APPLICATION OF SURFACE MODIFIED DIATOMITE AND BRICKS AS ADSORBENTS FOR REMOVAL OF FLUORIDE CONTAMINANTS FROM WATER SAMPLES COLLECTED FROM LAKE BARINGO

BY

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DECLARATION

Declaration by the Candidate

This thesis is my original work and has not been presented for a degree in any other University. No part of this thesis may be reproduced without the prior written permission of the author and/or Moi University.

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DEDICATION

I dedicate this work to my parents who have been inspirational and supportive throughout my research and study. May God bless them.

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ABSTRACT

High fluoride in drinking water is detrimental to health. Cases of dental and crippling fluorosis have been reported in Lake Baringo in Kenya due to the high fluoride in the lake, which serves as the source of drinking water. The high cost of fluoride removal is an impediment to the efforts for fluoride removal in drinking water. Diatomite and brick are cheap and locally availabe materials in Kenya with potential to remove fluoride but have not been adequately assesed for fluoride adsorption. The main aim of this study was to test the application of surface modified diatomite and bricks as adsorbents for removal of fluoride contaminants from water. The specific objectives of the research were to: develop and optimize aluminum hydroxide surface modified diatomite and brick adsorbent mixture; characterize the diatomite and brick adsorbents in terms of physical features and chemical composition; test the performance of optimized mixture of surface modified diatomite and bricks on fluoride removal from water; and determine the adsorption capacity of the optimized mixture of surface modified diatomite and bricks in the removal of fluoride from water samples collected from Lake Baringo in adsorption columns. Diatomite and brick adsorbents were characterized using scanning electron microscopes equipped with energy dispersive spectroscopy (SEM-EDS). Surface modified diatomite mixed with brick was tested for fluoride removal through batch adsorption and column experiments. Diatomite samples were modified using aluminium hydroxide. Mixture of diatomite and brick samples were optimized for fluoride removal through response 1surface methodology (RSM) using Box-Wilson central composite design (CCD). Fluoride removal studies by batch experiments showed that 28g/L dose of the surface modified diatomite sufficiently removed fluoride to the World Health Organization (WHO) acceptable limit of 1.5mg/L from initial concentration of 10mg/L from fluoride contaminated water simulated in the laboratory. Similarly, 300g/L dose of brick powder was required to achieve the same recommended level. RSM optimization showed that a mixture of 18.4 g of surface modified diatomite and 177.8g of brick could be successfully used to reduce the fluoride levels in water from 10mg/L to 1.5mg/L in 30minutes. Isotherm studies showed that the adsorption of fluoride by surface modified diatomite followed Freundlich adsorption isotherm, with a regression coefficient (R^2) of 0.9753 compared to Langmuir (R^2 =0.8954). The adsorption of fluoride by brick followed the Langmuir adsorption mechanism (R^2 =0.9804) as compared to Freundlich adsorption (R^2 =0.9372). Kinetic studies revealed that the removal of fluoride by both surface modified diatomite and brick conformed to the pseudo-second order kinetic model. Similarly, the optimized mixture of surface modified diatomite and brick demonstrated high conformity to the pseudo second order kinetic model (R^2 =0.9908). Column studies found the breakthrough point to be reached in 1 hour with 5 bed volumes and fluoride uptake capacity of 0.01mg/g of the mixed adsorbent material. The data fit well to the linearized Thomas kinetic model with the regression coefficient of 0.9695. A maximum fluoride uptake capacity of 0.02465mg/g was obtained with a Thomas rate constant of 3.9606mlmg^{-1}min^{1}. In conclusion, the results indicated that the optimized mixture of surface modified diatomite and brick has high potential for fluoride removal. It is recommended to be used as adsorbents for fluoride removal in areas affected by high fluoride levels in Kenya. Further studies on improving the fluoride uptake capacity of brick are suggested to improve its effectiveness when combined with surface modified diatomite.

