

JIMMA UNIVERSITY
COLLEGE OF NATURAL SCIENCES
DEPARTMENT OF CHEMISTRY



**ADSORPTIVE REMOVAL OF FLUORIDE FROM WATER USING
POLYACRYLAMIDE MODIFIED DIATOMITE**

**A THESIS SUBMITTED TO DEPARTMENT OF CHEMISTRY, JIMMA
UNIVERSITY, FOR THE PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR MASTER DEGREE OF SCIENCE IN
CHEMISTRY (ANALYTICAL)**

JUNE 2019

JIMMA, ETHIOPIA

**ADSORPTIVE REMOVAL OF FLUORIDE FROM WATER USING
POLYACRYLAMIDE MODIFIED DIATOMITE**

BY

EMMANUEL NICOLA CORNELIO

ADVISORS:

FEKADU MALAK (PhD)

FUAD ABADIRO (MSc)

JUNE 2019

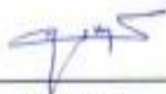
JIMMA, ETHIOPIA

SCHOOL OF GRADUATE STUDIES
JIMMA UNIVERSITY
COLLEGE OF NATURAL SCIENCES
MSc THESIS APPROVAL SHEET

We, the undersigned, member of the Board of Examiners of the final open defense by Emanuel Nicola have read and evaluated his/her thesis entitled "*Adsorptive removal of fluoride from water using polyacrylamide modified diatomite*" and examined the candidate. This is therefore to certify that the thesis has been accepted in partial fulfillment of the requirements for the degree Master of Science in **Chemistry (Analytical)**.

Dr. Fikadu Melak

Name of Advisor (1)



Signature

04- Jul-2019

Date

Mr. Fuad Abduro

Name of Advisor (2)



Signature

July 04/2019

Date

Dr. Shimeles Addisu

Name of the Internal Examiner



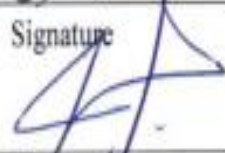
Signature

July-01-2019

Date

Dr. Alamavhu Paulos

Name of the External Examiner



Signature

July-01-2019

Date

Acknowledgement

In the beginning, I would like to give my great thanks to God, the almighty for his showers grace and blessing throughout my research. I would like to convey my ample thanks to advisor my Fekadu Melak (PhD) and my Co-advisor Fuad Abadiro (MSc) for their response, patience, and suitable approach throughout their advice to my work. I would take these lessons from my advisor in my life career. Also, I would like to express my appreciation to Jimma University and to the College of Natural Sciences and Department of Chemistry in particular for my admission as a postgraduate candidate. I would not forget to give abundant thanks to anyone that supports me spiritually, morally, financially, technically throughout the research of my master degree.

List of Abbreviations

EPA	Environmental Protection Agency
GRAS	General Recognized As Safe
HDPE	High-Density Polyethylene
PAMs	Polyacrylamides
SDWA	Safe Drinking Water Act
RTILs	The Room Temperature Ionic Liquids
WHO	World Health Organization

Table of Contents

Page

ABSTRACT.....	X
CHAPTER ONE.....	1
1.1 BACKGROUND.....	1
1.2 STATEMENT OF THE PROBLEM.....	3
1.3 OBJECTIVES.....	4
1.3.1 General objective.....	4
1.3.2 Specific objective.....	4
1.3.3 The significance of the study.....	4
1.3.4 Scope of the study.....	4
CHAPTER 2.....	5
2. LITERATURE REVIEW.....	5
2.1 NATURAL EXISTENCE OF FLUORIDE ION.....	5
2.2 TOXICITY OF FLUORIDE.....	6
FIGURE 1 SHOWING DENTAL AND SKELETAL FLUOROSIS.....	7
2.3 REMOVAL OF FLUORIDE.....	7
2.3.1 Removal of fluoride via modification of adsorbents.....	7
2.4 POLYACRYLAMIDES.....	8
2.4.1 Cationic polyacrylamides.....	9
2.5 DIATOMITE.....	9
2.6 ION EXCHANGE.....	10
2.6.1 Influence of pH value.....	10
2.6.2 Influence of other anions on fluoride precipitation.....	11
2.6.3 Adsorption isotherm.....	13
CHAPTER 3.....	16
3. MATERIAL AND METHODS.....	16
3.1 CHEMICAL AND MATERIALS.....	16
3.2 SOLUTION PREPARATION.....	16
3.3 PREPARATION OF PAM.....	16
3.4 MODIFIED DIATOMITE.....	17
3.4.1 CHARACTERIZATION OF ADSORBENTS.....	17
3.5 BATCH ADSORPTION.....	17
3.6 ISOTHERMAL.....	18
3.7 EFFECTS OF PARAMETERS.....	18
3.7.1 Effect of contact time.....	18
3.7.2 The Chemical Kinetics.....	18
3.7.3 Effect of pH.....	19
3.7.4 Concentration variation.....	19
3.7.5 Desorption study.....	19
CHAPTER 4.....	20

4.	RESULTS AND DISCUSSION	20
4.1	ADSORBENT CHARACTERIZATION	20
	FIGURE 4: FT-IR FOR PAM MODIFIED DIATOMITE BEFORE AND AFTER ADSORPTION.....	20
4.2	TIME EFFECTS.....	21
4.6	KINETIC STUDIES OF ADSORPTION	29
4.7	COMPARISON OF ADSORPTION CAPACITIES OF DIFFERENT ADSORBENTS FOR FLUORIDE REMOVAL ...	31
4.8	CONCLUSIONS.....	33
5.1	RECOMMENDATIONS.....	33
5	REFERENCES	34

List of Tables

TABLE 1. INFLUENCE OF FLUORIDE CONCENTRATION ON HUMAN HEALTH ^{1B, 6}	6
TABLE 2: SHOWING SOME STUDIES ON A NANO-FILTRATION PROCESS FOR REMOVAL OF FLUORIDE ⁶	13
TABLE 3: PARAMETERS FOR PLOTTING LANGMUIR AND FREUNDLICH ISOTHERMAL MODEL FOR UNMODIFIED DIATOMITE.....	25
TABLE 4: PARAMETERS FOR PLOTTING LANGMUIR AND FREUNDLICH ISOTHERMAL MODEL FOR PAM MODIFIED DIATOMITE.....	26
TABLE 5: LANGMUIR AND FREUNDLICH VALUE	29
TABLE 6: KINETIC PARAMETERS FOR ADSORPTION OF FLUORIDE IONS ONTO ADSORBENTS AT ROOM TEMPERATURE	30
TABLE 7: COMPARISON OF ADSORPTION CAPACITIES FOR DIFFERENT ADSORBENTS FOR FLUORIDE REMOVAL.....	32

List of Figures

FIGURE 1 SHOWING DENTAL AND SKELETAL FLUOROSIS	7
FIGURE 2 POLYACRYLAMIDE.....	8
FIGURE 3: ADSORPTION ISOTHERM	14
FIGURE 4: FT-IR FOR PAM MODIFIED DIATOMITE BEFORE AND AFTER ADSORPTION.....	20
FIGURE 5: EFFECT OF TIME ON DEFLUORIDATION USING MODIFIED DIATOMITE; INITIAL CONCENTRATION 100 MG/L, PH 5.6 SHAKING SPEED 150 RPM ADSORBENT DOSE 1G/L, AT ROOM TEMPERATURE.....	21
FIGURE 6: THE FLUORIDE REMOVAL CAPACITY BY MODIFIED DIATOMITE INITIAL CONCENTRATION 100 MG/L, SHAKING SPEED 150 RPM, AND ADSORBENT DOSE 1 G/L AT ROOM TEMPERATURE. 23	
FIGURE 7: EFFECT OF ADSORBENT DOSE ON FLUORIDE REMOVAL CAPACITY USING PAM MODIFIED DIATOMITE, INITIAL FLUORIDE CONCENTRATION 100 MG/L, PH OF 4, SHAKING SPEED 150 RPM FOR THE DURATION OF 60 MINUTES AT ROOM TEMPERATURE.	24
FIGURE 8: EFFECT OF CONCENTRATION VARIATION ON UNMODIFIED ADSORBENT FOR FLUORIDE REMOVAL CAPACITY, INITIAL FLUORIDE CONCENTRATION 100, 125, 150, 300, 500, AND 1000	

MG/L, PH OF 4, SHAKING SPEED 150 RPM FOR THE DURATION OF 60 MINUTES AT ROOM TEMPERATURE.	25
FIGURE 9: EFFECT OF CONCENTRATION VARIATION ON THE ADSORBENT CAPACITY FOR REMOVAL OF FLUORIDE USING PAM MODIFIED DIATOMITE AT PH 4.0 – 5.5, SHAKING SPEED 150 RPM, ADSORBENT DOSE 0.06G, AT ROOM TEMPERATURE.....	26
FIGURE 10: LANGMUIR ADSORPTION ISOTHERM FOR FLUORIDE ON PAM MODIFIED DIATOMITE, PH 4.0 – 5.5, ADSORBENT DOSE 0.02G, 60 MIN, AT ROOM TEMPERATURE. SLOPE OF THE CURVVE = $1/Q_M$, INTERCEPT OF CURVE = $1/K_L Q_M$, SD = 0.00984,.....	27
FIGURE 11: FREUNDLICH ADSORPTION ISOTHERM FOR FLUORIDE ON PAM MODIFIED DIATOMITE, PH 4.0 – 5.5, ADSORBENT DOSE 0.02G, 60 MIN, AT ROOM TEMPERATURE. SLOPE = $1/N$, INTERCEPT = $\log K_F$, SD = 0.724682,	27
FIGURE 12: LANGMUIR ADSORPTION ISOTHERM FOR FLUORIDE ON PAM MODIFIED DIATOMITE, PH 4.0 – 5.5, ADSORBENT DOSE 0.02G, 60 MIN, AT ROOM TEMPERATURE.	28
FIGURE 13: FREUNDLICH ADSORPTION ISOTHERM FOR FLUORIDE ON PAM MODIFIED DIATOMITE, PH 4.0 – 5.5, ADSORBENT DOSE 0.02G, 60 MIN, AT ROOM TEMPERATURE.	28
FIGURE: 14: PSEUDO –FIRST AND SECOND ORDER PLOT FOR F^- ADSORPTION ONTO PAM MODIFIED DIATOMITE, FLUORIDE INITIAL 100 MG/L; PH: 5.4; ADSORBENT DOSE 0.05G, SHAKING SPEED 150 RPM AT ROOM TEMPERATURE.....	30

Abstract

The problem of fluoride removal from drinking water is an urgent task for many regions of the world. Therefore, this study was initiated to develop polyacrylamide modified diatomite powder for the effective removal of fluoride. Batch scale adsorptive removal was performed as a function of solution pH, contact time, initial fluoride concentration, and agitation speed at room temperature. Results of the study revealed that 93.2 mg/g maximum adsorption capacity was obtained using polyacrylamide modified diatomite at optimal conditions of solution pH 4.0, contact time 1h, adsorbent dose of 1 g/L, when evaluated from initial fluoride concentration variation data. It was found that the Langmuir isotherm model better fitted to the experimental data, indicating monolayer adsorption of fluoride upon the adsorbent. Polyacrylamide modified diatomite was found to be a promising material for the removal of fluoride from fluoride bearing water.

Keywords: Diatomite powder, Polyacrylamide, Adsorption capacity, fluoride removal, water

Chapter one

1.1 Background

Fluorine is not found as a free element in nature due to its reactivity with other minerals, and the most common form of minerals of fluoride occurrence are as fluorspar, cryolite, fluorapatite, and sellaite (MgF_2)¹. Naturally, fluoride comes from water when minerals such as fluorite CaF_2 , cryolite Na_3AlF_6 and fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$ dissolved in water. A little amount of fluoride is vital for human organisms, and high concentration is toxic ².

Fluoride is existing in all water sources on the surface water with different level from minimally detectable to and high concentrations. About 60% of Pakistan, the African area, Thailand, China, and Sri Lanka are more exposed to fluoride in the water sources. Less than one-half per cent of U.S. residents which are depending on the community water system for drinking exposed to about 2 ppm, while one-tenth of 1% exceeds 4 ppm. But in Colorado reported the highest level of fluoride ranging from 2 to 13.7 ppm fluoride ³. Basically, elevated concentrations of fluoride are common when conditions mainly in calcium-poor aquifers.

Fluoride concentration is often low in the range of ppm, but fluoride absorbed rapidly and distributed by systematic circulation into intracellular and extracellular water of tissues; moreover about 90% of fluoride absorbed its burden the body since it will be taken in bones and teeth. Blood plasma reflects the concentration of the fluoride to entire soft tissues and organs ⁴. The regular water consumption can enable us to estimate the fluoride concentration per litre and led to the determination of the intake concentration of fluoride by mankind ². Fluoride intake via drinking water in small amounts (0.5–1.5 mg/L) is vital in preventing dental caries. Fluoride at higher concentrations ($\sim > 1.5$ mg/L), fluoride causes dental to skeletal fluorosis. It is estimated that about 200 million people, from 25 countries worldwide, including Ethiopia, suffer from fluorosis due to fluoride contamination ⁵. Consequently, guideline for fluoride consumption in water is set by the World Health Organization (WHO) as MCL of 1.5 mg/L, which gives rooms for international standards on drinking water suggested for human health; likewise in the United States, the Environmental Protection Agency (EPA) gives high indulgent to upgrade the drinking water standard with respect to WHO ²⁻³. The Safe Drinking Water Act (SDWA) designated the Environmental Protection Agency (EPA) to be an agency responsible safe level of drinking

water through the regulation setting for controlling the quality of drinking water. The SDWA defines any physical, chemical, biological or radiological substances in drinking water as “contaminations” regardless of its effect on human health ³.

