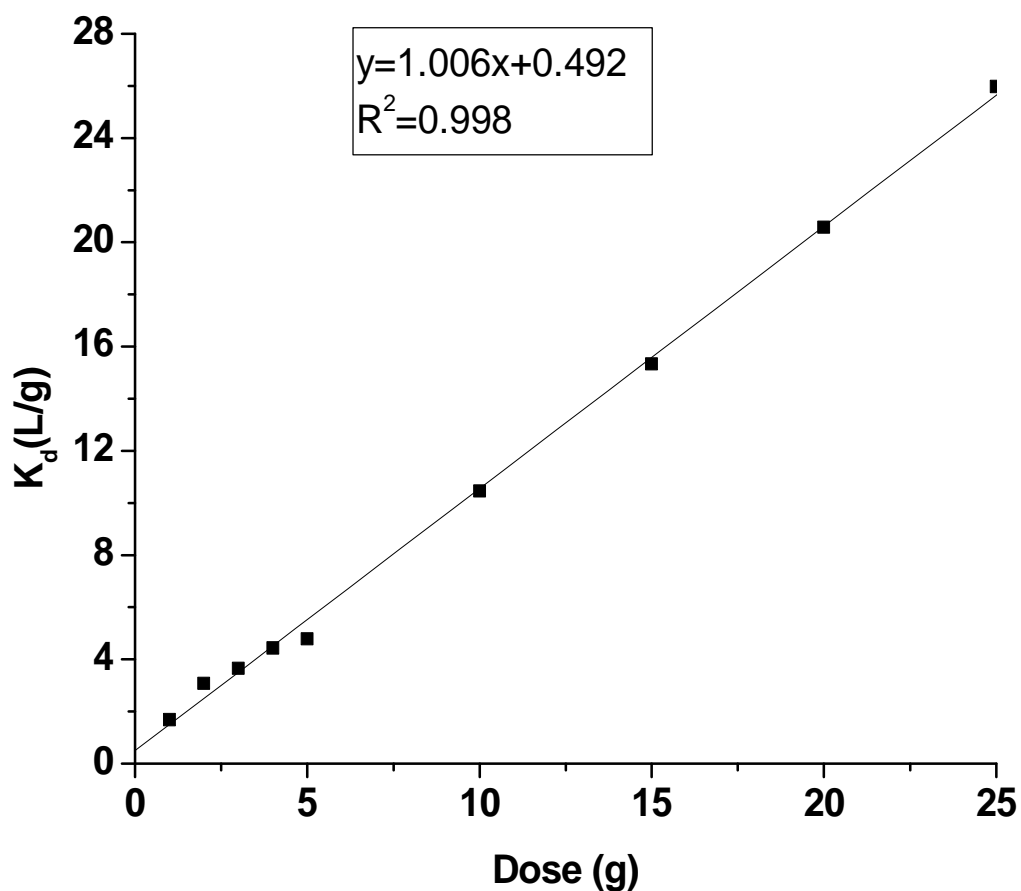


Fig. 7. The plot of K_d value as a function of adsorbent dose (pH ~ 6.0).

5.8. Effect of initial fluoride concentration

Figure 8 shows that fluoride adsorption efficiency was declined from 91 to 66% as initial fluoride concentration increased from 2.0 to 29 mg/L. However, fluoride adsorption capacity increased from 0.019 to 0.213 mg/g with the increase in initial fluoride concentration from 2.0 to 29 mg/L.

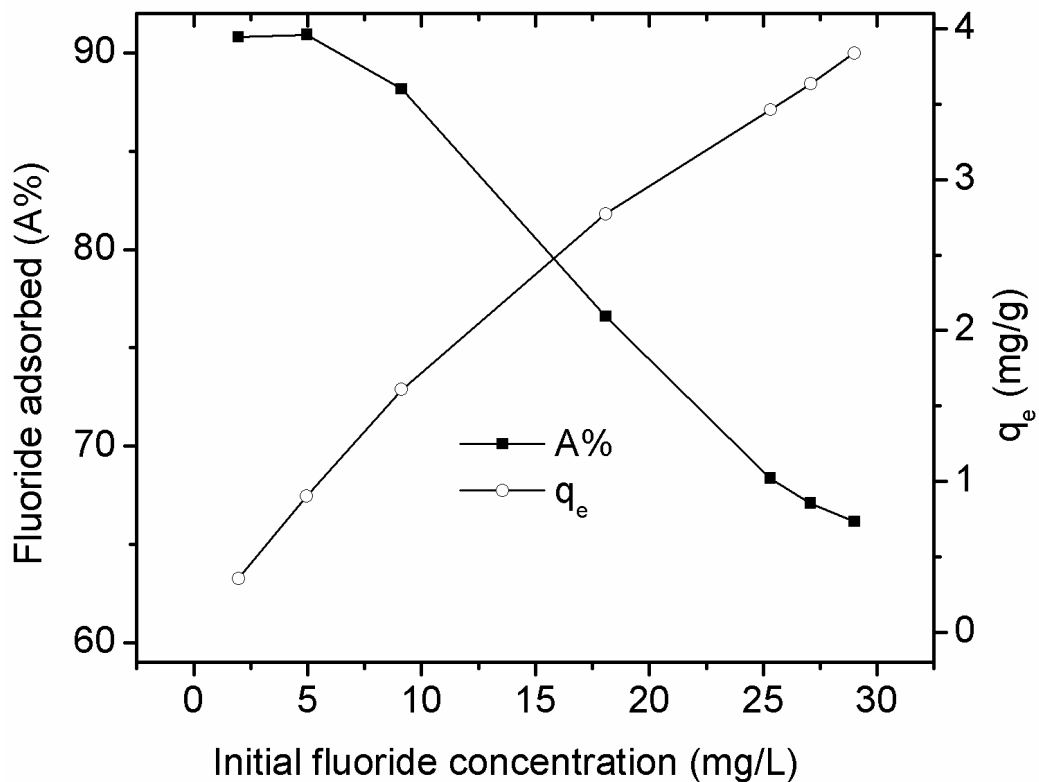


Fig. 8. Fluoride removal as a function of initial fluoride concentration (particle size: < 0.075 mm, adsorbent dose: 5.0 g/L, contact time: 120 min, pH: ~ 6.0 and agitation rate: 150 rpm).

5.9. Adsorption isotherm

It was observed that the Freundlich and Langmuir isotherms described well the equilibrium adsorption data with the coefficients of determination values of 0.993 and 0.983 respectively. However, the Freundlich isotherm described the equilibrium data better as the value of the coefficient of determination for Freundlich was greater and the value of the chi-square was less. The parameters of the Freundlich, Langmuir and Dubinin-Radushkevich isotherms are given in Table 3.

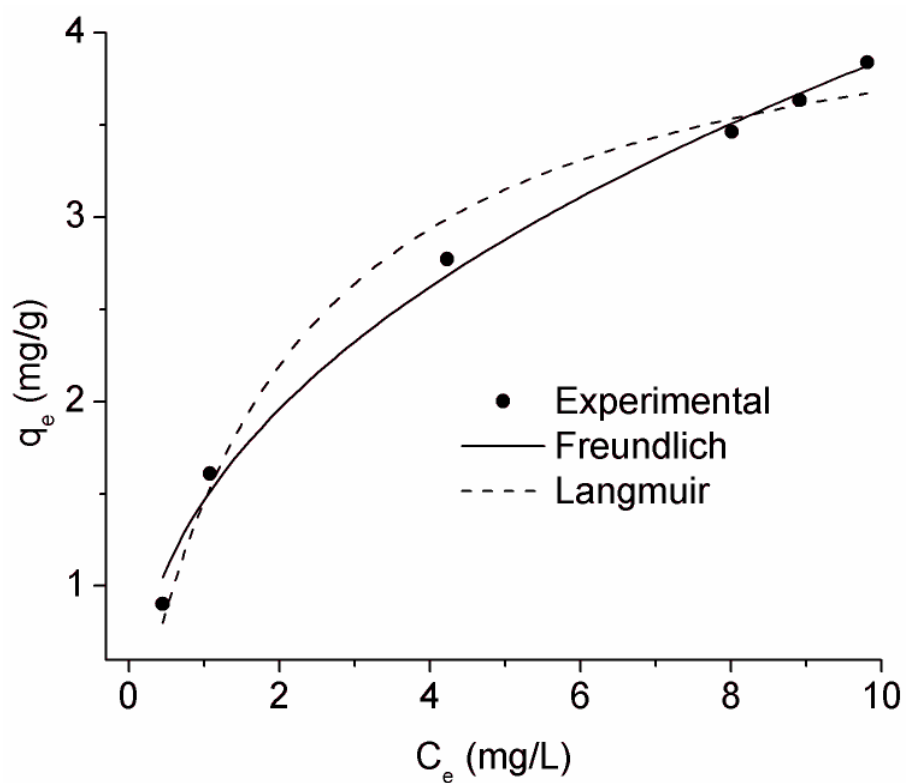


Fig. 9. Equilibrium isotherms of fluoride adsorption onto IO ($[F^-]_0$: 10 mg/L, particle size: < 0.075 mm, adsorbent dose: 1.0-25 g/L, contact time: 120 min, agitation rate: 150 rpm and pH: ~ 6.0).