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ABBREVIATIONS AND ACRONYMS

ADIL	African Diatomite Industries Limited
$Al(OH)_3$	Aluminium Hydroxide
ANOVA	Analysis of Variance
BCE	Before the Common Era
BE	Backscattered Electrons
CCD	Central Composite Design
DOE	Design of Experiment
EDS	Energy Dispersive X-ray Spectroscopy
EPA	Environmental Protection Agency
HAp	Hydroxyapatite
IGRAC	International Groundwater Resources Assessment Centre
JICA	Japan International Cooperation Agency
NDC	Nakuru Defluoridation Company
RO	Reverse Osmosis
RSM	Response Surface Methodology
SDG	Sustainable Development Goals
SE	Secondary Electrons
TISAB	Total Ionic Strength Adjustment Buffer
UNDP	United Nations Development Programme
WASREB	Water Services Regulatory Board
WHO	World Health Organization

CHAPTER ONE: INTRODUCTION

1.1 Background

The sustainable development goal number 6 (SDG6) advocates for availability and sustainable management of water and sanitation for all (U N, 2018). Despite this, water scarcity is still a challenge that faces humanity day in day out. If no solution is sought to this problem, then it is predicted to escalate to higher levels. It is estimated that by the year 2050, at least one in four people will suffer recurring water shortages (Matić & Karleuša, 2020). Kenya is not spared from this situation with many people still lack access to clean and safe drinking water. Up to 18 million Kenyans face a problem of accessing clean and safe drinking water (Mulwa et al., 2021), with 9.9 million Kenyans drinking from contaminated surface sources (Ocholla et al., 2022).

Fluoride is one of the major contaminants which need to be addressed as the world works towards achieving the standard development goal number six. Its presence in water is a subject that continues to attract attention. It is considered a double-edge sword in drinking water due to its positive and negative effects depending on the levels (Goldberg, 2018). Its addition to drinking water is a safe and simple means of preventing dental caries in children when the levels are within the set standard, but detrimental to health and can result in dental fluorosis when the levels are above the recommended limits (Harrison, 2005). The current World Health Organization (WHO) acceptable limit of fluoride is 1.5 mg/l (Demelash et al., 2019; Ghanbarian et al., 2021). It is noted that high levels of fluoride above this value carries with it a risk of dental and skeletal fluorosis (Guissouma et al., 2017).

Despite the legislation that regulates the fluoride levels in drinking water, cases of fluorosis are still reported in countries affected by fluoride. In Kenya for example, studies have established prevalence dental fluorosis among the people living in areas of high fluoride content to be up to 86% . Similarly, cases of crippling fluorosis have been reported for more than a decade in areas such as Lake Baringo (Matara, 2021; Mkawale, 2011). Reports estimate that by the year 2020, upto 4000 people from 10 villages around the lake had been affected by dental and skeletal fluorosis (Dominic, 2020).

The high cost of fluoride removal in water has resulted in fluoride contamination being ignored despite its devastating effects. Some places in Nakuru, Kenya, for example, has reported fluoride levels up to 7.6 mg/l in piped water (Wambu & Muthakia, 2011). It is therefore urgent that techniques which are simple and easy to deploy in water treatment are developed. This will help to fight the danger of fluoride in areas of high fluoride content in the water. Currently, there are several techniques of fluoride removal (Modi & Soni, 2013). These techniques include precipitation,ion exchange,membrane and adsoprtion techniques(Ingle et al., 2014).

The precipitation technique is mainly the Nalgonda technique which involves the addition of alum, lime, and bleaching powder, then mixing, flucculation sedimentation, filtration and finally disinifection(Waghmare & Arfin, 2015). Precipitation technique although it involves a simple design and is cost effective, the technique is tedious and requires daily operation. In addition, there is the danger of excess residual aluminium ions in water, which can cause the Alzheimer’s disease (Murutu et al., 2010). The ion exchange technique utilizes resins which removes fluoride through interraction with anions or cations. Although this technique can remove as high fluoride as 95% (Ingle et al., 2014), it has a drawback of ineficiency when other ions are present in water (Mondal & George, 2015). Additionaly, this technique is expensive due to the high cost of the resin used (Razbe, 2013). Membrane technique utilizes semi-permeable membrane in which the water molecules pass through the membrane due to hydraulic pressure, in the case of resverse osmosis or the ions in the water passes through the membrane and leavs the water molecules, because of electric current in an electro dialysis process (Ingle et al., 2014). This method is efficient in fluoride removal and is not affected by presence of other ions; however, the cost involved is very high (Waghmare & Arfin, 2015; Pillai et al., 2021)

Adsorption is considered a primary technique for fluoride removal (Lacson et al., 2021). This technique can remove upto 90% fluoride in water (Ingle et al., 2014). However, the cost of the adsorbents used in defluoridation is one of the challenges that derail the efforts of excess fluoride removal in water by adsorption (Dayananda et al., 2014; He et al., 2020). A search for cheap and easily accessible adsorbents for fluoride removal in water is therefore a subject of utmost importance.