There are many techniques used for fluoride determination in water including ion selective electrode, Colorimetric technique, Uv-Vis technique, Fluorescence Technique, Carbon Dots technique, and Back titration technique ⁶. In this finding the residue of fluoride was determined via back titration provides simple, low-cost, rapid and availability; the detection limit for the method is 5 mg/L ⁷.

Polyacrylamide PAM is a polymer with acrylamide monomers bonded connected by end to end configuration; and solid at room temperature. It's solid only being softened at 220~230 °C and its solution subjecting to significant degradation only at above 110 °C. Polyacrylamide is insoluble in organic solvent such as acetone, alcohols, benzene, toluene, xylene, gasoline, kerosene, diesel fuel, but soluble in water. Polyacrylamide can react with alkaline with partial hydrolysis of polyacrylamide. It will have imidization reaction in strongly acidic ($\text{pH} \leq 2.5$) which will reduce its solubility in water.

Polyacrylamide is easily soluble in cold water form transparent adhesive solution. Increasing the temperature does not affect its solubility and only affects its dissolution when the concentration is increased to a high viscosity.

Polyacrylamide has a moderate hygroscopic property, if not exposed to position of high temperatures, the powdered polyacrylamide can subject to long-term storage. The viscosity of polyacrylamide solution has a linear correlation with its molecular weight; in addition, the higher the temperature, the lower the viscosity ^{8,9}. The carboxyl group in a long-chain yields anionic polyacrylamide; the amino group yields cationic version. Because of the existence of amino group or carboxyl group in the long-chain of polyacrylamide, it is easy for flocculation when encountering aluminum ions ¹⁰. Polyacrylamide itself is non-toxic, but if it contains some monomers which is not polymerized (a double bond), it would be toxic to humans ¹¹.

1.2 Statement of the problem

Adsorption is promising techniques applied for reducing the fluoride concentration in the water, but it is not the only one available. For reasons being low cost, easier for application etc., numbers of the most effective adsorbents are increasing for the last decades. The coagulation and precipitation are mostly resulting wet sludge difficult in removal and could result on co-existing ions, which could led to the formation of sludge with a high content of toxic aluminum fluoride concentration residuals. Membrane filtration is sensitive for fouling, in addition to running capital is high. Ion-exchange more expensive removal technique and ion interfering is another difficulty facing it, and formation of toxic solid waste involved during the process. Occurrence of fluoride above the recommended level by the WHO in drinking water should have high attention in order to reduce health risk introduced by its consumption. Several fluoride removal techniques are available including adsorption, precipitation, coagulation, ion exchange, filtration, membrane, electrodialysis, reverse osmosis, and Donnan dialysis. And these methods have good capacity removal, but are very expensive and not ample in compare to adsorption technique. Method of water defluoridation is already present, but people still are looking for low-cost and available adsorbents with high removal capacity. If adsorbents are wisely selected adsorption could be the preferred option in developing countries to remove fluoride from water. Since polyacrylamide has no report of toxicity and it possess amide group which is easily can be converted to positive surface in acidic medium, it became a better modifier for removal of negative species from water including fluoride.

1.3 Objectives

1.3.1 General objective

To prepare polyacrylamide (PAM) modified diatomite for the adsorptive removal of fluoride from water

1.3.2 Specific objective

- To prepare modified diatomite using PAMs for adsorption
- To investigate the adsorption capacity of the adsorbent for fluoride removal
- To optimize adsorption influencing parameters including pH, contact time, and concentration variation.

1.3.3 The significance of the study

This study will enable effective removal of fluoride from water. In addition to that, the method will encourage others to scale up to support studies. The method will open a chance for other researchers in acquiring information on modifying the surface of adsorbents for adsorption via the formation of homogeneous mixture ways.

1.3.4 Scope of the study

The scope of the study was acquiring idea about modification of diatomite surface by polyacrylamide for removal of fluoride from water at room temperature where the optimal time, pH, and adsorbent dose had been figure out.

Chapter 2

2. Literature Review

2.1 Natural existence of fluoride ion

Volcanic rocks and Precambrian rocks are the most suppliers of fluoride in the nature ¹². Fluoride form about 0.08% of the earth's crust exists in form of minerals, geochemical deposits and it enters the food chains via drinking water, consumption and cereals. Fluoride concentration snake into water physically while degradation of fluoride present in the rocks ¹³. The large content of fluoride is found in alkali metals rocks rather than volcanic rocks. In water the concentration of fluoride range between 0.01 to 0.03 mg/L; but human exposure to fluoride differ from place to another geographically and frequent consumption of human to fluoride comes through water intake ².

Health effects related to excessive fluoride consumption had been reported on the population around Rift Valley areas¹⁴. There is definite proof that fluoride has a main consequence on demineralization and remineralization of dental hard tissue, and it's hinder because of acid production from cariogenic bacteria¹⁵. The core of successful therapy is by dissolving the fluoride. Fluoride source is their fluorapatite or precipitate calcium fluoride, which is not dissolving rapidly such are other studies reported. The calcium fluoride coated at neutral pH by pellicle proteins and the main reason for this phosphate, at lower pH value dissolution of calcium fluoride, occurs and the coating disappears ¹⁵⁻¹⁶.

Fluoride can be both essential and toxic depend and its presence on food content ¹³. According to WHO, it is not advisable to consume more than 1.5 mg/L from drinking water.

Several fluoride removal techniques are available including adsorption, precipitation, coagulation, ion exchange, filtration, membrane, electrodialysis, reverse osmosis, and Donnan dialysis ¹⁷. At these times there is no adsorbent specified for removal of certain toxic minerals from water, and most of the researchers are looking for an optimal combination of different adsorbents in every situation. Enhancing the surface of adsorbents, it increases its adsorption properties to show batter adsorption capacity ¹⁸.

All agriculture by-product adsorbent required modification before using it as an adsorbent. They must undergo pretreatment in order to prevent high chemical oxygen demand, and biological

demand, organic soluble materials release by plant biomass and increase adsorption efficiency. Both of socio-culture acceptance and religion restrictions are account as one of the major factors which hindered the application of other adsorbents especially bone char.

2.2 Toxicity of fluoride

Fluoride toxicity exists either naturally or anthropogenic ¹⁹. The Rift Valley area in Ethiopia is facing the serious medical problem concerning dental and fluorosis; which arise due to the consumption of drinking water obtained from drilling wells ^{14, 20}. Naturally, the groundwater reported a high concentration of fluoride; especially when it used for household consumptions; since most of the area depends on the direct intake of the groundwater which possesses a high content of fluoride, their exposure to such amount of fluoride for a period may be led to health problem ²¹.

Fluoride can be considered as an essential mineral in the range of low consumption. However, when fluoride > 1.5 mg/L in drinking water could cause dental as well as skeletal fluorosis, some report are indicated below in table 1 and figure. The United States of America, Africa and Asia recorded high fluoride concentration on groundwater more than 30 mg/L. A large number of people in the worldwide consumes more the 1.0 mg/L fluoride from drinking water; but most of them are living in the tropical countries, whereby they are facing the worse problem as a result of hot climate ^{1b}. Fluorosis is predominant in more than 20 developed and developing nations; and When fluoride consumed in surplus, it results to some diseases such as osteoporosis, arthritis, brittle bones, cancer, infertility in women, male sterility, brain damage, Alzheimer syndrome, and thyroid disorder ²².

Table 1: Influence of fluoride concentration on human health ^{1b, 13}

Fluoride concentration in mg/L	Health effects
< 0.5	Dental Carries
[F ⁻] 0.5 – 1.5	Optimum dental health
1.5 – 4	Dental fluorosis
4.0 – 10	Dental and skeletal fluorosis
> 10	Crippling fluorosis



Dental fluorosis

Skeletal fluorosis

Figure 1 showing dental and skeletal fluorosis

2.3 Removal of fluoride

A fluoride removal methods generally have two main subdivision, and they are membrane and adsorption^{17b}. There are several types of adsorption techniques used for removal of fluoride from water, such as precipitation – coagulation, membrane-based process, ion-exchange techniques, and in addition to adsorption; which is more appreciated techniques due to its economic status and simplicity action. Also it renders high efficiency, easy accessibility, environmental benignity, and since adsorbents characterized by the recycled principle²³.

2.3.1 Removal of fluoride via modification of adsorbents

Different solid materials are used as adsorbent for removal of fluoride by either ion-exchange or surface reaction; meanwhile the adsorbent can be assessed through its adsorption capacity in dilute solutions; a pH and time are necessary for fluoride removal, stability, regeneration capacity, possible interferences with other ions, and especially, cost and accessibility²³. Normally the adsorption of fluoride on the solid surface pass through some stages, and it can be summarized as flows

- Transport of a fluoride ion on a solid surface from bulky solution medium through an ambient film, and is called external mass transfer
- Fluoride ion adsorb on the surface

- Exchange of particles between adsorbent with respect to the chemistry of the solid surface and transfer of adsorbed fluoride ion are called internal surface for adsorbent materials (intraparticle diffusion)

And these are the theories observed during the adsorption process^{1b}. The prices of organic polymers used in carbon modified adsorbents can be considered one of the most insignificant remarks for modification of the adsorbents. but still there are my input such as lower dosages, filter backwash saving, reduced filter loading, increase turbidity removal and reduced sludge might counterbalance the whole price in favor of organic polymers in the long run²⁴.

2.4 Polyacrylamides

Polymers are widely applied for water purification for more than four decades. It gives lower coagulant, less volume of sludge and it raises uptake of ions from water figure 2 below showing train of polyacrylamide with both tail and loops. Also, polymers improved the reduction of aluminum when applied for water treatments; furthermore, it enhances the ability of low settling flocs at low-temperature coagulation or treatment of soft colored water²⁵.

Treatments of raw water always accompany with some physiochemical process, such coagulation and flocculation of suspended solids containing sludge. The cationic polymers are mainly and mostly contained ammonium group with a formal positive charge regardless of pH, and they are called strong electrolytes polymers¹¹. While if the electrolyte acquires cationic properties in acidic media it said to be weak electrolytes polymers.

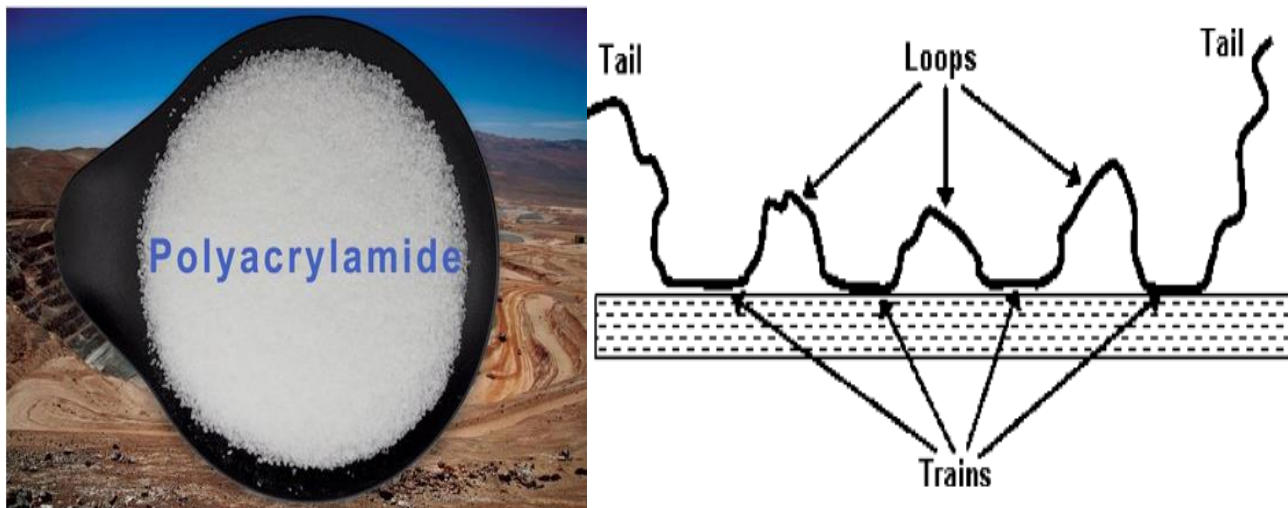


Figure 2 polyacrylamide

A cationic polyacrylamide ranging from 10 – 80 % roughly is hydrolyzed from ester group, where it results in loss of cationic charge with respect to pH, it the particle surface has an affinity to polymer segments. And the affinity between the surface site needed and polymer segment are recommended not to be great, according to different points of attachment ²⁶.