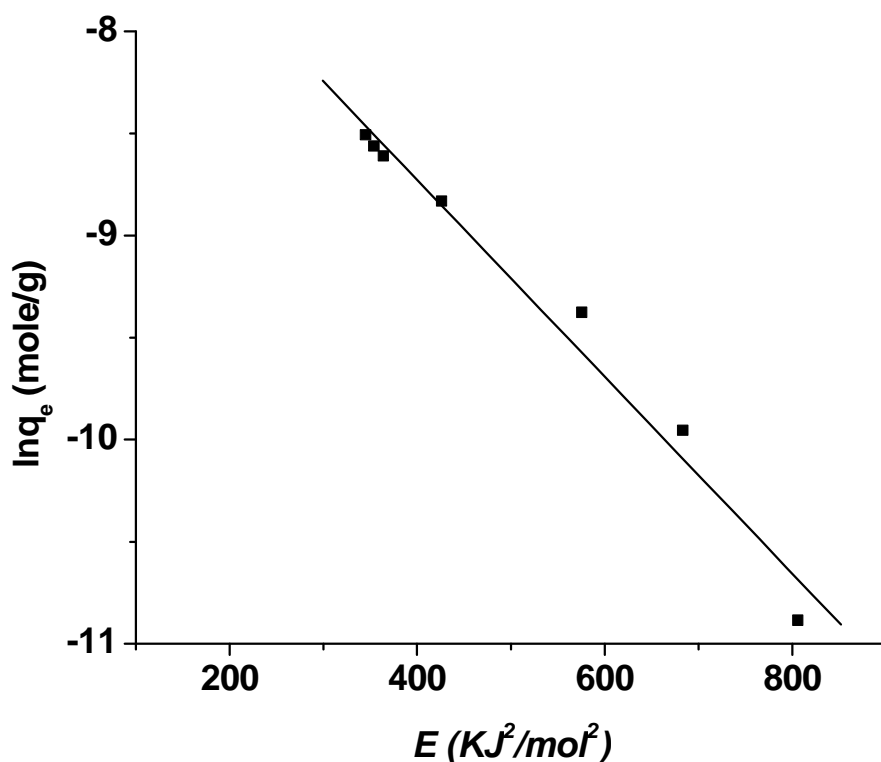


Fig. 10. D-R isotherm of fluoride adsorption onto IO ($[F^-]_0$: 10 mg/L, particle size: < 0.075 mm, adsorbent dose: 5.0 g/L, contact time: 120 min, agitation rate: 150 rpm, pH: ~ 6 and temperature: 22 ± 2 °C).

Table 3. Equilibrium isotherm parameters of fluoride adsorption onto IO.

Freundlich		Langmuir		D-R	
Parameters	Value	Parameter	Value	Parameter	Value
K_f (mg/g)	1.465	q_{\max} (mg/g)	4.433	q_s (mg/g)	21.159
$1/n$	0.420	b (L/mg)	0.490	E (kJ/mol)	10.206
R^2	0.993	R^2	0.983	R^2	0.978
χ^2	0.010	χ^2	0.024		

5.10. Effect of competing anions

The influence of competing anions on the fluoride adsorption efficiency is illustrated in Figure 11. It was observed that fluoride adsorption efficiency was significantly (p -value < 0.05) affected by phosphate, carbonate and bicarbonate within the concentration range tested (5.0-200 mg/L). However, the presence of sulphate, nitrate and chloride did not significantly (p -value > 0.05) affect fluoride adsorption efficiency within the concentration range tested (5.0-200 mg/L).

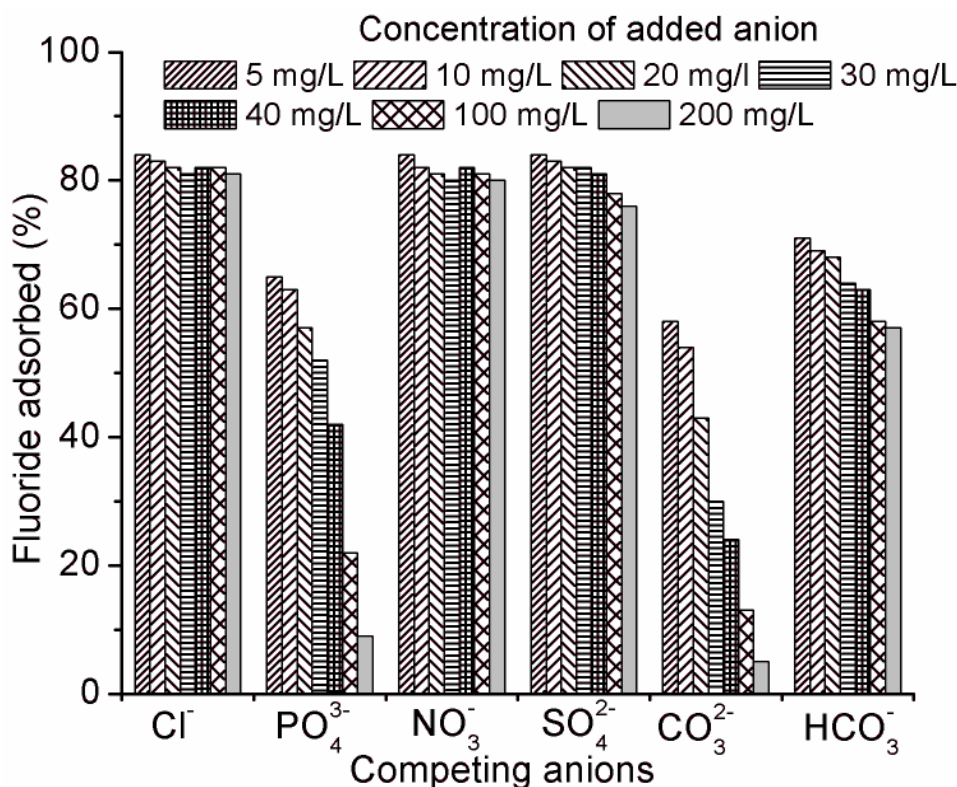


Fig. 11. Fluoride removal at different anions concentrations ($[F]_0$: 10 mg/L, particle size: < 0.075 mm, adsorbent dose: 5.0 g/L, contact time: 120 min, pH: ~ 6.0 and agitation rate: 150 rpm).

5.11. Desorption experiment

The reusability of an adsorbent mainly depends on the ease with which adsorbate is released from the spent adsorbent. The regenerative properties of the fluoride loaded IO was investigated using NaOH solution of different concentrations. The percentage of fluoride desorbed at

different concentrations of NaOH is shown in Figure 12. It was observed that the percentage of fluoride desorbed increased from 17 to 52% with the increase of the concentration of NaOH from 0.01 to 0.5 M.