1.2 Problem Statement

The levels of fluoride ions in Lake Baringo are alarming and life threatening. While the research done by Geothermal Development Company (GDC) in the area reports fluoride levels around the lake, as high as 50ppm (Mutonga, 2014). Gikunju reports a value of 5.2 ppm in the lake water (Gikunju et al., 1992). Despite the different quantities reported by each, the values are way far above the recommended value of 1.5 mg/l for safe drinking as per the WHO guidelines (WHO, 2006).

The findings above by GDC are a clear indicator that options such as borehole drilling for solution of the problem in the area are not an option for consideration. The comparative values above indicate that the area around the lake could indeed have higher fluoride content than the values in the lake. The only promising solution is therefore an efficient treatment method at an affordable cost to be rolled out to the residents of the area. This is only possible with the use of locally available materials.

The available commercial treatment techniques such as the reverse osmosis (RO) are expensive and have associated challenges as well such as removal of all the ions in water (Ingle et al., 2014). There is therefore room for further research.

1.3 Justification

Diatomite is one locally available material in Kenya. Deposits of this mineral have been identified in Baringo in addition to the current deposits being mined at Kariandusi. The material is 500 times cheaper than activated commercial carbon and is effective as activated carbon in filtration process (Akafu et al., 2019). The effectiveness of the adsorbent in defluoridation is low but can be improved by surface modification (Akafu et al., 2019). Bricks have also been found to remove fluoride due to the iron and aluminum content it has among other elements (Selvaraju & Pushpavanam, 2009; Swarnakar et al., 2007). A mixture of surface modified diatomite and brick in fluoride removal have not been accessed this work tested the potential of a mixture of surface modified diatomite and brick as cheap adsorbent for fluoride removal in water.

1.4 Objectives

1.4.1 Main Objective

The main objective of this work was to test the application of surface modified diatomite and bricks as adsorbents for removal of fluoride contaminants from water.

1.4.2 Specific Objectives

The specific objectives of this research work were:

1. To develop and optimize aluminum hydroxide surface modified diatomite and brick adsorbent mixture.
2. To characterize the diatomite and brick adsorbents in terms of physical features and chemical composition.
3. To test the performance of optimized mixture of surface modified diatomite and bricks on fluoride removal from water.
4. To determine the adsorption capacity of the optimized mixture of surface modified

   diatomite and brick in the removal of fluoride from water samples from Lake Baringo in adsorption columns.

1.5 Research Questions

The specific objectives were addressed by the following three research questions:

i. What is the optimum mixture of surface modified diatomite and brick in fluoride removal?

ii. What are the physical features and chemical composition of diatomite and brick used in this study?

iii. How is the performance of the optimized surface modified diatomite and brick adsorbent mixture in removal of fluoride in water?

iv. What is the performance of the developed optimum mixture of surface modified diatomite and bricks on fluoride removal for water sampled from Lake Baringo in column setups?

1.6 Significance of the Study

The findings of this study are of benefit to researchers and communities which live in the areas affected by high fluoride concentrations in water. The results suggested that an optimized mixture of surface modified diatomite and brick can be used in the removal of fluoride in water. The test and determination of the effectiveness of the diatomite-brick hybrid method gave an insight into the effectiveness of hybrid technique in combating the adverse effects of high fluoride concentrations in the affected areas. This insight is of great importance to researchers in fluoride removal because it has shed light on the potential of hybrid adsorbents in removal fluoride (Lacson et al., 2021). The affected communities , which live in areas with water containing high concentration of fluoride, particularly Lake Baringo region, will benefit from the findings of this work. This research identified and proposed a fluoride removal solution which can be customized for household use in the form adsorption column. The proposed mixture of the adsorbents is economically viable and affordable to the locals in the affected areas. The optimized mixture of surface modified diatomite and brick can be recommended for fluoride removal in areas affected by fluoride concentration in water.

1.7 Limitations of the Study

The study was limited by the following factors:

i The sample collected was in one section of the lake, Kampi ya Samaki.

ii The sample collection and study were carried out during the dry season. The concentration of fluoride may vary in the lake based on the seasons.

1.8 Assumptions of the Study

The following assumptions were made in the study:

i The collected sample is representative of the water in the lake.

ii The simulated water in the lab has similar characteristics to the water in the lake.

iii There effects of competing ions were negligible with respect to the fluoride removal from the water samples collected from the lake.