2.4.1 Cationic polyacrylamides

The cationic polyacrylamide (CPAM) possesses higher molecular weight, and higher stability property; with a wide range of application in water treatment, especially in flocculation. Furthermore, it increases adsorption capacity and bridge for suspending species ²⁷.

A copolymers of acrylamide and the cationic ester acryloyloxyethyltrimethyl-ammonium chloride, are broadly used in the water industry^{10, 26}. The methacrylate analogue is also commercially available ²⁶.

2.5 Diatomite

Diatomite is a biochemical sedimentary rock ²⁸. It deposits from an accumulation in oceans or fresh waters of amorphous silica (opal, $\text{SiO}_2 \cdot n\text{H}_2\text{O}$) cell wal of dead diatoms that are microscopic single-cell aquatic plant (algae). And diatomite rock is a loose, earthy or loosely cemented porous and lightweight rock of sedimentary origin, mainly formed by fragments of armor (skeletons) of diatom algae ²⁹. Diatomite Composed mainly of the skeletons of a very common type of marine plankton - diatoms. Diatoms are tiny plants that float near the ocean surface ³⁰. Because of porosity and high surface area, diatomite is highly sorbent and is very useful in the clean-up of leaks in the automotive, industrial, janitorial and waste remediation industries ³¹.

The method for modification of the diatomite surface features are many, and on depend on its applications. HCl is used for modification of diatomite surface in order to be used for as filter support. The surface will be unsafe when OH group removed from diatomite surface area. Sodium hydroxide NaOH and manganese oxide MnO_2 are used to improve adsorption capacity of diatomite surface for removal of heavy metals such as Pb^{2+} , Cu^{2+} and Cd^{2+} from wastewater. Diatomite powder possesses high sorption capacity because it has large surface area and low bulking value. Typical diatomite composed of 80% to 90% SiO_2 , alumia 2% to 4%, and

hematite 0.5% to 2%, with an analytical ignition loss of 4% to 6%. The high quality diatomite contained about 94% silica because it is inert to the most chemical reaction and is resistant to very high temperature ³².

2.6 Ion exchange

Commonly the adsorption of the organic substance onto carbonaceous substance accompany with heat-releasing; and isotherms of fluoride ion onto bone char BC measured at various temperature 283, 297, and 313 K respectively and the results show that as the temperature increases the adsorption amount increase. And this tells us that the adsorption of fluoride ion on the bone char is an endothermic reaction whereby the phosphate ions on the bone char exchange with fluoride ion ³³.

In the water treatment ion exchange resins used to the most popular procedures for softening the water source by exchanging sodium ions for hardness ions in addition to calcium and magnesium. Through the ion-exchange the common presentations in the water will target, such as fluoride and other ions; calcium ion can be used as selective ions for removal of fluoride. Calcium act as strong acid cation – exchange resin and it form the insoluble compound with fluoride ion in water with the window ranged from low to high concentrations. The remarkable challenge in ion-exchange is the formation of a highly concentrated waste by-product stream that presence as a removal problem ³⁴.

2.6.1 Influence of pH value

The pH, anions, concentrations, and intrinsic binding affinities have both direct and indirect influence on fluoride reaction with the positive ions ²². In equation I pH-value plots as a function of titrant addition, obtained in acid-base titrations, it appears that it can be adequate to solve the pH as

$$\text{Function of volume } H_{\text{corr}} = \text{pH} + ef \left| \frac{\text{pH} - \text{pH}_{\text{cal}}}{\text{pH}_{\text{cal}}} \right| \dots\dots\dots I$$

Where *ef* is an empirical parameter and has a relation with the inverse of cell efficiency, is empirical calibration pH and pH_{corr} is the corrected pH from potential systematic error to achieve 100% cell efficiency at 25°C ³⁵.

The fluoride before the formation of precipitation range from 4.5 to 10.1, and it can be adjusted with a buffer solution; the fluoride precipitation is slow and incomplete at low pH and it formed large crystal at about pH = 11. Co-precipitation can exist in null alcohol and excess of an acid or alkali before precipitation pH = 6.5 and after precipitation pH = 4.0³⁶.

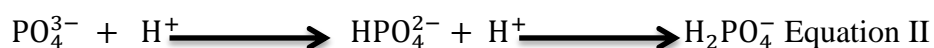
A very low quantity of CaF₂ precipitation is forming in the short-term application of neutral fluoride, and huge quantity exists when enamel change by initial caries lesions; which means the formation of CaF₂ increases as pH of the fluoride solution decrease, calcium fluoride form merely at 300 ppm fluoride concentration when the pH is adjusted to neutral. Spontaneously formation of calcium fluoride precipitation can occur on pH 5 where fluoride concentration is about 100 ppm³⁷.

At the pH 4.6, 7.0, and 9.2 fluoride exhibit isotherms adsorption on the BC at 293 K; the quantity of fluoride adsorbed increased with a decrease on pH value, which means phosphate ion can easily yield to fluoride ion at lower pH value because phosphate ion is more dissociated in al lower pH solution. In sequence, the solubility of calcium fluoride and calcium phosphates are 2.5 mg/100 mL and 1.7 mg/100 mL which means that calcium fluoride is more stable than calcium phosphate, and decreasing on pH of solution enhance the solubility of calcium phosphate³³.

2.6.2 Influence of other anions on fluoride precipitation

The Anions such as sulfate, nitrate, carbonate, chloride, bicarbonate, and phosphate effects adsorption of fluoride ion because they contain the same negative such as fluoride ions, and they exhibit amendment of their electrostatic charge at the solid surface²².

The existence of other anions such as Cl⁻, SO₄²⁻, and NO₃⁻ has no influence on fluoride removal but carbonate bicarbonate HCO₃⁻ effects because it increases the pH where it decreases the precipitation^{22, 38}. The fluoride removal shows that it increases with decreasing the pH in governor for PO₄³⁻ influence. The influence of decrease on pH for the phosphate while fluoride removal by illustrating by this equation



The phosphate concentration in the aqueous solution decrease by the above equations.

In the equation II the result of the decrease in pH below 11; whereby almost all PO_4^{3-} will be converted or if there any traces its impact will not be significant on fluoride removal. At the pH < 1.6 CaF_2 precipitation is not affected by the presence of phosphate ion³⁹. The charge ratio radius $\frac{Z}{r}$ is the reliability of the co-existing anions the affects fluoride selectivity at the removal process PO_4^{3-} (3/2.38) > SO_4^{2-} (2/2.30) > F^- (1/1.33) > HCO_3^- (1/1.56) > NO_3^- (1/1.79) > Cl^- (1/1.81) the phosphate is much greater than other anions; this enables phosphate to influence in reaction of calcium with fluoride ions, but bicarbonate is almost similar to fluoride which makes bicarbonate more fit to form a compound with calcium ion. The large radius of sulphate makes it have no significant effect on fluoride removal^{38b, 40}.

At the high pH, OH^- displaced F^- from the solid and fluoride ions changed to complexes; fluoride concentration increased in with decreased of pH⁴¹.

A nano-filtration process for removal of fluoride from water has some limitation, which is reported below on table 2, such pH, co-existing ions interferes, cost, ...etc. which many hinder removal of fluoride from water.

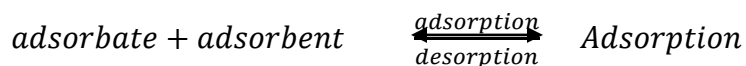
Table 2: showing Some Studies on a nano-filtration process for removal of fluoride ¹³

Outcome	Remark
<ul style="list-style-type: none"> ▪ Nano hydroxide chitin composite possesses higher adsorption capacity of 2840 mg/F/kg than nanohydroxyapatite which showed removal capacity of 296 mg/F/kg 	<ul style="list-style-type: none"> ▪ Presence of co-anion effects fluoride removal
<ul style="list-style-type: none"> ▪ Coated granules with a coating amount of 27.5% had a fluoride adsorption capacity of 2.22/g at pH 7 	<ul style="list-style-type: none"> ▪ It works at neutral pH, no need for pH adjustment
<ul style="list-style-type: none"> ▪ Fluoride removal effected by phosphate ion. Fluoride removal happened through isomorphic substitution of fluoride in brucite 	<ul style="list-style-type: none"> ▪ Cost effective recovery of material Improvement in the fluoride adsorption capacity
<ul style="list-style-type: none"> ▪ The adsorbent has a high affinity for fluoride and adsorption is rapid 	<ul style="list-style-type: none"> ▪ Adsorption depends upon temperature pH, adsorbent dose
<ul style="list-style-type: none"> ▪ Effective in fluoride removal, removal capacity is 68 mg/g 	<ul style="list-style-type: none"> ▪ Due to super magnetic and magnetization property removal of adsorbent after treatment is easy
<ul style="list-style-type: none"> ▪ The tightness of membrane plays a major role in removal efficiency 	<ul style="list-style-type: none"> ▪ The effect of pH on the removal rate is low. The promising technique, based on results technical device can be designed

2.6.3 Adsorption isotherm

The method of Adsorption is regularly studied through graphs know as adsorption isotherm. It is the graph between the concentration of adsorbate adsorbed on the surface of adsorbent and pressure at constant temperature ⁴². There are many types of adsorption isotherms such as Freundlich, and Langmuir.

In the process of adsorption, adsorbate gets adsorbed on adsorbent.



Representation of Le-Chatelier principle, the direction of equilibrium would shift in that direction where the stress can be relieved.

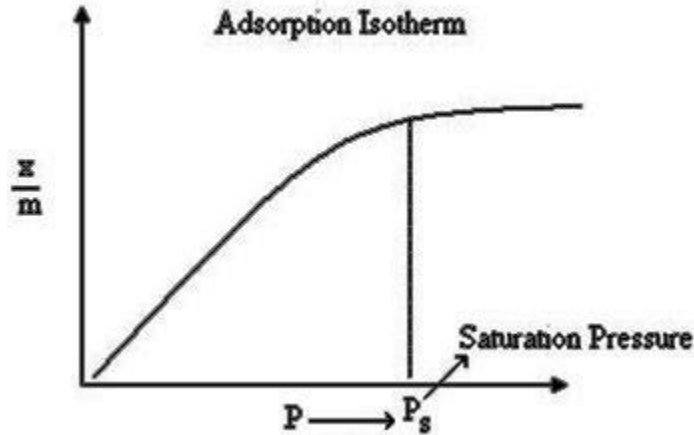


Figure 3: Adsorption Langmuir Isotherm model.

From the graph, we can predict that after saturation pressure P_s , adsorption does not occur anymore. This can be explained by the fact that there are limited numbers of vacancies on the surface of the adsorbent⁴³.

In 1909, the equation III Freundlich gave an empirical expression demonstrating the isothermal variation of adsorption of an amount of gas adsorbed by unit mass of solid adsorbent with pressure

$$\frac{x}{m} = kP^n \dots\dots\dots \text{III}$$

Where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p and k , n are constants whose values depend upon adsorbent and gas at particular temperature⁴⁴.

In 1916 Langmuir proposed another Adsorption Isotherm known as Langmuir Adsorption isotherm. This isotherm was based on different assumptions one of which is that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules⁴⁵.

A linear form of the Langmuir equation can be expressed as in equation IV

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b_L} \dots\dots\dots \text{IV}$$

Where q_e is the quantity of fluoride ion adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), and q_m and b_L are Langmuir constants related to the maximum adsorption capacity (mg/g) and energy of adsorption (L/mg)

The adsorption obeys the Langmuir equation since $\frac{C_e}{q_e}$ Vs C_e become straight-line and $\frac{1}{q_e}$ is the slope where $\frac{1}{q_m b_L}$ is the intercept.

The Langmuir equation V provides information about number of active sites at homogenous distributed surface of adsorbents. The interaction between the adsorbed molecules when the affinity is similar for mono molecular layer

$$R_L = \frac{1}{1 + b_L C_e} \dots\dots\dots V$$

Where R_L value is type of adsorption either unfavorable if ($R_L > 1$), linear if ($R_L = 1$), favorable when ($0 < R_L < 1$), and irreversible when ($R_L = 0$).

The Freundlich isotherm model equation VI relates to adsorption on heterogeneous surfaces where interactions between the adsorbed molecules occur, and is not limited to the formation of a monolayer. The model assumes that when the adsorbate concentration increased with increased of adsorbate on adsorbent surface.

$$\log \log q_e = \log K_f + \frac{1}{n} \log C_e \dots\dots\dots VI$$

Where q_e is the quantity adsorbed at equilibrium (mg/g), K_f is the Freundlich constant, $1/n$ is the heterogeneity factor which is associated to the capacity and intensity of the adsorption, and C_e is the equilibrium concentration (mg/L). The values of K_f and $1/n$ can be obtained from the slope and intercept of the plot of $\log q_e$ against $\log C_e$. Value of $1/n$ ranges from 0 to 1 and the closer this value to zero, the more heterogeneous the adsorbent surface.