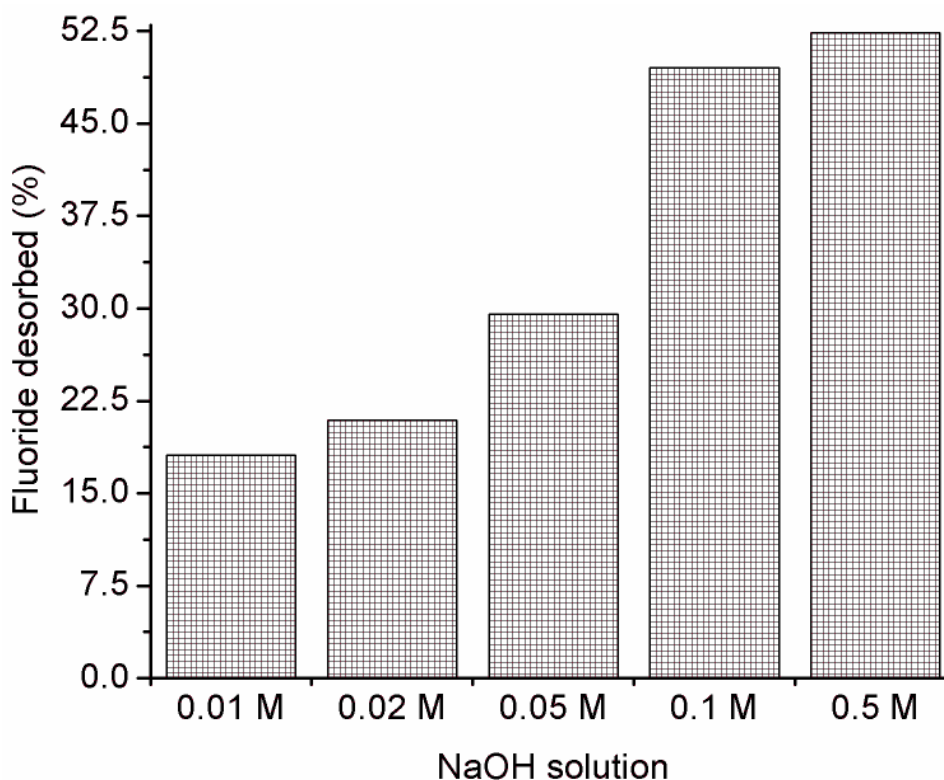


Fig. 12. Percentage of fluoride desorbed as a function of NaOH concentration (particle size: < 0.075 mm, adsorbent dose: 5.0 g/L, contact time: 120 min and agitation rate: 150 rpm).

5.12. Removal of fluoride from natural groundwater

The efficiency of locally available geomaterial as a defluoridating material is greatly affected by the anions that naturally co-exist with fluoride in the groundwater. To evaluate the fluoride adsorption efficiency of IO under fluoride contaminated groundwater was investigated under identical conditions of batch adsorption experiments. For this purpose a sample of fluoride contaminated groundwater was collected and its physico-chemical properties were analyzed according the Standard Methods for the Examination of Water and Wastewater (Clesceri *et al.*, 1997). The physico-chemical characteristics of the groundwater sample are given in Table 4. The sample of ground water contained 14.22 mg/L fluoride. Then, after batch adsorption, 14.22 mg/L

fluoride content of the water was reduced to 1.17 mg/L fluoride, which showed that ~ 89 % fluoride removal efficiency.

Table 4. Physico-chemical characteristics of groundwater

Composition	Value
PO ₄ ³⁻ (mg/L)	0.05
NO ₃ ⁻ (mg/L)	0.06
SO ₄ ²⁻ (mg/L)	310
CO ₃ ²⁻ (mg/L)	20
HCO ₃ ⁻ (mg/L)	0
Cl ⁻ (mg/L)	3.998
F ⁻ (mg/L)	14.22
DO (mg/L)	5.63
PH	7.76
EC (μS/cm)	1180
Turbidity (NTU)	3.55
Temperature (°C)	21.1

CHAPTER SIX

DISCUSSIONS

It was found that fluoride adsorption increased with the increase in contact time and attained equilibrium at 120 min with maximum adsorption efficiency and maximum adsorption capacity of ~ 86% and ~ 0.095 mg/g respectively. This is possibly due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high (Darchen *et al.*, 2010). Nevertheless, increase in contact time beyond 120 min did not increase adsorption efficiency which might be due to fewer adsorption sites and a lower fluoride concentration (Chen *et al.*, 2010). The obtained result is comparable with equilibrium time attained for fluoride removal studies on red mud at 120 min (Cengeloglu *et al.* 2009), rice husk at 120 min (Attar *et al.*, 2009), kanuma mud at 120 min (Chen *et al.*, 2010) and significant deviate with bleaching powder at 60 min (Devotta *et al.*, 2009), montmorillonite at 180 min (Tor, 2006), activated silica gel and activated rice husk ash at 100 min (Banerjee *et al.*, 2012) and waste residue from alum manufacturing process at 60 min (Chandravanshi *et al.*, 2007).

Likewise, the kinetic study showed that higher adsorption rate was observed within 120 min with fluoride adsorption efficiency of ~ 86 % at equilibrium time of 120 min. The kinetic data indicated that the fluoride adsorption onto IO obeys the pseudo-first-order kinetic with coefficient of determination (R^2) value of 0.822 at which calculated equilibrium adsorption capacity q_e (0.119 mg/g) is consistent with the experimental value (~ 0.095 mg/g). The Pseudo-first-order kinetic rate constant (k_1), calculated from the slope of the plot of $\log(q_e - q_t)$ versus t was found to be $0.024 \text{ g mg}^{-1} \text{ min}^{-1}$ for initial fluoride concentration of 10 mg/L. This rate is not quick compared with value reported for using bauxite ($2.80 \text{ g mg}^{-1} \text{ min}^{-1}$) for 10 mg/L fluoride (Anand and Sujana, 2011), but quicker compared with value reported for using natural stilbite zeolite modified with Fe (III) ($0.0085 \text{ g mg}^{-1} \text{ min}^{-1}$) for 5.0 mg/L fluoride (Cheng *et al.*, 2011), indicating that the diffusion of fluoride into the cavity of iron ore has a significant influence on adsorption process. The intraparticle diffusion rate constant (k_p) value obtained from the slope of plot of q_t versus square root of time was found to be $0.0103 \text{ mg g}^{-1} \text{ min}^{-1/2}$ for the initial fluoride

concentration of 10 mg/L. As shown in Figure 2, the linear portion of plot is not passing through the origin, which indicates the fluoride adsorption onto IO is a complex procedure. Both the surface adsorption as well as intraparticle diffusion contributes to the rate determining step.

In this study, the adsorption of fluoride was dependent on the pH of the solution. The percentage of fluoride adsorbed and fluoride adsorption capacity progressively increased from 62 to ~ 86% and 0.07 to ~ 0.095 mg/g as the pH of the solution increased from 3.0 to ~ 6.0 respectively. At pH ~6.0 maximum adsorption efficiency (~ 86%) and maximum adsorption capacity (~ 0.095 mg/g) were achieved. At pH ~ below 6.0, the decrease in fluoride adsorption efficiency and fluoride adsorption capacity were possibly due to the formation of hydrofluoric which would reduce the coulombic attraction between the oxides surface and the fluoride ions (Devotta *et al.*, 2009). At pH ~ above 6.0, both adsorption efficiency and adsorption capacity dramatically decreased which might be due to stronger competition for active sites between fluoride and hydroxyl ions (Dongre *et al.*, 2006). The results are in agreement with the previous studies on bauxite at pH 6.4 (Anand *et al.*, 2011), natural stilbite zeolite modified with Fe (III) at pH 6.94 (Cheng *et al.*, 2011), lanthanum impregnated chitosan flakes at pH 5.0 (Das *et al.*, 2011), Zirconium (IV)-ethylenediamine hybrid material at pH 2.0-7.0 (Dey *et al.*, 2012), aluminum oxide embedded with Fe₃O₄ nanoparticles at pH 6.5 (Cai *et al.*, 2010), red mud at pH 5.5 (Cengeloglu *et al.*, 2011), calcined Mg-Al-CO₃ layered double hydroxides at pH 6 (Duana *et al.*, 2006), montmorillonite at pH 6.0 (Tor, 2006), pumice at pH 3.0 (Fatehizadeh *et al.*, 2011) and granular ceramic at pH 5.0-8.0 (Chen *et al.*, 2010).

From the present study, it was noticed that the percentage of fluoride adsorbed and adsorption capacity progressively increased as agitation rate increased achieving the maximum value of ~ 86% and ~ 0.095 m/g at 150 rpm respectively. This might be due to at higher agitation rate better contact between the adsorbent and adsorbate is possible (Dongre and Tembhurkar, 2006). This result is in agreement with a study on the fluoride removal using five soil samples collected from the highland areas around Addis Ababa (Bardsen *et al.*, 1997).

It was also observed that percentage of fluoride adsorbed increased from 13 to ~ 86% with decrease in particle size of the adsorbent from > 4.75 to < 0.075 mm. With respect to the obtained result, smaller particle sized definitely improved the fluoride adsorption efficiency by

increasing availability of more specific surface areas on the adsorbent surface (Dongre *et al.*, 2006). This finding is in agreement with previous studies on fluoride removal using synthetic hydroxyapatites (Gao *et al.*, 2009), low grade coal (Borah and Dey, 2009) and *phyllanthus emblica* (Alagumuthu and Veeraputhiran, 2011) in which higher percentage of fluoride adsorption achieved at smaller particle size.