CHAPTER TWO: LITERATURE REVIEW

2.1 Introduction

The presence of fluoride in water bears both positive and negative effects depending on the concentration (Goldberg, 2018). It is considered a safe and simple means of preventing dental caries in children when the levels are within the set standard, but detrimental to health and can result in dental fluorosis when the levels are above the recommended limits (Harrison, 2005). The cost of the adsorbents used in the removal of fluoride is one of the challenges that derail the efforts of excess fluoride removal in water. This calls for the exploration of cheap and locally available adsorbents. Diatomite and brick are such cheap adsorbents that can be tested for fluoride removal (Swarnakar et al., 2007; Selvaraju & Pushpavanam, 2009; Akafu et al., 2019).

2.2 Fluoride Occurrence

Fluorine is the ninth element in the periodic table and is the lightest member of the halogen group (Fawell et al., 2006; Ryde, 2020). It is the most reactive and most electronegative element. However, it is never found in its molecular form in the environment but rather in its combined state in the form of fluoride (Fawell et al., 2006). It is the 13th most abundant element and constitutes 0.06-0.09% of the earth’s crust (Fawell et al., 2006; Peckham & Awofeso, 2014).

Fluorides occur naturally in soil, water, plants, and animals in trace quantities. It is usually deposited in bones and teeth of humans and animals when ingested (Harrison, 2005). However, exposure to fluorides among human beings can also take place through food and fluoride containing supplements (Kanduti et al., 2016). In ground water, the geogenic sources of fluoride are the fluoride bearing rocks (Ali et al., 2016).

The problem of fluoride contamination in water is prevalent worldwide with extreme concentration of fluoride in ground water being confined to the arid and semi-arid regions of Asia and Africa (Ali et al., 2016). The geographical belts of high fluoride concentration in ground water have been noted to extend from Syria through Jordan, Egypt, and all the way to Algeria in North Africa, as shown in by the map in Figure 2.1 (a) (Adelana et al., 2011). As shown in Figure 2.1 (b), Kenya is among the countries in Africa that experiences the challenge of very high fluoride concentration in its ground water (Malago et al., 2017).

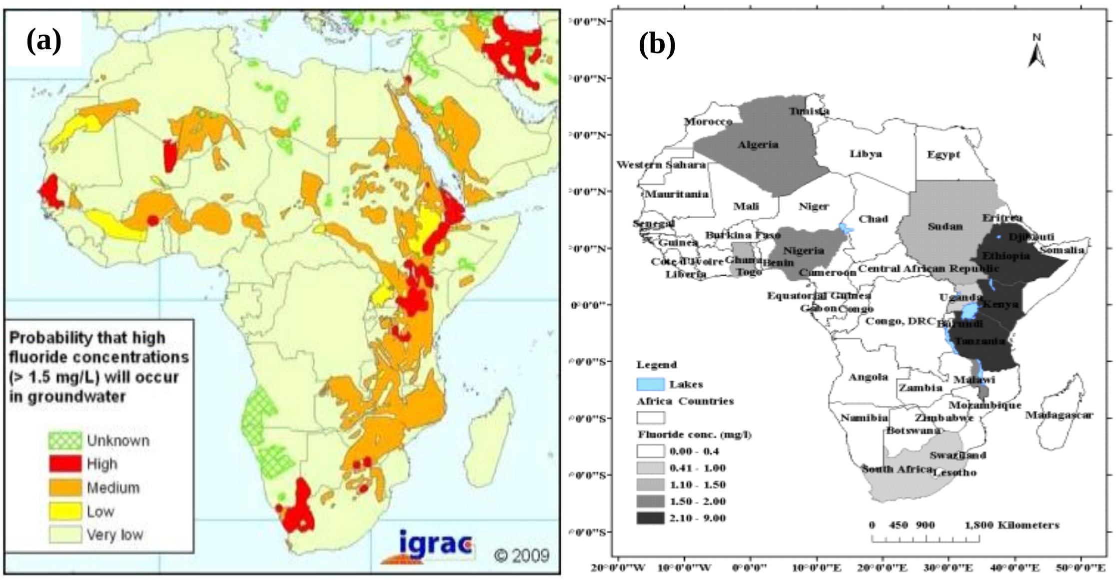

Figure 2.1: Fluoride in Africa. (a) Probability map of fluoride occurrence in Africa (IGRAC 2009), (b) African countries with high fluoride in water.