Chapter 3

3. Material and Methods

3.1 Chemical and materials

Reagents NaF (98%, Finkem, Italy) analytical grade for standard and working fluoride solution preparation, NaCl, acrylamide and hydrogen peroxide, Mohar's Salt (BDH chemicals Ltd, England) and, NaOH (Labmerk chemicals, India) and HCl (Riedel-De Haen, Germany), and methanol alcohol were used throughout the experiment. A stock solution of fluoride (0.05 M) was prepared, and the stability of the stock solution was maintained by keeping it in the refrigerator during the experiment. Distilled water was used for the preparation of all solution and dilution series. And 0.05 stock solution disodium EDTA salt (Chemika, Mumbai) and 1M stock of Calcium chloride dihydrate was prepared. Working standard solutions of lower concentration for the whole was prepared by dilution method. Whatman filter paper (grade 1 and size 8.5 cm); from Whatman International Ltd was applied for filtration.

3.2 Solution preparation

A stock solution of 1000 mg/L F^- was prepared by dissolving 2.21 g of NaF (98%, Finkem, Italy) in distilled water and stored with Polyethylene plastic bottles. Calibration standards were prepared from 1000 mg/L F^- stock solution. 14.7 g of $CaCl_2 \cdot 2H_2O$ was used for the preparation of 1M in 100 mL as well as 9.3 g of disodium EDTA salt (Chemika, Mumbai) was dissolved in 500 mL to prepare 0.05 M. Working solutions of F^- was prepared by diluting the stock solution prior to each experiment. The applicability of the adsorbent was investigated for various parameters under batch adsorption. Fluoride residue at each sample was determined using back titration and EDTA was used as a suitable titrant for the excess calcium added.

3.3 Preparation of PAM

Polymerization of acrylamide with a redox system in aqueous solution; about 10 g of acrylamide was dissolved in a beaker containing 50 mL of distilled water. And the beaker start getting cold when acrylamide dissolved; then 0.08 g of Mohr's salt (Ferrous ammonium sulfate $FeSO_4 \cdot 7H_2O$) is added to the beaker containing acrylamide solution and the mixture was stirred till it is homogenized. During the stirring, about 5 mL of H_2O_2 is added to the solution and stirred for 2

minutes; H₂O₂ oxidized the ferrous ions to Ferric (Fe³⁺) ions which cause the solution to have a rusty color. The reaction produces OH· radical which initiate the polymerization reaction of acrylamide. After 30 minutes about five drops of concentrated hydrochloric acid were added. Finally adequate amount of methanol was added to precipitate the polyacrylamide ⁴⁶.

3.4 modified diatomite

About 40 g of powder diatomaceous earth acid washed filter aid (Northampton, U.K) was mixed gently with 6 g of freshly prepared polyacrylamide for 30 minutes till homogeneous paste was obtained. And the diatomaceous and polyacrylamide percentage was 87:13. The paste was dried in air at room temperature for a duration of 3 days till all water particle escaped from the mixture paste⁴⁷. A dried pate has been powdered and used as an adsorbent for fluoride removal.

3.4.1 Characterization of adsorbents

The prepared PAM modified diatomite adsorbent has been characterized by Fourier Transforms Infrared (FTIR) spectroscopy. Both used and unused adsorbents has dried; then packed in a very thin film and introduced to the FTIR analyzer.

3.5 Batch adsorption

A batch adsorption experiments were carried out in 50 cm³ high-density polyethylene (HDPE) bottles. The sorbent was added to the solution in the bottles, and proper shaking was achieved for the mixture at 150 rpm and 25 °C for duration 60 minutes. The aqueous phase was separated from the sorbent through filtration. The filtered sample was analyzed for fluoride through back titration. Triplicate batch adsorption was performed at room temperature. The fluoride uptake capacity was calculated as in equation VII:

$$q = \frac{(C_o - C_e)}{m} \times V \dots\dots\dots VII$$

Where q is adsorbed fluoride (mg/g), while C_o and C_e are the initial and equilibrium concentration of fluoride in the solution (mg/L), respectively, V is the solution volume (L), and m is the adsorbent dosage (g).

The removal per cent (%) of fluoride was be calculated using the following equation VIII:

$$\text{Removal (\%)} = \frac{(C_o - C_e)}{C_o} \times 100 \dots\dots\dots\text{VIII}$$

Doses of 1 g of sorbent were used for investigating the effects of sorbent dosage and the fluoride initial concentration ⁴⁸.

3.6 Isothermal

Adsorption data described broadly by using Langmuir and Freundlich adsorption isothermal models. The equation IX shows Langmuir model depends on the assumption of maximum uptake on a saturated monolayer of analyte molecules presences on the adsorbent surface; adsorbate molecules were not migrated since the energy of adsorption remains fixed. The uptake always occurs at constant and restricted sites; where lateral interaction and steric hindrances involved in adsorbed molecules; the Langmuir isothermal model equation as follows ^{48b}.

$$q_e = \frac{(C_o - C_{eq})V}{w} \dots\dots\dots\text{IX}$$

Where q_e is the amount of fluoride removed from solution (mg/g); C_o is an initial concentration of fluoride in solution before mixing with adsorbent (mg/L); C_{eq} is the equilibrium concentration of fluoride left in the solution after the experiment (mg/L); V is the solution volume (L), and W is weight of the adsorbent in (g).

3.7 Effects of parameters

3.7.1 Effect of contact time

The effect of contact time on adsorption was studied to find the equilibrium time. Removal capacities are increased with increasing contact time until the state of equilibrium is reached. A pre-trial experiment has been performed until 24 h before the actual experiment to estimate the equilibrium time.

3.7.2 The Chemical Kinetics

Pseudo –First order Kinetic Model

The uptake of amount of solute per mass of sorbent (mg/g) at any time, and equilibrium respectively, and k_1 is the rate constant for the first-order sorption in 1/min. The intercept obtained from a plot of $(q_e - q_t)$ versus t gives $\log(q_e)$ as slope and intercept $k_1/2.303$ as in

equation X⁴⁵. Later from the capacity (q_e) of adsorbent at equilibrium and first-order sorption rate constant (k_1) was evaluated from the slope and intercept.

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \dots \dots \dots X$$

Pseudo-Second order Kinetic model

Since the adsorption follow Langmuir equation, the has represented by equation XI

$$\frac{t}{q_t} = \frac{1}{k_t q_e^2} + \left(\frac{1}{q_e}\right)t \dots \dots \dots XI$$

The initial rate was figure out by the equation XII

$$h = k_2 q_t^2$$

Where k_2 is the rate constant, and q_t is the fluoride adsorbed at any time t ⁴⁹.

3.7.3 Effect of pH

The initial pH (pH 2.5 – 10.2) of the solution was optimized as to which pH provide efficient removal of contaminants. The favorite solutions for all runs were prepared by dilution of stock solutions at medium pH of 5.5. The solution pH was adjusted by adding buffers. Prior to each viral experiment⁵⁰.

3.7.4 Concentration variation

About seven serial diluted solutions were prepared for the batch concentration variation study. The concentrations of fluoride started from 50 mg/L to 1000 mg/L where selected to saturate saturated⁵¹ and with fixing of some other parameters. Back titration was used for measuring fluoride concentration in the residuals after each sample has been filtered.

3.7.5 Desorption study

The adsorbent capacity was determined through adsorption dose. The amount of adsorbent was varied from smaller weight to the highest weight per liter of solution. Both treated and untreated diatomite were examined for fluoride removal under various parameters. As the mass transfer increase, adsorbent dose decrease with respect to ion mobility and it reflect the capacity of the surface area toward binding with the fluoride ion⁵². The adsorbent dose was studied in the ranges of: 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2, 3.0, 5.0, 6.0, and 10 g/L.

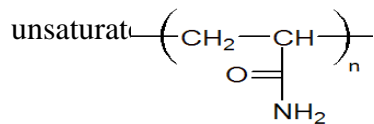
Chapter 4

4. Results and Discussion

In this finding, a polymerization, batch adsorption removal, and back titration experiment were carried out, and various parameters such contact time, pH, dose, and concentration variation of fluoride has been investigated in room temperature. The outcome data were applied for interpretation of adsorbent characterization, adsorbent capacity, and evaluation of the kinetics of fluoride on to modified diatomite.

4.1 Adsorbent Characterization

The FT-IR characterization was carried out before and after adsorption in the range 400–4000 cm^{-1} for PAM modified diatomite for detection of functional groups and to predict the mechanism of adsorption responsible (Fig. 4). A typical FTIR spectrum of PAM modified diatomite has the following characteristic absorption bands: strong bands at 3409 and 3436 cm^{-1} are associated with the –OH of water or N-H stretching vibrations (stretch, medium)⁵³, before and after adsorption, showing intensity and frequency shifts upon adsorption of fluoride. The modes observed at 3196 and 2942 cm^{-1} could be asymmetric and symmetric CH_2 stretching vibrations. The lowering of the frequencies in polyacrylamide could be mainly due to the unsaturat



The peak at 1085 cm^{-1} might be attributed to the asymmetric stretching models of Si–O–Si

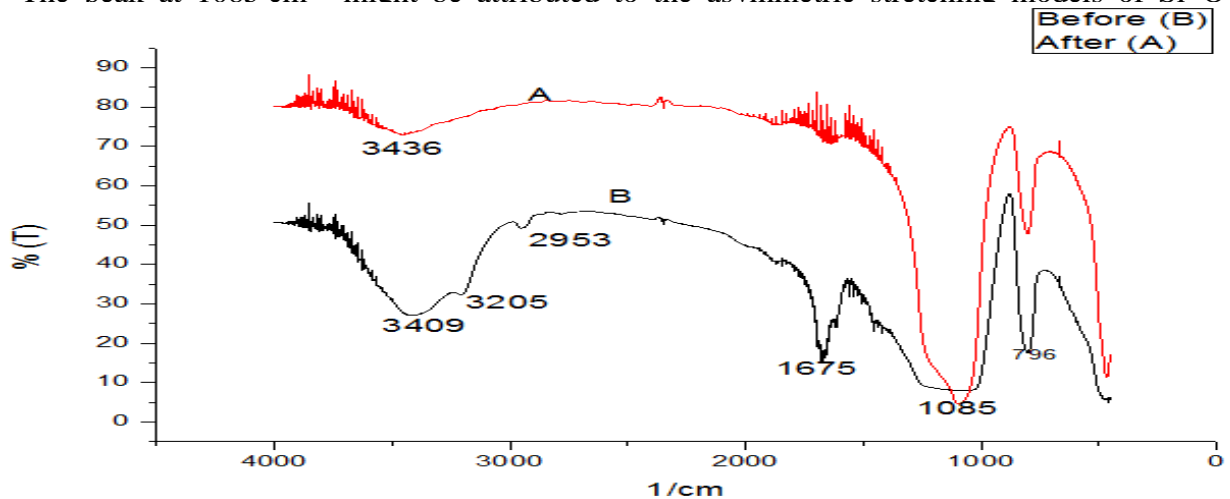


Figure 4: FT-IR for PAM modified diatomite before and after adsorption

4.2 Time effects

The fluoride adsorption capacity on PAM modified diatomite was performed to define the equilibrium time. The results revealed that natural diatomite provided a 12.4 mg/g which is negligible amount of removal capacities as compared to PAM modified diatomite with all other parameters being remained the same. Thus, the experiment was focused on the use of PAM modified diatomite for fluoride removal. The experimental result showed that a rapid rate of fluoride uptake during the first 40 min. contact time, followed by equilibration, where adsorptions desorption remains constant. The rapid fluoride ion removal from aqueous solution during the initial stage of contact time is presumably due to the fact that initially, all adsorbent sites were vacant⁵⁴.

Although it seems equilibrium attains after 40 minutes (Fig. 5), 60 minutes have been used as working time to avoid uncertainties in equilibration. And the removal capacity was found to be 92 mg/g at the pH of 5.6, 1 g/L adsorbent dose and 100 mg/L as initial concentration at room temperature.