The results in this study show that fluoride adsorption efficiency increased from 37 to ~ 86% with an increase in adsorbent dose from 1.0 to 5.0 g/L which possibly due to the increase in availability of active sites resulting from an increase in dose of the adsorbent (Gao *et al.*, 2009). However, higher dose of the adsorbent (greater than 5.0 g/L) only increase the amount of sludge, without causing a significant change on fluoride adsorption efficiency of the adsorbent. This might be due to the strong inhibition of fluoride species mobility in the adsorbent due to the overlapping of active sites at higher dosage, thus leaving some binding sites unsaturated (Chandravanshi *et al.*, 2007). It was also required to bring down the fluoride level to the maximum permissible limit for fluoride in drinking water, i.e., to the WHO proposed upper limit, 1.5 mg/L fluoride in drinking water. The obtained result is in agreement with the research conducted by Darchen *et al.* (2010), who found that as dose of the new charcoal that contain calcium compounds increased from 0.4 to 4.0 g/L, the defluoridation yield increased from 27.5 to 93.3% and Devotta *et al.* (2008), who also found that as dose of the hydrated cement increased from 2.0 to 20 g/L, the percentage of fluoride removal increased from 47.46 to 92.37%. Similarly, Duana *et al.* (2006) found that the percentage of fluoride removal increased with increase in dose of the adsorbent and largest percentage removal of 90% was exhibited at 4.0 g/1.8 L of calcined Mg-Al-CO₃ layered double hydroxides. On the other hand, fluoride adsorption capacity decreased from 0.205 to ~ 0.095 mg/g with increase in dose of the adsorbent which was possibly due to the fixed initial fluoride concentration (Chandravanshi *et al.*, 2006). To maintain maximum adsorption capacity and high adsorption efficiency, the surface loading (i.e., the mass ratio of fluoride to adsorbent dose) should be lower than the optimum value (i.e., the surface loading for optimum fluoride removal, ~ 86%, obtained is ~ 0.095 mg/g or less).

The distribution coefficient (K_d) increased with an increase in adsorbent dose at constant pH ~ 6.0, indicating the heterogeneous nature of the surface of the adsorbent. If the surface is

homogeneous, the K_d values at a given pH should not change with adsorbent concentration (Cengeloglu *et al.*, 2002).

In addition, in this study it was observed that fluoride adsorption efficiency decreased from 91 to 66% with an increase in initial fluoride concentration from 2.0 to 29 mg/L. The decrease of the removal percentage could be attributed to the insufficient active sites of the adsorbents, which was caused by the occupation of the fluoride ions, as the more fluoride ions in solution the more active sites were occupied, and then the lower removal percentage achieved (Gao *et al.*, 2009). However, the adsorption capacity increased from 0.019 to 0.213 mg/g increasing initial fluoride concentration from 2.0 to 29 mg/L which might be due to the utilization of less accessible or energetically less active sites because of increased diffusivity and activity of fluoride upon the increased concentration. The adsorption sites present on the interior surface of a pore may not be as easily accessible because of the resistance to the pore diffusion (Chandravanshi *et al.*, 2007). The obtained result is in agreement with the previous study on fluoride removal using rice husk by Attar *et al.* (2009), who found that as initial fluoride concentration increased from 5.0 to 23 mg/L adsorption efficiency decreased from 75 to 40%. Similarly, Alagumuthu and Veeraputhiran (2011) found that as initial fluoride concentration increased from 2.0 to 10 mg/L adsorption efficiency decreased 87.95 to 47.22% using *Phyllanthus emblica* as adsorbent.

It was observed that both Freundlich and Langmuir isotherms well described the equilibrium isotherm data of fluoride adsorption onto IO. However, the Freundlich isotherm better described the equilibrium data with higher coefficient of determination and less chi-square values. The k_f value obtained in this study (1.465 mg/g) is greater than those of reported for using hydrated cement (0.07419 mg/g) (Devotta *et al.*, 2008), pumice (0.31 mg/g) (Fatehizadeh *et al.*, 2011) and lanthanum impregnated chitosan flakes (1.27 mg/g) (Das *et al.*, 2011). Indirectly this shows that better fluoride adsorption capacity (mg/g) using IO relative to those adsorbents listed above. The calculated value of R_L for an initial fluoride concentration of 10 mg/L is found to be 0.169, which indicates that this system is favorable for adsorption.

The coefficient of determination (R^2) value for the D-R isotherm was 0.977. The monolayer sorption capacity (q_s) and mean sorption energy (E) were found to be 21.16 mol/g and 10.206 kJ/mol for the adsorption of fluoride onto IO respectively. The E value ranges from 0 to 8.0

kJ/mol for physisorption and from 8.0 to 16 kJ/mol for chemisorption (Asai *et al.*, 2008). The value of E , which is 10 kJ/mol, suggesting that the mechanism for the adsorption of fluoride onto IO is dominantly chemisorption. Similar observation has been made previously by Chandravanshi *et al.* (2007) who found that the mechanism for the adsorption of fluoride on the waste residue from alum manufacturing process is a combination of chemical and physical in nature.

Fluoride contaminated drinking water containing other co-existing anions such as chloride, nitrate, sulfate, phosphate, carbonate and bicarbonate that can compete with fluoride during the adsorption process for the active sites on IO. Hence, in this study, it was observed that fluoride adsorption efficiency was significantly (p -value < 0.05) affected by phosphate, carbonate and bicarbonate within the concentration range tested (5.0-200mg/L). This might be due to competition of these anions with fluoride for active sites (Anand *et al.*, 2011). It was also observed from the batch study on the effect of pH that fluoride adsorption decreased in highly alkaline pH. However, the presence of sulphate, nitrate and chloride did not significantly (p -value > 0.05) affect fluoride adsorption efficiency within the concentration range tested (5.0-200 mg/L). The slight improvement in fluoride removal efficiency in the presence of nitrate and chloride could be due an increase in the ionic strength of the solution and/or a weakening of lateral repulsion between adsorbed fluoride ions, which in turn lead to an increase in fluoride adsorption (Asai *et al.*, 2008). Therefore, the effect of other anions concentration on fluoride removal by IO followed the order of Carbonate>Phosphate >Bicarbonate>Nitrate>Chloride >Sulfate. The obtained result is in agreement with work done on fluoride removal by Devotta *et al.* (2008) for hydrated cement, by Devotta *et al.* (2009) for bleaching powder and by Das *et al.* (2011) for lanthanum impregnated chitosan flakes indicating that the presence of carbonate and bicarbonate showed negative effect while chloride, nitrate, and sulfate did not affect the fluoride removal. Also similar observation have been reported by Alagumuthu *et al.* (2010) for *Cynodon dactylon*-based thermally activated carbon for fluoride removal indicating that chloride and nitrate ions did not significantly affect fluoride removal even at a concentration of 500 mg/L.

Regeneration of any exhausted adsorbent is a crucial factor in any sorption process for improving the process efficiency and tackling the adverse public health impacts due to excess concentration of fluoride in drinking water. Hence, in the present study, the percentage of fluoride desorbed

increased as the concentration of NaOH increased from 0.01 to 0.5 M showing that the adsorbed fluoride on adsorbent is not effectively desorbed which might be due to the strong bond formed between adsorbed fluoride and the adsorbent. Similar result was obtained by Biswas *et al.* (2010) on synthetic iron (III)-aluminum (III)-chromium (III) ternary mixed oxide loaded fluoride desorbed up to 90% with 0.5 M NaOH.

In the present study, it was observed that fluoride adsorption efficiency of ~ 89% and adsorption capacity of 0.178 mg/g were achieved using natural groundwater containing 14.22 mg/L fluoride at 120 min contact time using 15 g/L IO. The lower fluoride removal efficiency as compared to the removal efficiency achieved in aqueous solution might be due to the competing anions for binding sites on surface of the adsorbent (Anand and Sujana, 2010). However, the result obtained by Das *et al.* (2011) shows that 90% fluoride was removed from field water sample by using 1.0 g/50 mL of the lanthanum impregnated chitosan flakes as an adsorbent.