2.3 Fluoride in Kenya

The fluoride levels in the Kenyan water vary significantly. The ground water sources across the country have been identified to have varied concentration of fluoride with several cases exceeding 5 mg/l of fluoride (Nair et al., 1984). Table 2.1 shows a summary of the fluoride concentration across the country in terms of percentages of ground water sources for the various regions. It is evident from Table 2.1 that Kenya has a problem of fluoride across the country, with a greater prevalence in the Nairobi, Eastern, the Rift Valley and Central regions in which more than 10% of the ground water sources have registered fluoride levels above 5 mg/l.

Table 2.1: Summary of the fluoride concentration across the country in terms of percentages of ground water sources (Nair et al., 1984).

Region	% Ground water source with F- above 5 mg/l
Nairobi	37.5
Eastern	22.1
Rift Valley	17.9
Central	13.6
Nyanza	9.7
Northeastern	7.8
Western	7.7
Coast	4.3

The rivers in Kenya are noted to have lower levels of fluoride than that WHO recommended value of 1.5 mg/l in drinking water (Gaciri & Davies, 1993). However, the groundwater and the lake water in Kenya are noted to have much higher fluoride levels (Gaciri & Davies, 1993), with the rift valley lakes recording higher levels of fluoride (Njenga, 2004). The high fluoride levels above 1.5 mg/l pose the danger of dental fluorosis in the areas affected. Research in Nakuru for example, has shown that fluoride concentration between 0.1 mg/l and 72 mg/l in drinking water (Gevera et al., 2019). The mean fluoride concentration in the boreholes and other hydrological sources is 11.08 mg/l (Gevera & Mouri, 2018). This has resulted in a high prevalence of dental fluorosis in the area, with prevalence of 86% and 79.49% in Gilgil and Egerton -Njoro respectively (Gevera et al., 2019). The children in areas such as Njoro division, have registered 48.3% moderate to severe dental fluorosis (Moturi et al., 2002).

2.4 Fluoride in Lake Baringo

Lake Baringo is among the few freshwater lakes in the Rift Valley region of Kenya. By virtue of being a freshwater lake, it serves as a source of drinking and potable water. Research, however, indicates the presence of high fluoride level in the lake. According to the research carried out by the Japanese government in partnership with the government of Kenya in the year 1999 to 2002, Lake Baringo region has a high fluoride content. The report associated the high fluoride content in the area with the intense tectonic activity within the Rift Valley (JICA, 2002). The findings by JICA agreed with the work by Gaciri and Davies, which attributed the main source of fluoride to the emissions of volcanic activity in the East African rift system (Gaciri & Davies, 1993).

The research done by JICA found out that, 20% of water ponds around the Lake Baringo area contain fluoride content exceeding 3ppm (JICA, 2002). The water sourced from lake, which is the source of drinking water for the region, has been reported to record as high levels as 5.2 mg/l (Gikunju et al., 1992). Evidence of dental fluorosis has also been reported among the residents of the lake shore, with cases being identified among the students of Kampi ya Samaki primary school (Näslund & Snell, 2005). This is a school which is located near the lake.

2.5. Effects of Fluoride in Drinking Water

The deficiency of fluoride in the body during tooth formation results in enamel demineralization. However, benefits are available for fluoride concentrations up to 1.5mg in drinking water. Levels between 0.5-1.5 mg/l prevent dental cavities (Guissouma et al., 2017). This therapeutic effect of fluoride at this concentration is achieved by the re-mineralization of the teeth and the bones (Srivastava & Flora, 2020; Kashyap et al., 2021). Higher concentrations beyond this have adverse negative effects.

Some of the adverse effects include dental and skeletal fluorosis. According to WHO guidelines, exposure to high fluoride levels can lead to mottling teeth (Guissouma et al., 2017).

Fluoride levels between 1.5-4.0 mg/l predisposes one to the risk of dental fluorosis. On the other hand, fluoride concentrations above 10 mg/l poses the risk of crippling fluorosis (Lacson et al., 2021). Figure 2.2 provides images of the effect of fluoride, a case of dental fluorosis in human beings and animals (Figure 2.2 (a) and Figure 2.2 (c)) and skeletal fluorosis in humans (Figure 2.2(b)).

Figure 2.2: Effects of excess fluoride in drinking water. (a) Dental Fluorosis in humans (b)Skeletal fluorosis in humans (c)Dental fluorosis in animals.