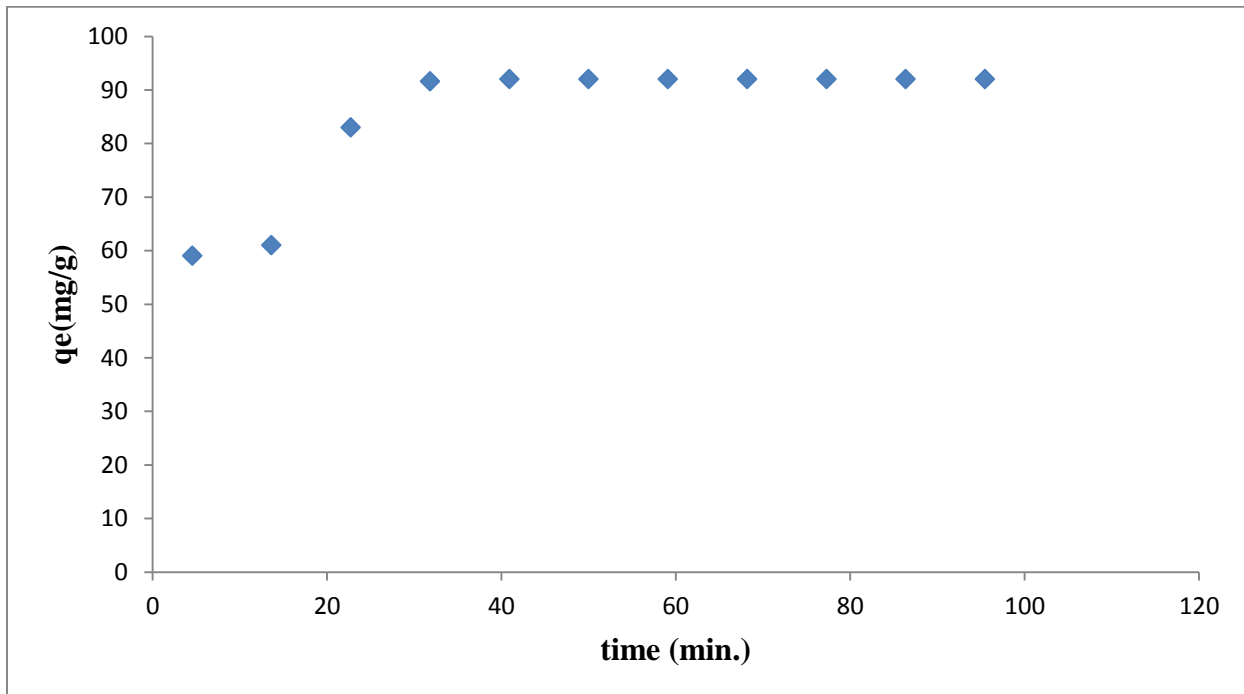
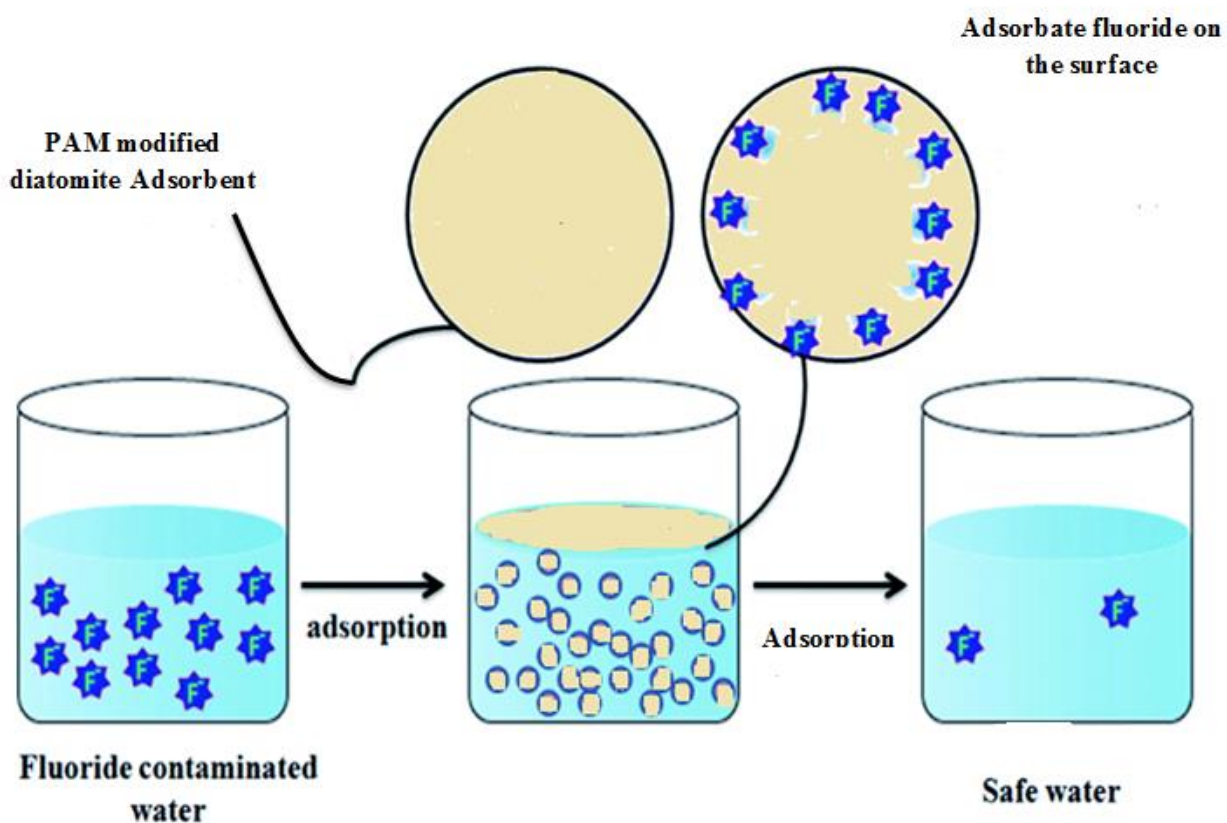


Figure 5: Effect of time on removal of fluoride using modified diatomite; initial concentration 100 mg/L, pH 5.6 shaking speed 150 rpm adsorbent dose 1g/L, at room temperature

4.3 Effects of pH

The influence of solution pH for fluoride removal was presented in Fig. 6. It was shown that the removal of fluoride using PAM modified diatomite was effective over an initial pH range of 4-5.5. Similar mechanisms were proposed in aluminum based adsorbents for fluoride removal in the previous literature⁵⁵.

Because the adsorbent surface is positive at lower pH values fluoride removal is highly expected at this range in acidic medium.



The percentage of fluoride removal was high at pH range from 4 to 5.5, but showed a decrement at neutral pH. And starts shooting up to the higher pHs. A decrease in fluoride removal below pH 4 is might be due to the washing of modifier from the diatomite, while decrease above 5.5 is due to the presence of hydroxide ion OH^- which has the high potentiality to compete with fluoride for the positive surface of the adsorbent. Since hydroxide OH^- and fluoride similar size, charge, and size; which make them to have the same mobility¹³.

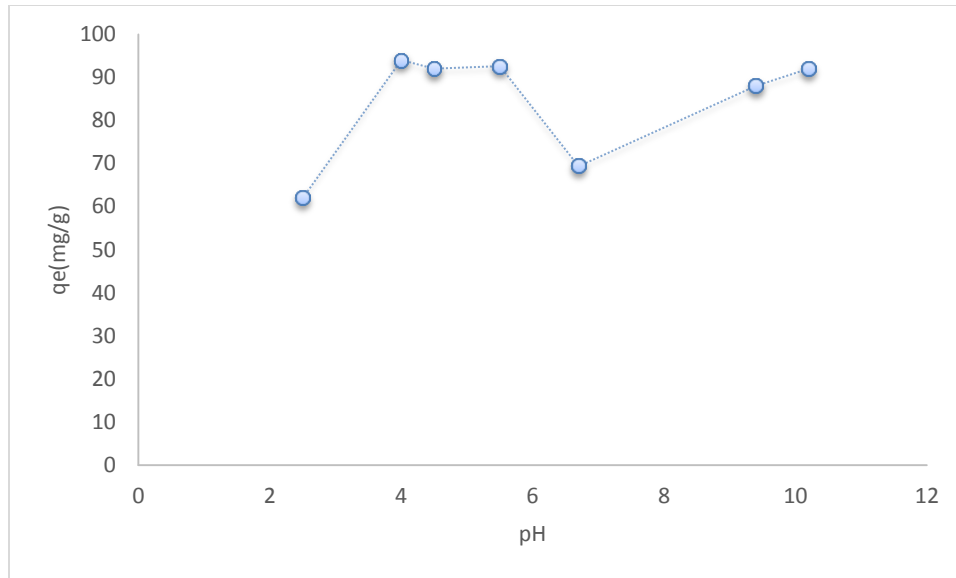


Figure 6: the fluoride removal capacity by modified diatomite initial concentration 100 mg/L, shaking speed 150 rpm, and adsorbent dose 1 g/L at room temperature.

4.4 Adsorbent dose

The adsorbent dose varied from initial dose of 0.02, 0.04, 0.06, 0.08, 0.15, 0.20, 0.25, 0.30, and 0.50 g respectively in each 50 mL where the duration is 60 minutes, and the fluoride initial concentration was 100 mg/L, room temperature condition. It is found that the removal capacity is inversely proportional to dose variations as shown in Fig. 7. The maximum capacity on this dose variation was found to be 93.2 mg/g which was obtained at a smaller dose of 0.02 g/L due to greater saturation of the adsorbent.

The result shows the smallest capacity removal is about 0.45 mg/g when the dose of 10 g/L, which indicate the availability of more adsorbents sites are likely for fluoride removal. A 2 g/L considered being the optimum dose for fluoride removal using modified diatomite with polyacrylamide. The dose of modified diatomite indicated a decrease in capacity with an increase in adsorbent dose; since the fluoride initial concentration is constant for all doses, it would be distributed over the range of added adsorbent doses, hence fluoride per gram adsorbed would decrease⁵⁶.

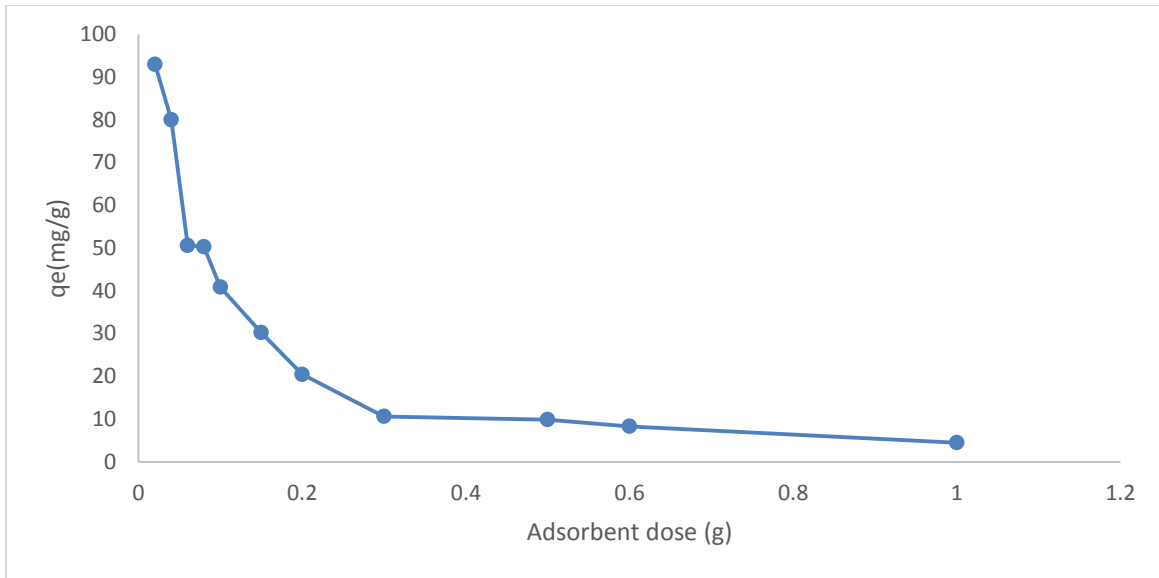


Figure 7: Effect of adsorbent dose on fluoride removal capacity using PAM modified diatomite, initial fluoride concentration 100 mg/L, pH of 4, shaking speed 150 rpm for the duration of 60 minutes at room temperature.

4.5 Concentration variation

Fluoride removal at batch basis was studied at optimal conditions (pH of 4, shaking speed 150 rpm, a dose of 1 g/L, and duration of 60 minutes) at room temperature under initial concentration variation. The adsorption capacities vs initial concentration was used to express the data for unmodified and modified adsorbents (Fig. 8 & 9). The maximum capacity of PAM modified diatomite as explained from the Langmuir model was 93.00 mg/g. The Langmuir and Freundlich model parameters were described in Table 3. Langmuir model described the relationship between the adsorbate and the fixed homogeneous active surfaces undergoing adsorption, being all active sites with equal size and shape⁵⁷. Whereas the Freundlich isotherm model assumes a heterogeneous surface with the possibility of adsorbate-adsorbate interaction. The non-linear forms of both models are given by the following equations:

Langmuir: $q_e = q_{max} * b * C_e / (1 + b * C_e)$

Freundlich: $q_e = K * C_e^{1/n}$

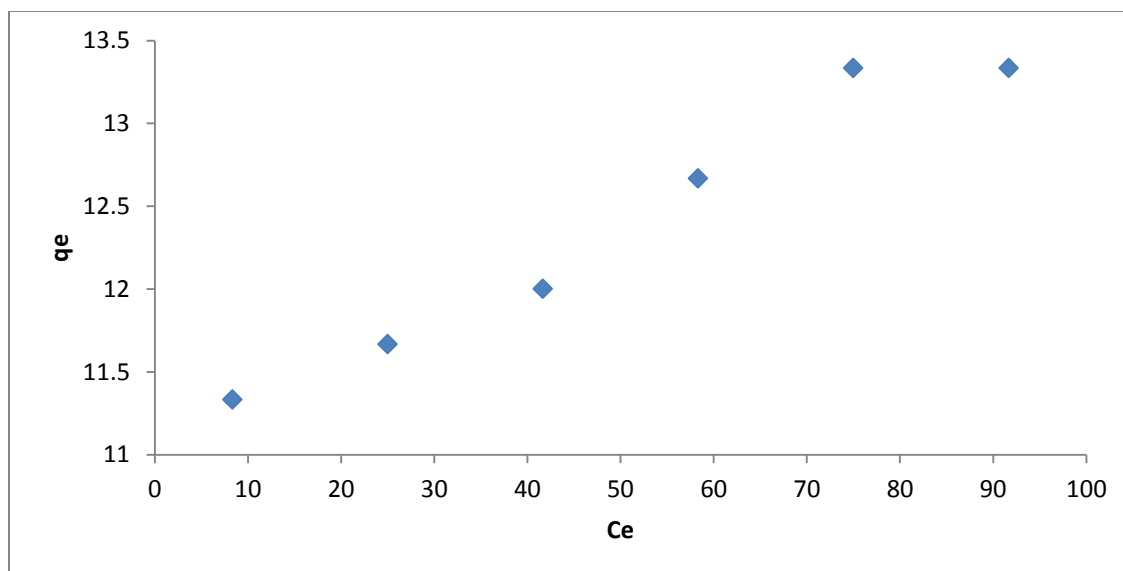


Figure 8: Effect of concentration variation on unmodified adsorbent for fluoride removal capacity, initial fluoride concentration 100, 125, 150, 300, 500, and 1000 mg/L, pH of 4, shaking speed 150 rpm for the duration of 60 minutes at room temperature. [triplicate]

In figure 8, the maximum capacity of unmodified adsorbent was about 13.3 mg/L showed at higher fluoride concentration.