CHAPTER SEVEN

7. CONCLUSIONS AND RECOMMENDATIONS

7.1. Conclusions

The results of this research showed that good fluoride removal efficiency from aqueous solution using IO as an adsorbent and could be useful for tackling the adverse public health impacts. The loading capacity of IO for fluoride was ~ 0.095 mg/g within equilibrium of 120 min at laboratory room temperature (22 ± 2 °C). The optimum fluoride removal was observed at pH of ~ 6.0 indicating that IO could be a promising adsorbent for the defluoridation technology. Carbonate, bicarbonate and phosphate showed significant negative effect on fluoride adsorption efficiency. However, chloride, nitrate and sulfate did not significantly affect fluoride adsorption efficiency. Therefore, it can be noted that the effect sequence for anions adsorption on IO is in the order: $\text{CO}_3^{2-} > \text{PO}_4^{3-} > \text{HCO}_3^- > \text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$. The adsorption process was fitted well to both the Freundlich and Langmuir isotherm models indicating that the homogenous and heterogeneous distribution of active sites on the surface of IO. Kinetic study indicated that the adsorption process followed a pseudo-first-order kinetic model. In conclusion based on the study findings, IO has a potential to remove fluoride from water.

7.2. Recommendations

Further investigation is needed on the exact regeneration cycle, loss of metals during regeneration process, adsorption mechanism as well as stability of the adsorbent at experimental conditions. Also continuous flow experiment and field trial have to be further investigated to optimize and scale up to large scale.

REFERENCES

- Abbaspour, K., Amini, M., Johnson, C., Möller, K., Mueller, K. and Sarr, M. (2008) Statistical modeling of global geogenic fluoride contamination in groundwaters. *Environ Sci. Technol*, 42(10): 3662–3668.
- Alagumuthu, G. and Veeraputhiran, V. (2011). Treatment of high fluoride drinking water using bioadsorbent, *Research Journal of Chemical Sciences*, 1(4): 49-54.
- Alagumuthu, G., Veeraputhiran, V. and Venkataraman, R. (2010). Fluoride sorption using *Cynodondactylon*-based activated carbon, *Chemistry Research Centre*, Tamilnadu, India, 65(1): 23-35.
- Anand, S., Giles, D., Mishra, B., Mohapatra, M. and Singh, P. (2009). Review of fluoride removal from drinking water, *Journal of Environmental Management*, 91(1): 67-77.
- Anand, S., Pradhan, H. and Sujana, M. (2009). Studies on sorption of some geomaterials for fluoride removal from aqueous solutions, *Journal of Hazardous materials*, 161(1): 120-125.
- Anand, S., Soma, G., Sujana, M. and Vasumathi, N. (2009). Studies on fluoride adsorption capacities of amorphous Fe/Al mixed hydroxides from aqueous solutions, *Journal of Fluorine Chemistry*, 130(8): 749-754.
- Anand, S. and Sujana, M. (2011). Fluoride removal studies from contaminated groundwater by using bauxite, *Desalination*, 267(2-3): 122-127.
- Arijit, G., Biswas, K., Kaushik, G. and Uday, C. (2010). Fluoride removal efficiency from aqueous solution by synthetic iron(III)-aluminum (III)-chromium(III) ternary mixed oxide, *Desalination*, 255(1-3): 44-51.
- Asai, S., Eskandarpour, A., Ochieng, A. and Onyango, M. (2008). Removal of fluoride ions from aqueous solution at low pH using schwertmannite, *Journal of Hazardous Materials*, 152(2): 571-579.

- Attar, S. and Deshmukh, S. (2008). Equilibrium analysis for batch studies of adsorption of fluoride in water using Activated Alumina Rand D 6S1-X., *Int. J Chem. Sci.*, 6(4): 1903-1910.
- Attar, S., Deshmukh, S. and Wagmare, D. (2009). Investigation on sorption of fluoride in water using rice husk as an adsorbent, *An Interactional Quarterly Scientific Journal*, 8(2): 218.
- Ayoob, S. and Gupta, K. (2006). Fluoride in drinking water: a review on the status and stress effects, *Crit. Rev. Environ. Sci. Technol.* 36: 433–487.
- Bailey, K., Chilton, J., Dahi, E., Fawell, J., Fewtrell, L. and Magara, Y. (2006). WHO, Fluoride in drinking water, *International Water Association (IWA) Publishing*, UK, London: 1900222965.
- Bardsen, A., Bjorvatn, K., Kvalheim, A. and Tekle-Haimanot, R. (1997). Defluoridation of drinking water by the use of clay/ soils, 2nd International Workshop on Fluorosis Prevention and Defluoridation of Water, *Int. Soc. Fluoride Res.*, Bergen, Norway and Addis Ababa, Ethiopia.
- Banerjee, A., Baur, T., Bhaumik, R., Datta, K. and Mondal, k. (2012). A comparative study on the batch performance of fluoride adsorption by activated silica gel and activated rice husk ash, *International journal of environmental sciences*, 2(3): 1648-165.
- Benghalem, A., Ghaffour, N., Ramdani, A. and Taleb, S. (2010). Removal of excess fluoride ions from Saharan brackish water by adsorption on natural materials, *Desalination*, 250(1): 408-413.
- Bhend, S., Mosler, H. and Huber, A. (2007). Determinants of exclusive consumption of fluoride free water: a cross-sectional household study in rural Ethiopia, *Journal of public health*, 20(3): 269-278.
- Borah, L. and Dey, C. (2009). Removal of fluoride from low TDS water using low grade coal, *Indian journal of chemical technology*, 16(4): 362.

- Bulut, V., Duran, C., Gundogdu, A., Kemer, B., Ozdes, D. and Soylak, M. (2009). Removal of fluoride ions from aqueous solution by waste mud, *Journal of Hazardous Materials*, 168 (2-3): 889-890.
- Bushera, A., Fekadu, A., Mekonnen, Y. and Tekle-Haimanot, R. (1995). Fluoride levels in water and endemic fluorosis in Ethiopian Rift Valley, 1st International Workshop on Fluorosis Prevention and Defluoridation of Water, *Int. Soc. Fluoride Res.*, Addis Ababa University (Ethiopia).
- Cai, Y., Jiang, G., Shia, Y., Wanga, J., Wanga, T., Wub, F. and Zhaoa, X. (2010). Removal of fluoride from aqueous media by Aluminum oxide embedded with Fe₃O₄ magnetic nanoparticles, *Journal of Hazardous Materials*, 173(1-3): 102-109.
- Cengeloglu, Y., Ersoz, M. and Kir, E. (2002). Removal of fluoride from aqueous solution by using red Mud, *Separation and Purification Technology*, 28(1): 81-86.
- Chandravanshi, S., Nigussie, W. and Zewge, F. (2007). Removal of excess fluoride from water using waste residue from alum manufacturing process, *Journal of Hazardous Materials*, 147(3): 954-956.
- Chandravanshi, S., Shimelis, B. and Zewge, F. (2006). Removal of excess fluoride from water by aluminum hydroxide, *Bull. Chem. Soc. Ethiop.*, 20(1): 22-30.
- Chang, M. and Liu, J. (2007). Precipitation removal of fluoride from Semi-conductor wastewater, *Journal of Environmental Engineering*, 133(4): 1.
- Chen, N., Chen, R., Feng, C., Li, M., Sugiura, N. and Zhang, Z. (2010). Removal of fluoride from aqueous solution by adsorption onto Kanuma mud, *Water science and Technology*, 62(8): 863-864.
- Chen, N., Chen, R., Feng, C., Li, M., Zhang, Z. and Sugiura, N. (2010). Fluoride removal from water by granular ceramic adsorption, *Journal of Colloid and Interface Science*, 348(2): 579-584.