A summary of the range of fluoride concentration in water with the associated effects is provided in Table 2.2 (Jamwal & Slathia, 2022).

Table 2.2: Summary of the fluoride concentration with the associated health effects.

Concentration of Fluoride (mg/l)	Effect on Health
0.0 − 0.5	Limited growth and fertility, dental caries
0.5 − 1.5	Promote dental health, prevents tooth decay
1.5 − 4.0	Dental fluorosis (mottling of teeth)
4.0 − 10.0	Dental & skeletal fluorosis (pain in back and neck bones)
> 10.	Crippling fluorosis

2.6 Fluoride Level Guidelines

The guidelines on safe and beneficial fluoride concentration in water are provided in the standards given by the WHO although bodies in charge of environment and water in various countries also provide and implement country specific guidelines. WHO set the pre 1993 acceptable fluoride concentration in drinking water at 6 mg/l (Addison et al., 2020). This value, however, was found to be high. A new permissible limit was set at 1.5 mg/l fluoride concentration in the year 1984 and reaffirmed in 1993 (WHO, 2006).

Several countries have set their own standards as well. These guidelines are based on the climatic conditions which determine the risk of exposure (Frazão et al., 2011). Some countries simply adopted the WHO standard as their country specific standard, for example Kenya and Malawi (Addison et al., 2020). In Kenya, Water Services Regulatory Board (WASREB) recommended a value of 3 mg/l as the acceptable fluoride concentration (WASREB, 2008). However, this limit was found to be high. In the efforts to fight the effects of high fluoride concentration in drinking water, Kenya joined other countries in adopting the current WHO acceptable value of 1.5 mg/l as the limit for fluoride in drinking water (Rusiniak et al., 2021).

Similarly, Malawi adopted the former WHO value of 6 mg/l of fluoride concentration in drinking water (Addison et al., 2020). South Africa on the other hand is among the countries that uses its own set standards, different from the WHO guideline on fluoride concentration in the water. The country uses 0.75 mg/l fluoride concentration as the acceptable limit in drinking water (Murutu et al., 2012)

2.7 Fluoride Measurement Techniques

Several techniques have been devised to measure the fluoride concentration in water. The available techniques include the ion selective electrode method, SPADN's method, the automated complex-one method, ion chromatography method, the flow injection method and the Palintest method. The ion-selective electrode method and the SPADN's method are the most common (Baird et al., 2021). On the other hand, the Palintest method is a simple and easy to use technique.

2.7.1 SPADNs Method

This method has a linear analytical range of 0 to 1.4 mg/l fluoride concentration(Baird et al., 2021). The use of non-linear calibration can extend the range to 3.5 mg/l. The method is calorimetric and the colour development is virtually instantaneous in its application. The colour determination is made photometrically using either filter photometer or spectrophotometer.

The principle in the SPADNS fluoride determination method is based on the reaction between the fluoride and the zirconium dye lake. Fluoride reacts with the dye lake and the portion of the dye lake dissociates into a colorless complex anion ($ZrF6^{2-}$), and the dye. A curve developed from the standards is used to determine the fluoride concentration of the sample. Some substances in the water samples may adversely affect this method. Among these include the trivalent ions. pH also influences the SPADNS method (Baird et al., 2021). The method is provided under EPA’s sampling and compilation methods as EPA 340.1 method (Keith, 1996).

2.7.2 Ion Selective Electrode Method

This method uses fluoride electrode sensors. This involves potentiometric determination of the total solubilized fluoride in water with the help of a standard single junction sleeve –type reference electrode and a pH meter with expanded millivolt scale or selective ion meter with direct concentration scale for fluoride (Keith, 1996). The method analyses the simple fluoride ions as opposed to total fluoride (Keith, 1996). The method is suitable for measurement of fluoride concentrations in the range of 0.1 to 10 mg/l (Baird et al., 2021). The addition of prescribed buffer usually frees this method from the common interferences that would adversely affect the SPADN’s calorimetric method (Baird et al., 2021). The common buffer in use is the total ion adjustment buffer (TISAB). The degree of interference is usually dependent on the number of polyvalent cations present, the concentration of the fluoride ions and the pH of the sample. The addition of the pH 5.0 buffer containing strong chelating agents preferentially complexes the Al^{3+} ions (which are the common cause of interference), silicon ions, Fe^{3+} ions and eliminates the pH problem.