Table 3: parameters for plotting Langmuir and Freundlich isothermal model for unmodified diatomite

Conc mg/L	C_e	q_e	$1/C_e$	$1/q_e$	$\text{Log } C_e$	$\text{Log } q_e$
100	66	11.33	0.015	0.088	1.820	1.054
125	90	11.67	0.011	0.086	1.954	1.067
150	115	12.00	0.009	0.083	2.061	1.079
300	264	12.67	0.004	0.079	2.422	1.103
500	460	13.33	0.002	0.075	2.663	1.125
1000	960	13.33	0.001	0.075	2.982	1.125

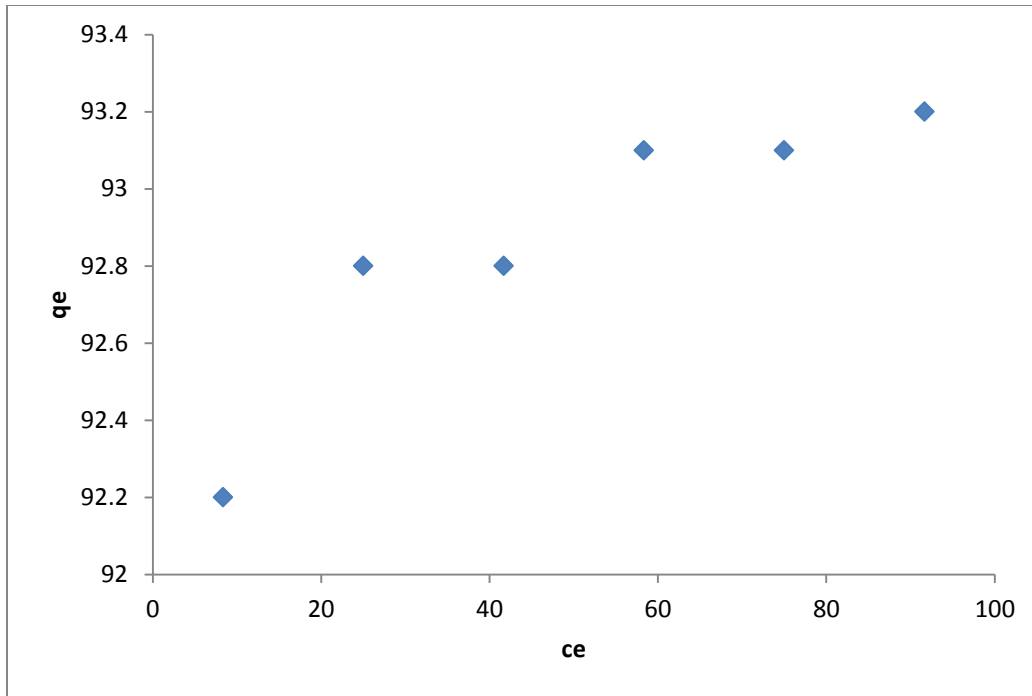


Figure 9: effect of concentration variation on the adsorbent capacity for removal of fluoride using PAM modified diatomite at pH 4.0 – 5.5, shaking speed 150 rpm, adsorbent dose 0.06g, at room temperature

In figure 9, the capacity of PAM modified adsorbent is about 93.2, which is much higher than the capacity of unmodified reported in figure 8. This indicated the efficiency of PAM modified diatomite toward fluoride removal.

Table 4: parameters for plotting Langmuir and Freundlich isothermal model for PAM modified diatomite

Conc mg/L	C_e	q_e	$1/C_e$	$1/q_e$	Log C_e	Log q_e
100	6.9	93.1	0.145	0.011	0.839	1.969
125	32.2	92.8	0.031	0.011	1.508	1.968
150	56.8	93.2	0.018	0.011	1.754	1.969
300	206.9	93.1	0.005	0.011	2.316	1.969
500	407.2	92.8	0.002	0.011	2.610	1.968
1000	907.8	92.2	0.001	0.011	2.958	1.965

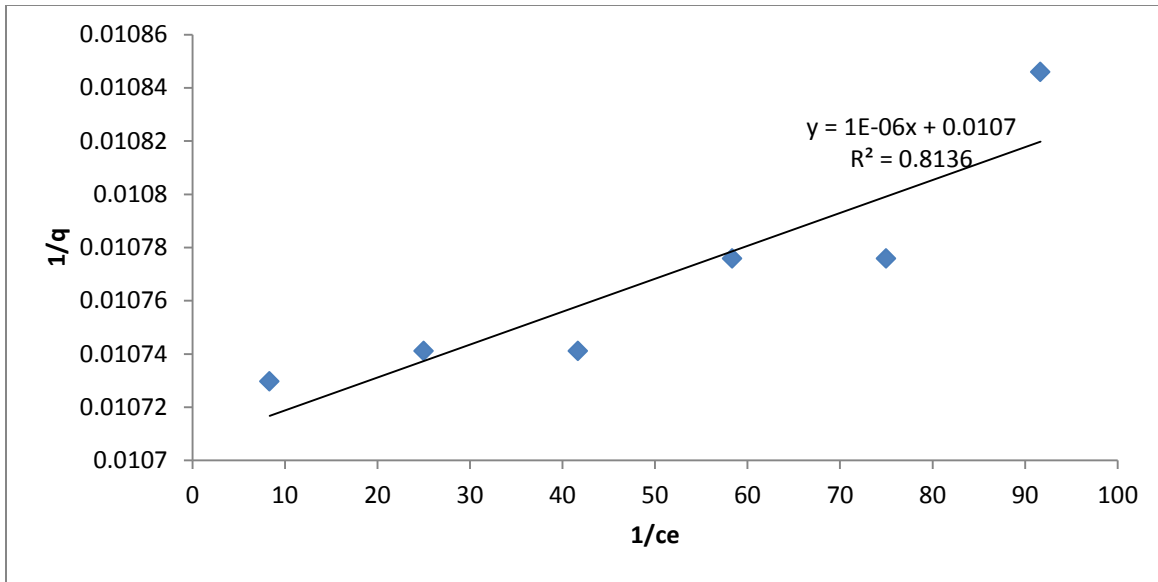


Figure 10: Langmuir adsorption isotherm for fluoride on PAM modified diatomite, pH 4.0 – 5.5, adsorbent dose 0.02g, 60 min, at room temperature. Slope of the curve = $1/q_m$, intercept of curve = $1/K_l q_m$, SD = 0.00984,

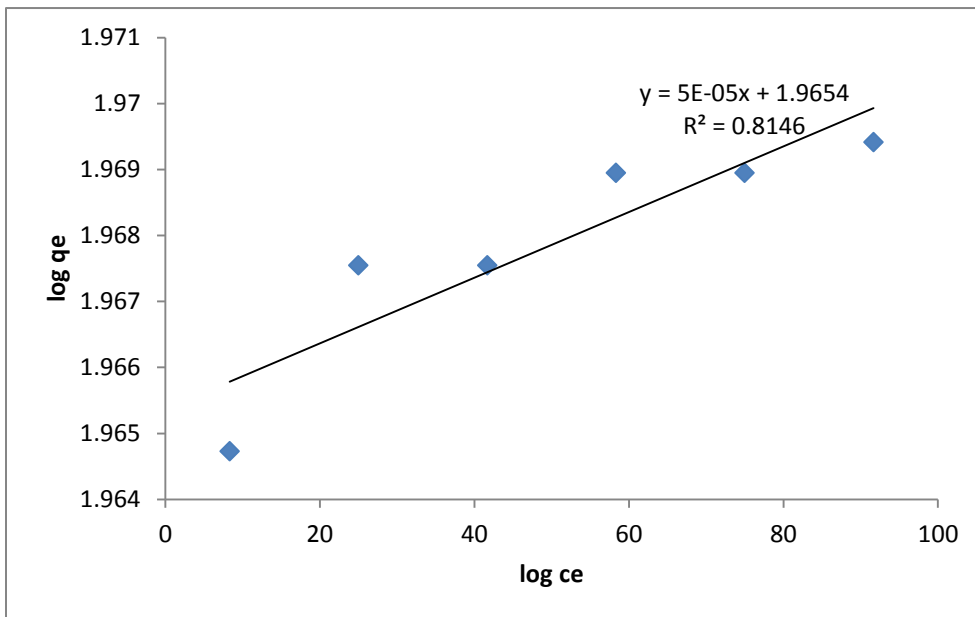


Figure 11: Freundlich adsorption isotherm for fluoride on PAM modified diatomite, pH 4.0 – 5.5, adsorbent dose 0.02g, 60 min, at room temperature. Slope = $1/n$, intercept = $\log K_f$, SD = 0.724682,

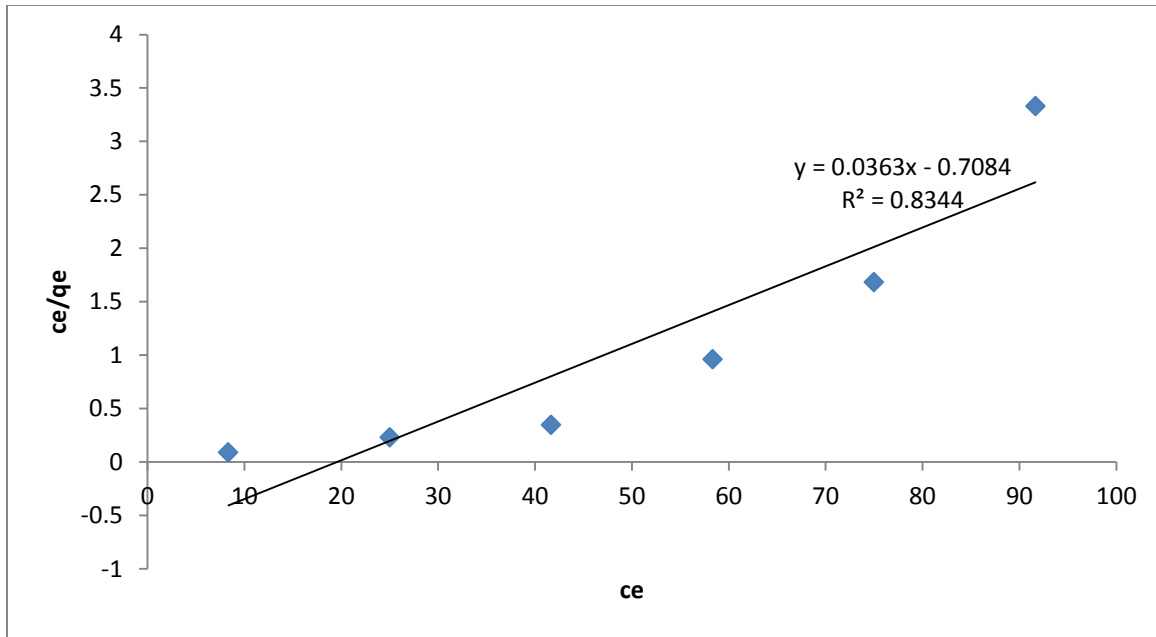


Figure 12: Langmuir adsorption isotherm for fluoride on PAM modified diatomite, pH 4.0 – 5.5, adsorbent dose 0.02g, 60 min, at room temperature. [is it differ from 10]