- Chen, N., Dirui, Y., Feng, C., Sugiura, N., Zhang, Z. and Zhu, Y. (2011). Preparation and characterization of porous granular ceramic containing dispersed aluminum and iron oxides as adsorbents for fluoride removal from aqueous solution, *Journal of Hazardous Materials*, 186(1): 863-868.
- Cheng, X., Dong, J., Fang, Q., Sun, Y. and Xu, J. (2011). Removal of fluoride from drinking water by natural stilbite zeolite modified with Fe (III), *Desalination*, 277(1-3): 121-127.
- Chidambaram, S., Ramanathan, A. and Vasudevan, S. (2003). Fluoride removal studies in water using natural materials, Newdelhi, India, 29(3): 339-344.
- Cirelli, A. and Miretzky, P. (2011). Fluoride removal from water by chitosan derivatives and composites: A review, *Journal of fluorine chemistry*, 123(4): 231-240.
- Clesceri, L., Eaton, A. and Greenberg, A. (1997). Standard methods for the examination of water and wastewater, 19th edition, Washington, DC.
- Darchen, A., Ngameni, E. and Tchomgui-Kamga, E. (2010). Evaluation of removal efficiency of fluoride from aqueous solution using new charcoals that contain calcium compounds, *Journal of colloids and Interface Science*, 346(2): 494-499.
- Das, S., Jagtap, S., Rayalu, S. and Yenkie, M. (2011). Synthesis and characterization of lanthanum impregnated chitosan flakes for fluoride removal in water, *Desalination*, 273(2-3): 267-275.
- Devotta, S., Dhawade, P., Jagtap, S., Kagne, S., Kamble, S. and Rayalu S. (2008). Hydrated cement: A promising adsorbent for the removal of fluoride from aqueous solution, *Journal of Hazardous Materials*, 154(1-3): 88-95.
- Devotta, S., Jagtap, S., Kagne, S., Rayalu, S. and Thakare, D. (2009). Bleaching powder: A versatile adsorbent for the removal of fluoride from aqueous solution, *Desalination*, 243(1-3): 22-31.

- Dey, R., Jhaa, U., Mishrab, S., Pateld, R., Patnaikc, T. and Swaina, S. (2012). Fluoride removal performance of a new hybrid sorbent of Zr(IV)-ethylenediamine, *Chemical Engineering Journal*, 184(1): 72-81.
- Dongre, Sh. and Tembhurkar, A. (2006). Studies on fluoride removal using adsorption process, *Journal of Environmental Science & Engineering*, 48(43): 151-156.
- Duana, X., Evans, G., He, J., Lv, L. and Wei, M. (2006). Factors influencing the removal of fluoride from aqueous solution by calcined Mg-Al-CO₃ layered double hydroxides, *Journal of Hazardous Materials*, 133(1-3): 119-128.
- Evelt, J. and Liu, C. (2003). Soil Properties- Testing, Measurment, and Evaluation, Banta Book Company, USA: 0-13-093005-9
- Fan, X., Parker, D. and Smith, M. (2003). Adsorption kinetics of fluoride on low cost materials, *Water Research*, 37(20): 4929-4937.
- Fatehizadeh, A., Malakootian, M., Moosazadeh, M. and Yousefi, N. (2011). Fluoride removal from aqueous solution by pumice: case study on Kuhbonan water, *African Journal of Environmental Science and Technology*, 5(4): 299-300.
- Federal Democratic Republic of Ethiopia, Ministry of Water Resources (2002). Ethiopian Guidelines Specification for Drinking Water Quality, Addis Ababa.
- Feenstra, L., Griffioen, J. and Vasak, L. (2007). Fluoride in groundwater: Overview and evaluation of removal methods, *International Groundwater Resources Assessment Centre*, Utrecht, Netherlands.
- Felgenhauer, S. and Perkovich, A. (2008). Fluoride & Boron, North Island Labs Newsletter: 3(1).
- Gao, N., Guan, X., Su, T., Tang, Y. and Wang, J. (2009). Fluoride adsorption onto activated alumina: Modeling the effects of pH and some competing ions, *Colloids and Surfaces A Physicochemical and Engineering Aspects*, 337(1-3): 33-38.

- Gao, S., Hu, F., Li, H., Sun, R., Wei, Z. and Zhao, H. (2009). Size-dependent defluoridation properties of synthetic hydroxyapatites, *Journal of Fluorine Chemistry*, 130(6):550-556.
- Ghorai, S. and Pant, K. (2004). Investigations on the column performance of fluoride adsorption by activated alumina in a fixed-bed, *Chemical Engineering Journal*, 98(1-2): 165.
- Green facts on fluoride (2002). Facts on health and Environment, <http://www.greenfacts.org>.
- Heibati, B., Mahvi, H., Mesdaghinia, A. and Yari, A. (2012). Fluoride Adsorption by Pumice from Aqueous Solutions, *E-Journal of Chemistry* <http://www.ejchem.net>, 9(4): 1843-1853.
- Hoshyaripour, G., Janpoor, F., Khatibikamal, V. and Torabian, A. (2010). Fluoride removal from industrial wastewater using electro coagulation and its adsorption kinetics, *Journal of Hazardous materials*, 179(1-2): 280.
- International Commission on Occupational Health Newsletter (1999). 7(2): 3-4.
- Jamode, A., Jamode, S. and Sapka, S. (2004). Defluoridation of water using inexpensive adsorbents, *J. Indian Inst. Sci.*, 84(5): 64-163.
- Johnson, A., Mutheki, P., Osterwalder, L., Rohner, R., Samuel, E. and Zewge, F. (2011). Introducing fluoride removal filters to Ethiopia, community and household water systems, Sandec News.
- Karthikeyan, J. and Vivek, M. (2011). Removal of fluoride from water using low-cost materials, Fifteenth International Water Technology Conference, 1(2): 13.
- Kaseva, M. (2006). Optimization of regenerated bone char for fluoride removal in drinking water: a case study in Tanzania, International Water Association (IWA) Publishing 2006, *Journal of water and health*, 4(1): 139-147.
- Kloos, H. and Tekle-Haimanot, R. (1999). Distribution of fluoride and fluorosis in Ethiopia and prospects to control, *Tropical Medicine and International Health*, 4(5): 355-364.

- Kumar, D. and Salim, J. (2011). Comparative Study of batch adsorption of fluoride using commercial and natural Adsorbent, *Research Journal of Chemical Sciences*, 1(7): 68-75.
- Maheshwari, C. and Meenakshi, S. (2006). Fluoride in drinking water and its removal, *Journal of Hazardous Materials*, 137(1): 456-463.
- Rao, N. (2003). Fluoride And Environment- Review, Proceedings of the Third International Conference on Environment and Health, Chennai, December, 15-17 December, Chennai: York University, Indian: 386-399.
- Sidelil, A., Steenbergen, V. and Tekle-Haimanot, R. (2011). High Fluoride, Modest Fluorosis: Investigation in drinking water supply in Halaba (SNNPR, Ethiopia), *Journal of Water Resource and Protection*, 3(2): 120-126.
- Tor, A. (2006). Removal of fluoride from an aqueous solution by using montmorillonite, *Desalination*, 201(1-3): 267-276.
- World Health Organization (1994). Fluorides and Oral health. Report of a WHO Expert Committee on Oral Health Status and Fluoride use, Geneva, World Health Organization (WHO Technical Report Series 846).
- World Health Organization (2011). Guidelines for drinking-water quality, Fourth edition: 9789241548151.

APPENDICES

Appendix 1- Determination of fluoride

Alizarin Red photometric Method

Reagents

Stock fluoride solution: dissolve 0.2210 g anhydrous sodium fluoride, NaF, in distilled water and dilute to 1000 mL, 1.00 mL=100 $\mu\text{g F}^-$.

Standard fluoride Solution: dissolve 100 mL stock fluoride solution to 1000 mL with distilled water, 1.00 mL = 10.0 $\mu\text{g F}^-$.

Alizarin red solution: dissolve 0.75 g alizarin reds in distilled water and dilute to 1000 mL. If insoluble material is present, the filter protects from direct sunlight.

Zirconyl acid reagent: dissolve 133 mg zirconyl chloride octahydrate, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, in about 25 mL distilled water. Add 350 mL conc. HCl and dilute to 500 mL with distilled water. Cool to temperature and after 1 h the reagent is ready to use.

Sodium arsenite solution: dissolve 5.0 g NaAsO_2 and dilute to 1000 mL with distilled water, (Caution: Toxic 1 - avoid ingestion)

Procedures

- 1) Prepare the following series of fluoride standards by measuring the indicated volume of standard fluoride solution in to separate 100 mL graduated cylinders.