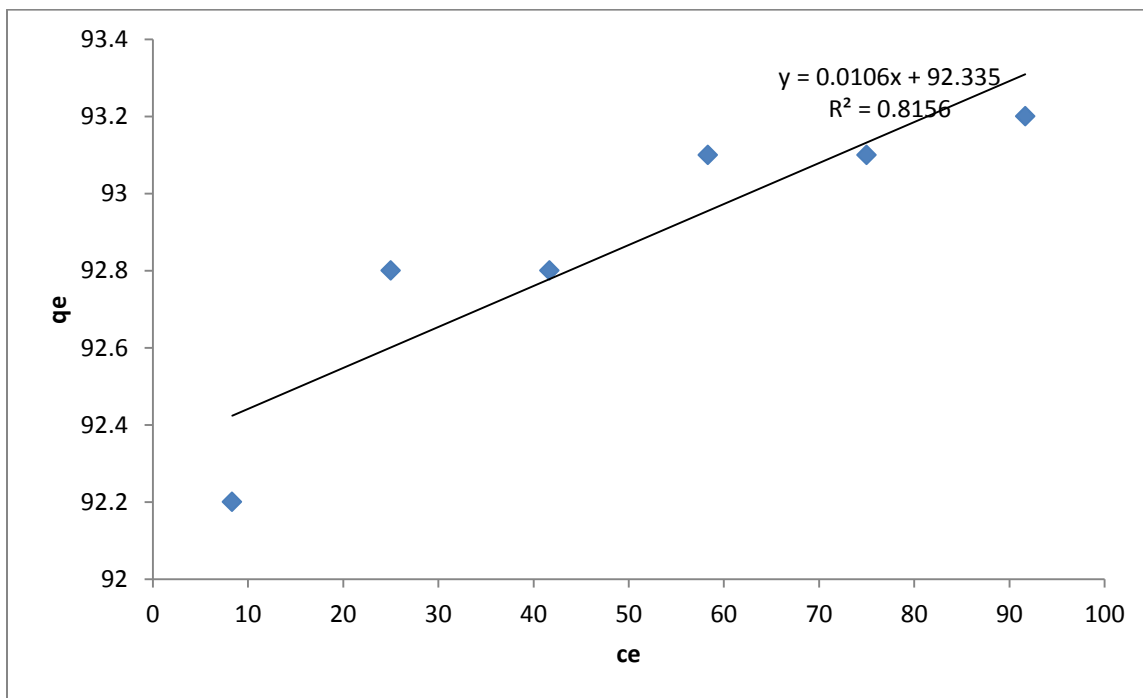


Figure 13: Freundlich adsorption isotherm for fluoride on PAM modified diatomite, pH 4.0 – 5.5, adsorbent dose 0.02g, 60 min, at room temperature. [fig 13 vs 11]

The adsorption equilibrium data were analyzed using Freundlich and Langmuir isotherm models in the concentration of fluoride ranged from 100 to 1000 mg/L. the concentration was selected based on limit of detection of the instrument used in determination. And the value of $n > 1$ is favorable for adsorption condition. Langmuir isotherm assumes monolayer attention of adsorbate on the surface of adsorbent.

Table 5: Langmuir and Freundlich value

Langmuir			Freundlich		
q_m	R_L	R^2	k_f	$1/n$	R^2
93.1	0.7084	0.8344	2.26	0.0106	0.8156

From the table 5, $0 < R_L < 1$ which indicate that favorability of the Langmuir isotherm model for removal of fluoride from water.

Langmuir isotherm constant $R_L = 0.7084$ which above 0 and below 1. In this case the adsorption process is favorable and obeyed type II. Freundlich isotherm constant, n , is a degree of deviation from linearity. The value of n is in agreement the adsorption is linear, but below linearity it is suggested that the relation is unfavorable, meanwhile if the n value is above agreement, adsorption is favorable 0.82. In this finding, the value of n at equilibrium was higher, which is in favorable with adsorption process.

4.6 Kinetic studies of Adsorption

The kinetic of adsorption system was study for determination of how rapidly or deliberately the rate constant of the reaction is during the adsorption process. At different time where the other parameters are constant, the kinetic studies were carried out. The kinetic data provides valuable information about the effectiveness of the adsorption process.

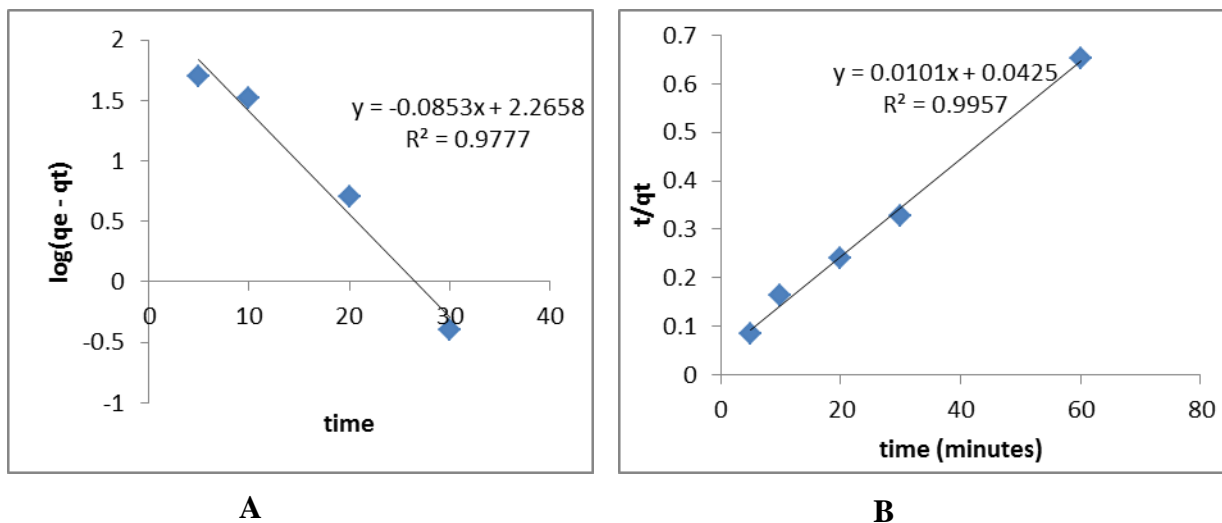


Figure: **14**: Pseudo –first and second order plot for F^- adsorption onto PAM modified diatomite, fluoride initial 100 mg/L; pH: 5.4; adsorbent dose 0.05g, shaking speed 150 rpm at room temperature.

As the rate of sorption increases the maximum capacity obtained, capacity at equilibrium q_e and capacity at any time, t , of the first order sorbed at initial concentration period, as in (Figure 14. A). fluoride ion sorption on PAM modified diatomite with 100 mg/L initial concentration at time 30 minutes. Where (figure 14 B) demonstrate the linearity of pseudo-second order model for sorption of fluoride ion by PAM modified diatomite with 100 mg/L as initial concentration at 60 minutes. The correlation of t/q_t versus time from the pseudo-second order rate 0.9957 is greater than 0.9777 for pseudo-first order model when the time is 60 minutes. Which means that this sorption is not a first order reaction and the system support a pseudo-second order model. Adsorption kinetic models applied for illustration of correlation coefficient, R^2 , and adsorption kinetic.

Table 6: Kinetic parameters for adsorption of fluoride ions onto adsorbents at room temperature

	$K_1 (min^{-1})$	$Q_e \left(\frac{mg}{g}\right)$	R^2
Pseudo-first order	1.169	59.00	0.9777
	$K_2 (min^{-1})$	$Q_e \left(\frac{mg}{g}\right)$	R^2
Pseudo-second order	0.0002	92	0.9957

The kinetics and correlation coefficient, R^2 , were calculated from the plots. Both pseudo – first order and pseudo second order has been used for understanding of adsorption kinetics. And the equation X and XI has been applied for calculating the pseudo – first and pseudo second.

Nevertheless, the values of coefficient, R^2 , showed that pseudo-second order model in (figure 14 and table 6) is well fit in compared to pseudo – first order.

4.7 Comparison of adsorption capacities of different adsorbents for fluoride removal

The values of adsorbent capacities of related work have been used for comparison of adsorptive capacities of an adsorbent. Some literature reported values of adsorption capacity at different pH values, and they are clearly shown in (Table 7)

Table 7: Comparison of adsorption capacities for different adsorbents for fluoride removal.

S/N	Adsorbents	pH	Adsorbent capacity Q_m (mg/g)	References
1	aluminum impregnated coconut	12	3.14	58
2	Fluoride Removal from Water By Calcium Materials	3-5	1.07	38c
3	adsorption of fluoride from water by modified banana peel	6.2-8.2	39.5	59
4	Hydrated Cement	7	1.92	60
5	activated carbon prepared coffee	2	0.41	61
6	Iron–tin bimetal	6.4	10.47	32
7	Waste residue from alum manufacturing process	3-8	332.5	52
8	Siliceous Mineral of a Kenyan Origin	3.4	12.4	62
9	trimetal Mg/Ce/Mn oxide-modified diatomaceous earth	4	12.63	63
10	Modified spent diatomaceous earth adsorbents	3.4	51.1	5
11	acid-activated diatomite	6	12.33	64
12	acid-activated ignimbrite material	6	8.8267	64
13	PAM modified diatomite	4-5.5	93.2	current work

4.8 Conclusions

A batch scale removal of fluoride using adsorptive experiments was performed as a function of solution pH, adsorbent dose, contact time, and agitation speed at room temperature. The study suggested that the batch defluoridation by using PAM modified diatomite was found to be promising due to the following main findings: high adsorption capacity of 96.23 mg/g, the possibility of working near neutral pH and short equilibrium time. Moreover, the possibility of degradation of the adsorbent is vital features of this work.

The experimental data for the batch adsorption process was fitted by Langmuir and Freundlich adsorption isotherm model with encouraged correlations.

5.1 Recommendations

- Another study for the removal of fluoride using cross-link modified PAM should carry out for diatomite.
- Another study should be carried out using modified diatomite under lower fluoride concentrations and the fluoride residual should be tested using an instrument such as an ion-selective electrode or Uv-Vis spectroscopy.
- Diatomaceous and PAM is highly encouraged to be used for adsorption, since they have no significant hazard to human.

5 References

1. (a) Mr J.K. Fawell, M. M. G., Dr P. Toft, Prof. Y. Magara & Mr P. Jackson,, Fluoride in Drinking-water. *WHI/SDE/WSH* **2003**, 3 (04), 17; (b) M. Mohapatra , S. A., B.K. Mishra, Dion E. Giles b, P. Singh Review of fluoride removal from drinking water. *Journal of Environmental Management* **2009**, 91 (2009), 67-77.
2. Odobasic, A. B. a. A., Determination of Fluoride and Chloride Contents in Drinking Water by Ion Selective Electrode. *Environmental Monitoring* **2011**, (04, November, 2011), 10.
3. SURAK', H. K. a. J. G., Determination of Fluoride by Conductometric Titration. *Analytical Chemistry Division* **1958**, 24 (1952), 1-4.
4. Inkielewicz, K., Fluoride_content_in_soft_tissues_and_urine_of_rats. *the International Society for Fluoride Research* **2003**, 36 (4), 263-266.
5. WOLDE, T. Fluoride removal using modified spent diatomaceous earth adsorbent ADDIS ABABA UNIVERSITY, ADDIS ABABA, ETHIOPIA, 2017.
6. (a) Meena Chakraborty, M. P., and Piyushkant Pandey, Spectrophotometric method vs ion selective electrode for field determination of fluoride in water and complex samples. *Research Journal of Chemical Sciences* **2017**, 7 (5), 31-37; (b) Coetzee, J.-H. N. a. P., Evaluation of the potentiometric determination of trace fluoride in natural and drinking water with a fluoride ISE. *WaterSA* **2007**, 33 (4), 519-530.
7. MURRAY, A. M. B. A. M. M. *Direct Titrimetric Determination of Fluoride in Natural Waters*; Bedford College: London, 1952; pp 642-645.
8. Clasen, W.-M. K. C., *Viscosimetry of Polymers and Polyelectrolytes* Professor Dr. Werner-Michael Kulicke: New York 2003; Vol. 2, p 139.
9. J. Pillai, P. D., Nalco Company, Flocculants and Coagulants: The Keys to Water and Waste Management in Aggregaten Production. *NALCO Company* **1990**, 1, 1-6.
10. Per M. Claesson, A. D., Orlando J. Rojas, Polyelectrolytes as adhesion modifiers. *Advances in Colloid and Interface Science* **2003**, 104 (2003), 53-74.
11. Valery F. Kurenkov, H.-G. H., and Fedor . Lobanov, Application of polyacrylamide fluocculats for water treatment *Thematic Division: Chemical Technologyn* **2002**, 3 (11), 31-39.
12. Redda Tekle-Haimanot, Z. M., Helmut Kloos, Clemens Reimann, Wondwossen Fantaye, Legesse Zerihun, Kjell Bjorvatn The geographic distribution of fluoride in surface and

groundwater in Ethiopia with an emphasis on the Rift Valley. *Science of the Total Environment* **2006**, 367 (2006), 182-190.

13. Kalpana Singh , D. H. L., Kailas L. Wasewar & Chang Kyoo Yoo, Removal of fluoride from aqueous solution: status and techniques. *Desalination and Water Treatment* **2013**, 51 (2013), 3233-3247.

14. Clemens Reimann, K. B., Bjørn Frengstad , Zenebe Melaku, Redda Tekle-Haimanot , Ulrich Siewers, Drinking water quality in the Ethiopian section of the East African Rift Valley I—data and health aspects. *The Science of the Total Environment* **2003**, 31 (1), 65-80.