Standard fluoride Solution, mL	Fluoride, $\mu\text{g}/100\text{mL}$
0	0
0.5	5
1.0	10
2.0	20
4.0	40

6.0	60
8.0	80
10.0	100

- 2) Add distilled water to the 100mL mark, and mix by inverting each cylinder four to six times.
- 3) Measuring the appropriate samples volume for the indicated fluoride range:

Standard volume, mL	Fluoride Range, mg/L
100	0.1-1.2
50	1.3-2.4
25	2.5-4.8

- 4) Place the clear and colorless samples in a 100 mL graduated cylinder. If necessary dilute to the 100 mL mark with distilled water and mix by inverting each cylinder four to six times.
- 5) Remove any residual chlorine from the sample by adding 0.05mL (1 drop) of sodium arsenite solution for each 0.1 mg of residual chlorine present in the samples and mix by inverting each cylinder four to six times.
- 6) Allow the standards and samples to come to the same temperature, because the color development depends critically on temperature. Adjust the temperature of samples and standards so that deviation among them is no more than 2.0 °C.
- 7) With a volumetric pipette, add 5.0 mL Alizarin red reagent & 5.0 mL Zinconyl acid reagent to each of the standards and samples. Complete the addition to the entire series of cylinders within 5 minutes.
- 8) Mix the contents by inverting four to six times.
- 9) Allow to stand for at least 1 h \pm 5 minutes.
- 10) Measure the standards and samples absorbance at 570 nm using distilled water to zero the spectrophotometer.
- 11) Construct a calibration curve using the standard series.

12) From the calibration curve determine the microgram fluoride in the sample making the necessary blank correction

$$Mg / L \text{ fluoride} = \frac{\mu g \text{ fluoride}}{mL \text{ of sample}}$$

Appendix 2- Determination of chloride

Argentometric Method.

Reagents

- a) Potassium chromate indicator solution: 50 g K_2CrO_4 was dissolved in distilled water and diluted to 1000 mL. $AgNO_3$ solution was added until a definite red precipitate is formed. Then stand 12 h. Filtered and diluted to 1.0 L with distilled water.
- b) Standard silver nitrate titrant, 0.0141 N: 2.395 g $AgNO_3$ was dissolved in distilled water and diluted to 1000 mL, and standardized against 0.0141N NaCl solution, 1.00 mL = 500 $\mu g Cl^-$, then stored in a brown bottle.
- c) Standard sodium chloride 0.0141 N: 824 g NaCl (dried at 140 °C) was dissolved in distilled water and diluted to 1000 mL, 1.00 mL=600 $\mu g Cl^-$.
- d) Special reagents for removal of interference:
 - i. Aluminum hydroxide suspension: 125 g of Aluminum potassium sulfate or aluminum ammonium sulfate was dissolved in 1000 mL distilled water. And Warmed to 60 °C and 55 mL conc. NH_4OH was added slowly with stirring. And stand about 1 hr and transferred to a large bottle, and precipitate was washed by successive additions, with thorough mixing and decanting with distilled water, until free from chloride.
 - ii. Phenolphthalein in indicator solution.
 - iii. Sodium hydroxide 1N.

Procedures

- 1) The appropriate sample volume for the indicated chloride range using the following table was measured and transferred to a 250 mL Erlenmeyer flask.

Sample Volume, mL	Alkalinity Range mg/L as CaCO ₃
100	1-50
50	51-100
25	101-200
10	201-500

- Color comparison blank was prepared by placing distilled water in a similar flask that having similar volume to that of the sample.
- 1.0 mL K₂CrO₄ indicator solution was added to the blank and the sample, and mixed.
- To the color comparison blank AgNO₃ was carefully added from a burette drop by drop titrant until the yellow color changes to a brownish tinge.
- Milliliter of silver nitrate titrant consumed was recorded.
- If the sample turns yellow, AgNO₃ titrate from a burette was gradually added. Then the flask was continuously shaken and adding the titrant until the sample turns the same continued.
- Silver nitrate titrant consumed was recorded.

Calculation:

$$mg / L \text{ of Chloride} = \frac{(A - B) \times N \times 35,450}{\text{mL of sample}}$$

Where, A= mL titration for sample

B= mL titration for blank and

N= normality of silver nitrate

Appendix 3- Determination of Nitrate

Phenoldisulphonic acid method

Reagents

- a) Standard silver sulfate solution: 4.40 g silver sulfate free from nitrate was dissolved in distilled water and diluted to 1000 mL, 1.00 mL = 1.00 mg /L.
- b) Ammonium hydroxide Conc: 12 N KOH solutions was prepared by dissolving 673 g KOH in distilled water and diluted to 1000 mL.
- c) EDTA reagent: 50 g disodium ethylenediamine tetracetate dehydrate was rubbed with 20 mL distilled water. The paste was weighed. 60 mL of concentrated ammonium hydroxide (NH₄OH) was added and mixed well to dissolve the paste.
- d) Stock nitrate solution: 9.7218 g anhydrous potassium nitrate was dissolved and diluted to 1000 mL with distilled water 1.0 mL = 100 µg N.
- e) Standard Nitrate solution: 50.0 mL stock nitrate solution was evaporated to dryness on water bath. The residue was dissolved by rubbing with 2.0 mL Phenoldisulphonic acid reagent, and diluted to 500 mL with distilled water, 1.00 mL = 10.0 µg N = 44.3 µg NO₃⁻

Procedures

- 1) The chloride content of the water sample was determined and 100 mL was treated with an equivalent amount of silver sulfate solution (1.0 mL for 1.0 mg Cl⁻) to precipitate the chlorides and the precipitated chloride was removed by centrifugation.
- 2) If the sample has color of more than 10 unit (on platinum cobalt scale), decolorized by adding 3.0 mL aluminum hydroxide suspension to 150 mL sample; stirred very thoroughly; allowed to stand for a few minutes; then filtered, the first portion of the filtrate was discarded.
- 3) The clarified filtrate was neutralized to ~ pH 7.0 in to an evaporating dish. Evaporated to dryness over a hot water bath.
- 4) 2.0 mL Phenoldisulphonic acid reagent was added and the residue was rubbed thoroughly to ensure dissolution of all solids

- 5) Diluted with 20 mL of distilled water and 6.0 to 7.0 mL NH₄OH was added with stirring until maximum yellow color is developed any resulting flocculent hydroxides were removed by filtration.
- 6) The filtrate of clear solution was transferred to a 50 mL volumetric flask. The dish, glass rod and filter paper was rinsed with distilled water, the rinsing was added to the flask until all the colored solution has been transferred.
- 7) Diluted to the 50 mL mark with distilled water, and mixed thoroughly
- 8) The absorbance was measured at a wavelength of 410 nm against a blank prepared from the same volumes of reagents as used for the samples.
- 9) Calibration curve was constructed in the range 0.0-2.0 mg/L NO₃-N by adding 0, 0.2, 0.5, 1.0, 3.0, 5.0 and 10 mL of standard nitrate solution to separate evaporating dishes and treating them in the same way as the sample. Milligram of NO₃-N in the sample was determined by reference to the calibration curve.

Calculation:

$$\text{mg/L NO}_3\text{-N} = \mu\text{g NO}_3\text{-N/mL sample}$$

$$\text{mg / L Nitrate} = \frac{\mu\text{g NO}_3 - \text{N} \times 4.427}{\text{mL sample}}$$

Appendix 4- Determination of Orthophosphate

Stannous Chloride Method

Reagents

- 1) Standard sodium hydroxide titrant, 0.1 N: 0.1 N was prepared by dissolving 4.0 g NaOH in CO₂ free water and diluting to 1000 mL. Then Standardized by titrating 40.00 mL KHC₈H₄O₄ solution using a 25 mL burette. Then after, titrated to the inflection point, which is close to pH 8.7. The normality of NaOH was calculated.
- 2) Phenolphthalein Indicator: 0.2 g phenolphthalein was dissolved into 200 mL deionized water and 200 mL ethanol.

- 3) Ammonium Molybdate Reagent: 25 g of $(\text{NH}_4)_6\text{MO}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was dissolved in 175 mL of distilled water. 280 mL conc. H_2SO_4 was added to 400 mL of distilled water. Then cooled, molybdate solution was added, and diluted to 1000 mL.
- 4) Stannous Chloride Reagent: 2.5 g of fresh stannous chloride was dissolved in 100 mL glycerol. Then heated on a hot plate (lowest setting) and stirred with a stirring rod to enhance dissolution.
- 5) Stock phosphate solution: 0.7165 g of anhydrous KH_2PO_4 was dissolved in distilled water and dilute to 1000 mL; 1.00ml = 500 g PO_4^{3-} - P.
- 6) Standard Phosphate Solution: 219.5 mg of potassium biphosphate (KH_2PO_4) was dissolved and diluted to 1000 mL; 1mL=50.0 g PO_4^{3-} - P.
- 7) Strong-acid solution: 300 mL conc. H_2SO_4 was dissolved to about 600 mL of distilled water. Then cooled, 4.0 mL conc. HNO_3 was added and diluted to 1000 mL.