15. Lincir, K. R. i.-G. a. I., Current Concept on the Anticaries Fluoride Mechanism of the Action. *Coll. Antropo* **2001**, 25 (2), 703-712.

16. M. Markovic, S. T., L. C. Chow, and S. Frukhtbeyn, Calcium Fluoride Precipitation and Deposition From 12 mmol/L Fluoride Solutions With Different Calcium Addition Rates. *Journal of Research of the National Institute of Standards and Technology* **2009**, 114 (September-October 2009), 293-501.

17. (a) Natrayasamy Viswanathan, S. M., Selective fluoride adsorption by a hydrotalcite/chitosan composite. *Applied Clay Science* **2010**, 40 (2010), 607-611; (b) Mirna Habuda-Stanić , M. E. R. a. A. F., A Review on Adsorption of Fluoride from Aqueous Solution. *materials* **2014**, 7 (2014), 6317-6366.

18. Sillanpää, E. I. M., The use of low-cost adsorbents for wastewater purification in mining industries. *Environ Sci Pollut Res* **2013**, 1 (9), 1-22.

19. M. Behbahani, M. R. A. M., M. Arami Techno-economical evaluation of fluoride removal by electrocoagulation process: Optimization through response surface methodology. *Desalination and Water Treatment* **2011**, 271 (2011), 209-218.

20. Lejalem Abeble Dagnaw, B. S. C., * Feleke Zewge, Fluoride content of leafy vegetables, irrigation water, and farmland soil in the rift valley and in non-rift valley areas of Ethiopia. *Fluoride in leafy vegetables* **2018**, 50 (4), 409-429.

21. D. Van Rooijen & G. Tadesse, G., Urban sanitation and wastewater treatment in Addis Ababa in the Awash Basin, Ethiopia. *Loughborough University* **2009**, 95 (1), 1-7.

22. Yasinta John, V. E. D. J. a. D. M., A Comparative Study on Removal of Hazardous Anions from Water by Adsorption: A Review. *International Journal of Chemical Engineering* **2018**, 2018 (15 February 2018), 1-12.

23. Luis Gómez-Hortigüela, J. P.-P., Raquel García, Yonas Chebudeb, Isabel Díaz Natural zeolites from Ethiopia for elimination of fluoride from drinking water. *Separation and Purification Technology* **2013**, 120 (1), 224-229.
24. Ngakfumbé, J. The Use of Organic Polymers in the Chemical Purification of Peat Derived Runoff Water. Master's Thesis, University of Oulu, OULUNYLIOPISTO 2013.
25. Hodge, S. A. B., Mustafa K. Tay, Hui Huang Shaffer, Milo S. P., Giant cationic polyelectrolytes generated via electrochemical oxidation of single-walled carbon nanotubes. *Nature Communications* **2013**, 4, 1989.
26. Gregory, B. B. a. J., Organic polyelectrolytes in water treatment *Water Research* **2007**, 41 (2007), 2301-2324.
27. ZHU, Z. J. a. J., Cationic Polyacrylamide: Synthesis and Application in Sludge Dewatering Treatment. *Asian Journal of Chemistry* **2014**, 26 (3), 629-633.
28. Bakr, H. E. G. M. M., Diatomite: Its Characterization, Modifications and Applications. *Asian Journal of Materials Science* **2010**, 2 (3), 121-136.
29. Tassadit Benkacem, B. H., Alain Chamayou, Henri Balard, Rachel Calvet, Physicochemical characterization of a diatomaceous upon an acid treatment: a focus on surface properties by inverse gas chromatography. *HAL archives - ouvertes.fr* **2016**, 294, 498-507.
30. Bakr, H. E. G. M. M., Hossam Elden Galal Morsy Mohamed Bakr. *Asian Journal of Materials Science* **2010**, 2 (3), 121-136.
31. Yıldız, N. *Diatomite: A New Substrate for Hydroponics*; Ataturk University: Turkey, 2008; pp 527-536.
32. Krishna Biswas, K. G., Uday Chand Ghosh, Adsorption of fluoride by hydrous iron(III)–tin(IV) bimetal mixed oxide from the aqueous solutions. *Chemical Engineering Journal* **2015**, 149, 196-206.
33. Ikuo Abe, S. I., Toshimitsu Tokimoto, Takeo Nakamura, Naohito Kawasaki, and Seiki Tanada Adsorption of fluoride ions onto carbonaceous materials. *Journal of Colloid and Interface Science* **2004**, 275 (2004), 35-39.
34. Tressaud, A., *Fluorine and the Environment* Alain Tressaud: University of Bordeaux I Pessac Cedex, France, 2006; Vol. 2, p 297.

35. Norma Rodríguez-Laguna, A. R.-H., 1 María Teresa Ramírez-Silva,1 LuceroHernández-García,1 andMario Romero-Romo2, An ExactMethod to Determine the Conductivity of Aqueous Solutions in Acid-Base Titrations. *Journal of Chemistry* **2015**, 13.
36. LEONARD, M. A., Determination of Fluoride by Complexometric Titration. *View Article Online* **1963**, 88, 404-406.
37. Adrian Lussi1, E. H. J. K., Fluorides – Mode of Action and Recommendations for Use. *Research and Science* **2012**, 122 (6 October 2011), 1030-1036.
38. (a) M. Mourabet A. El Rhilassi, H. E. B., M. Bennani-Ziatni, R. El Hamri, A. Taitai, Removal of fluoride from aqueous solution by adsorption on Apatitic tricalcium phosphate using Box–Behnken design and desirability function. *Applied Surface Science* **2012**, 258 (2012), 4402-4410; (b) Liang Chen, K.-S. Z., Jun-Yong He, Wei-Hong Xu†, Xing-Jiu Huang, Jin-Huai Liu Enhanced fluoride removal from water by sulfate-doped hydroxyapatite hierarchical hollow microspheres. *Chemical Engineering Journal* **2016**, 285 (2016), 616-624; (c) Sanghranta S. Waghmare, T. A., Fluoride Removal from Water By Calcium Materials: A State-Of-The-Art Review. *International Journal of Innovative Research in Science, Engineering and Technology* **2015**, 4 (9), 8090 -8102.
39. Brett D. Turner, P. J. B., and Scott W. Sloan, Impact of Phosphate on Fluoride Removal by Calcite. *Environmental Engineering Science* **2010**, 27 (8), 643-650.
40. Kowakhuk., E. E. Selective Fluoride Removal by Aluminum Precipitation & membrane Filtration The University of New Mexico, Albuquerque, New Mexico, 2011.
41. Amit Bhatnagara, E. K., Mika Sillanpääb, Fluoride removal from water by adsorption— A review. *Chemical Engineering Journal* **2011**, 171 (2011), 811-840.
42. Abechi E.S, G. C. E., Uzairu A, Kagbu J.A, Kinetics of adsorption of methylene blue onto activated carbon prepared from palm kernel shell. *Scholars Research Library* **2011**, 3 (1), 154-164.
43. G.Vijayakumar, R. T., M. Dharmendirakumar, Adsorption, Kinetic, Equilibrium and Thermodynamic studies on the removal of basic dye Rhodamine-B from aqueous solution by the use of natural adsorbent perlite. *J. Mater. Environ. Sci* **2012**, 3 (1), 157-170.
44. Arun Bahl, B. S. B., G.D Tuli *Essential of Physical Chemistry* Multicolour Edition UK, 2000; Vol. 26.

45. Z. Benmaamar, H. H., H. Boutoumi, H. Benmaamar,; S. Ould Baba Ali, A. B., A. Aggoun., A batch study of adsorption equilibrium and kinetic for methylene blue onto synthesized zeolite. *Journal of materials and Environmental Sciences* **2017**, 8 (2), 539-550.
46. Sarac, A. S., Redox polymerization. *Progress in Polymer Science* **1999**, 24, 1149-1204.
47. C.M. Li, C. Q. S., W. Chen, L. Pan, Electrochemical thin film deposition of polypyrrole on different substrates *Surface & Coatings Technology* **2005**, 198 (11), 474-477.
48. (a) Kamel Babaeivlni, A. P. K., Adsorption of fluoride onto crystalline titanium dioxide: Effect of pH, ionic strength, and co-existing ions. *Journal of Colloid and Interface Science* **2013**, 394 (2013), 419-427; (b) Merga Regassa, F. M., Wondessen Birke, Esayas Alemayehu, Defluoridation of Water Using Natural and Activated Coal. *International Advanced Research Journal in Science, Engineering and Technology* **2016**, 3 (1), 1-7.
49. Keno David Kowanga, E. G., Godfrey Omare Mauti, Eliakim Mbaka Mauti, Kinetic, sorption isotherms, pseudo-first-order model and pseudo-second-order model studies of Cu(II) and Pb(II) using defatted Moringa oleifera seed powder. *the Journal of Phytopharmacology* **2016**, 5 (2), 71-71.
50. Md. Saifur Rahaman, C. D. V., and Menachem Elimelech, Electrochemical Carbon-Nanotube Filter Performance toward Virus Removal and Inactivation in the Presence of Natural Organic Matter. *Environmental Science and technology* **2012**, 42 (2012), 1556-1564.
51. Poonam Tirkey, T. B., Sukalyan Chakraborty, Optimization of fluoride removal from aqueous solution using Jamun (*Syzygium cumini*) leaf ash. *Process Safety and Environmental Protection* **2018**, 115 (2018), 125-138.
52. Worku Nigussiea, F. Z., B.S. Chandravanshi, Removal of excess fluoride from water using waste residue from alum manufacturing process. *Journal of Hazardous Materials* **2007**, 147 (2007), 954-963.
53. Farsani, H. F. a. S. N., Modification of polyacrylamide- β -zeolite composite by phytic acid for the removal of lead from aqueous solutions. *Polish Journal of Chemical Technology* **2013**, 15 (1), 1-6.
54. Caili Dai, Z. X., YiningWu, Chenwei Zou, XuepengWu, TaoWang, Xu Guo and Mingwei Zhao, Design and Study of a Novel Thermal-Resistant and Shear-Stable Amphoteric Polyacrylamide in High-Salinity Solution *Polymers* **2017**, 9 (296), 1-12.

55. A.H. Essadki, B. G., Ch. Vial, H. Delmas, M. Bennajah, Defluoridation of drinking water by electrocoagulation/electroflotation in a stirred tank reactor with a comparative performance to an external-loop airlift reactor. *Journal of Hazardous Materials* **2009**, *168*, 1325-1333.
56. Fentahun Adeno, E. M., Feleke Zewge and Yonas Chebude, Adsorption Removal of Fluoride From Water using Nanoscale Aluminum Oxide Hydroxide (AlOOH) *Chemical Society of Ethiopia* **2014**, *28* (2), 215-227.
57. (a) Pavarajarn, S. P. a. V., Adsorption Study for Removal of Mn (II) Ion in Aqueous Solution by Hydrated Ferric (III) Oxides. *International Journal of Chemical Engineering and Applications* **2016**, *7* (4), 239-243; (b) Dada, A. O., Olalekan, A.P, Olatunya, A.M, DADA, O, Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn²⁺ Unto Phosphoric Acid Modified Rice Husk. *IOSR Journal of Applied Chemistry* **2012**, *3* (1), 38-45.
58. Naba Kumar Mondal , R. B., Jayanta Kumar Datta, Removal of fluoride by aluminum impregnated coconut fiber from synthetic fluoride solution and natural water. *Alexandria Engineering Journal* **2015**, *2015*, 1-121.
59. Bhaumik, R.; Naba Kumar Mondal , R. B., Jayanta Kumar Datta, Optimizing adsorption of fluoride from water by modified banana peel dust using response surface modelling approach. *Appl Water Sci* **2016**, *6*, 115-135.
60. Sadia Bibi, A. F., Assistant Professor Khadim Hussain, Naghma Haide, Evaluation of industrial based adsorbents for simultaneous removal of arsenic and fluoride from drinking water. *Journal of Cleaner Production* **2014**, *14*, 1-45.
61. Rao, T. G. A. H. V. M., Defluoridation of water by activated carbon prepared from banana (*Musa paradisiaca*) peel and coffee (*Coffea arabica*) husk. *Int. J. Environ. Sci. Technol* **2015**, *12* (4), 1857-1866.
62. Muthakia., E. W. W. C. O. O. W. A. G. K., Removal of Fluoride from Aqueous Solutions by Adsorption Using a Siliceous Mineral of a Kenyan Origin. *Clean Soil Air Water* *42* (4), 340-349.
63. Wilson M. Gitari, A. A. I., Jabulani R. Gumbo., Synthesis, characterization and batch assessment of groundwater fluoride removal capacity of trimetal Mg/Ce/Mn oxide-modified diatomaceous earth. *Arabian Journal of Chemistry* **2017**, *01* (002), 1-16.

64. Esengül Kır, H. O., Ismail Kır & Tugba Sardohan-Koseoglu, Removal of fluoride from aqueous solution by natural and acid-activated diatomite and ignimbrite materials. *Desalination and Water Treatment* **2016**, 2015, 1-13.