Procedures

- 1) The following series of phosphate standards were prepared by measuring the indicated volume of standard phosphate solution in to separate 100 mL graduated cylinders.

Standard Phosphate Solution, mL	Phosphate (PO_4^{3-}), $\mu\text{g}/100\text{ mL}$
0	0
1	5
2	10
3	15
4	20
5	25
6	30

- 2) To the sample, 0.05 mL of phenolphthalein indicator solution was added. If the sample turns pink, strong acid solution was added until the color is discharged.
- 3) With a measuring pipette, 4.0 mL acid-molybdate solution was added to each of the standards and sample.
- 4) Then mixed thoroughly by inverting each flask four to six times

- 5) With medicine dropper 0.5 mL (10 drops) of stannous chloride solution was added to each of the standards and sample
- 6) And mixed by inverting each flask four to six times
- 7) After 10 minutes, but before 12 minutes, the color was measured photometrically at 690 nm using distilled water as blank.
- 8) calibration curve was constructed using the standards

Appendix 5- Determination of Sulphate

Gravimetric Method with Ignition Residual

Reagents

- A. Methyl red indicator solution: dissolve 0.1 g methyl red sodium salt in distilled water and dilute to 100 mL.
- B. Hydrochloric acid HCl
- C. Barium Chloride solution: dissolve 100 g BaCl_2 in 1000 mL distilled water. Filter through a membrane filter or hard-finish filter paper prior use 1.0 mL is capable of precipitating approximately 40 mg SO_4 .
- D. Silver nitrate-nitric acid reagent: dissolve 8.5 g AgNO_3 and 0.5 mL conc. HNO_3 in 500 mL distilled water.

Procedures

Adjust the volume of clarified sample to contain approximately 50 mg of sulphate in a 25 mL volume. Lower concentrations of sulphates may be tolerated if it is impractical to concentrate the sample to the optimum level, but in such cases limit the total volume to 15 mL.

1. Adjust the pH with conc. HCl to pH 4.5-5.0, using a pH meter or the orange color of methyl red indicator. Then, add additional 1.0 to 2.0 mL HCl.
2. Heat the solution to boiling and while stirring gently, add warm barium chlorides solution slowly until precipitation appears to be complete. Then add about 2.0 mL in excess.
3. Digest the precipitate at 80-90 °C for not less than 2 h.

4. Filter and wash the precipitate with small portion of warm distilled water until the washings are free of chloride as indicated by testing with $\text{AgNO}_3\text{HNO}_3$ reagent. Be sure that all of the precipitate is transferred to the paper.
5. Place the filter paper and precipitate in ignited and weighed crucible and dry in the oven.
6. Ignite at 800°C for 1 h, cool in desiccator and weigh.
7. Calculation:

$$\text{mg / L sulphate} = \frac{\text{mg BaSO}_4 \times 411.6}{\text{mL sample}}$$

Appendix 6- Alkalinity

Titration Method

Reagents and apparatus

- a) Standard sulfuric acid or hydrochloric acid, 0.1 N: dilute 2.8 mL conc. H_2SO_4 (specific gravity 1.834-1.836, 96-99% W/W H_2SO_4) or 8.31 mL conc. HCl (specific gravity 1.174-1.189, 36-37% W/W HCl) to 1000 mL. Standardized against the standard NaOH solution prepared for acidity determination.
- b) Standard sulfuric acid or hydrochloric acid, 0.02 N: dilute 200 mL 0.1 N Standard acid to 1000mL with distilled water.
- c) Mixed bromocresol green-methyl red indicator solution: dissolve 0.02 g methyl red and 0.1 g bromo cresol green in 1000mL 95% ethyl alcohol.
- d) Phenolphthalein solution, alcoholic pH 8.3 indicator: same as for acidity.
- e) Sodium thiosulphate, 0.1 N. Look on reagent preparation for acidity test.

Procedures

- 1) Measure the appropriate sample volume for the indicated alkalinity range and transfer to a 250 mL Erlenmeyer flask

Sample volume, mL	Alkalinity range, mg/L CaCO_3
100	0-250
50	241-500

25	501-1000
----	----------

- 2) If necessary, remove the residual chlorine by adding 1 drop of sodium thiosulphate to each flask and mix.
- 3) Add two drop of phenolphthalein indicator solution and mix. If the sample turns pink, carbonate or hydroxide is present; proceed with step. If the sample remains colorless the water contains bicarbonate or acid. Skip step 4 and 5 go on to step 6.
1. If the sample turns pink, gradually add sulfuric acid titrant from the burette, shaking the flask constantly until the pink just disappears.
2. Record the milliliters acid consumed
3. To the same sample add 2 drop of mixed Bromocresol green or methyl red indicator solution
4. Titrate with small volume of sulfuric acid titrant until the color changes from Greenish blue to light pink
5. Record the milliliters acid consumed. Calculate the total volume of acid used in the p-alkalinity titration (if step 4 is carried out) and the m-alkalinity titration (step 7).
6. Calculation :

$$\text{Alkalinity mg/L as CaCO}_3 = \frac{A \times N \times 50}{\text{mL sample}}$$

Where

A = mL standard acid used

N = Normality of standard acid

- 7) Methyl orange indicator solution: dissolve 500 mg methyl-orange powder in distilled water and dilute to 1000 mL.
- 8) Phenolphthalein indicator solution, Alcoholic, pH=8.3 indicator: dissolve 8.0 g phenolphthalein in 500 mL 95% ethylene or isopropyl alcohol and add 500 mL distilled water. If necessary add 0.02 N NaOH drop wise until faint pink color appears.
- 9) Sodium thiosulphate, 0.1 N: dissolve 25 g Na₂S₂O₃.5H₂O and dilute to 1000 mL with distilled water.

Appendix 7- Total Dissolve Solids Dried at 180 °C

- 1) Filter measured volume of well-mixed sample through glass-fiber-filter, wash with three successive 10 mL volume of distilled water, allowing complete drainage between washings, and continue suction for about 3 minutes after filtration is complete.
- 2) Transfer filtrate to a weighed evaporating dish and evaporate to dryness on a steam bath if filtrate volume exceeds dish capacity successive portions to the same dish after evaporating.
- 3) Dry for at least 1 h in an oven at 103-105 °C, cool in a desiccators to balance temperature and weigh.
- 4) Calculation:

$$mg / L \text{ TDS} = \frac{(A - B) \times 100}{\text{mL sample}}$$

Where, A= Weight of dried residue + dish, mg and

B= Weight of dish, mg

Note:

1. Prepare glass-fiber-filter disk as in total suspended solids determination
2. Use glass-fiber-filter disks without organic binder. What man grade 934A, Gelman type A/E; Millipore type AP40; equivalent. Available in diameters of 2.2 cm to 4.7 cm.

Appendix 8- Soil Particle Density Protocol

1. Place distilled water in squirt bottle.
2. Measure the mass of the empty flask without cap. Record mass on the Soil Particle Density Data Sheet.
3. Measure out 25 g of dried, sieved soil. Place soil in the flask using the funnel. Since it is important to have 25 g of soil inside the flask, be careful to transfer all the soil into the flask and not to spill any soil outside the flask (Note: if soil is spilled outside the flask, does this step over with another 25 g sample).

4. Record the length of time since the soil was dried in an oven, and how the soil has been stored (e.g. in plastic bag, air tight container, other)
5. Measure the mass of the flask containing the soil (without the stopper/cap). Record the mass on the Soil Particle Density Data Sheet.
6. Use the squirt bottle to wash any soil sticking to the neck of the flask down to the bottom of the flask. Add about 50 mL of distilled water to the soil in the flask.
7. Bring the soil/water mixture to a gentle boil by placing the flask on a hot plate or holding it over a Bunsen burner. Gently swirl the flask for 10 seconds once every minute to keep the soil/water mixture from foaming over. Boil for 10 minutes to remove air bubbles.
8. Remove the flask from the heat and allow the mixture to cool. Once the flask has cooled, cap the flask and let it sit for 24 hours.
9. After 24 hours, remove the stopper/cap and fill the flask with distilled water so that the bottom of the meniscus is at the 100 mL line.
10. Weigh the 100 mL-soil/water mixture in the flask (without the stopper/cap). Record the mass of the mixture on the Soil Particle Density Data Sheet.
11. Place the bulb of the thermometer in the flask for 2-3 minutes. When the temperature has stabilized, record the temperature of the mixture on the Soil Particle Density Data Sheet.