2.7.3 Palintest Method

The Palintest method is a zirconyl chloride and Eriochrome cyanine R based calorimetric method. It uses a photometer in the analysis of fluoride in the water (Fernando et al., 2018; De Silva et al., 2020). This method is well outlined in the Palintest Photometer Method for the examination of water and wastewater (Nkasah et al., 2010) . The technique was developed by Palintest Company (England), which is a leading water analysis laboratory. The company develops new water analysis techniques and portable equipment for water analysis on site (Goncharuk et al., 2009).

2.8 Defluoridation Techniques

Defluoridation techniques can be broadly divided into three main categories which include: chemical additive methods, contact precipitation and adsorption method (Modi & Soni, 2013; Jamwal & Slathia, 2022). All the methods under each of these categories have their merits and demerits. Some of the limitations, for example of reverse osmosis method, include its capacity to remove excess fluoride in the water (Kashyap et al., 2021). In addition, some of the methods have proved to be expensive. Single treatment techniques are therefore inadequate in the removal of fluoride and employment of hybrid treatment methods is recommended (Lacson et al., 2021).

2.8.1 Chemical Additive Methods

The chemical additive methods involve the addition of soluble chemicals to the water to be treated. Fluoride is removed through precipitation, co-precipitation, or adsorption onto the formed precipitate. One such method which has found extensive use in fluoride removal is Nalgonda Technique. The Nalgonda Technique traces back its origin to 1961 research by National Environmental Engineering Research Institute (NEERI), in Nagpur India (Piddennavar & Krishnappa, 2013). It has been widely applied in India, Kenya, Senegal, and Tanzania for fluoride removal in drinking water (Ayoob et al., 2008; Bhatnagar et al., 2011)

The method basically involves the addition of alum and lime to the water. In other instances, bleaching powder is added to aid in disinfection. Although it is cheap and easily applicable, the use of Nalgonda Technique has associated problems. It has been found that the amount of residual aluminium from this method in the water is very high and lies between 2-7 mg/l of aluminium ions (Bhatnagar et al., 2011).The recommended standard residual aluminium in water as per WHO is 0.2 mg/l (Maheshwari, 2006; WHO, 2006).The residual aluminium ions in the water therefore resulting from the fluoride removal by the Nalgonda technique poses the danger of the premature senile dementia disease, also known as the Alzheimer's disease (Modi & Soni, 2013; Murutu et al., 2010; Selvam et al., 2017). Studies have shown that amounts of aluminium ions in water as low as 0.08 mg/l have the potential of causing the Alzheimer's disease (Islam & Patel, 2007; Singh et al., 2019).

2.8.2 Contact Precipitation Method

In contact precipitation method, calcium, and phosphate compounds in the presence of saturated bone charcoal act as the catalyst for the precipitation of the fluoride as calcium fluoride or fluorapatite. Currently, artificial bone char (Hydroxyapatite-HAp) is in use as a substitute for bone charcoal. There are challenges associated with this method which include the challenge of low defluoridation capacity by HAp (Xu et al., 2019). In addition, the hydroxyapatite dissociates in the process and the resulting product is acidic, which lowers the pH of the water (Sankannavar & Chaudhari, 2019).

2.8.3 Adsorption Method

This technique involves the passage of raw water containing fluoride ions in a bed of fluoride removing material. This method among others, has been identified as the best method as it offers satisfactory outcome in fluoride removal (Bhatnagar et al., 2011). It is an efficient method offering a low-cost process for fluoride removal in water (He et al., 2020). The mechanism of action includes both physical, chemical or ion-exchange.

However, the adsorptive column becomes saturated, and its efficiency becomes low, hence regeneration is necessary.

Several adsorbents have been developed and studied for application for their potential in fluoride removal (He et al., 2020). Among the adsorbents used include, activated carbon, bone char, calcium-based minerals, diatomite, and brick.

2.8.3.1 Activated Carbon

Activated carbon refers to a family of highly porous carbonaceous materials with millions of tiny interlocking pores (Rogans, 2012). It has a high internal surface area and is therefore very efficient in adsorption (He et al., 2020). Although activated carbon has good porosity and efficient adsorption for organic pollutants, its affinity to inorganic pollutants such as fluoride is low (He et al., 2020). The use of activated carbon in adsorption other than the high level of porosity is attributed to the ease in the regeneration process through heat treatment (Al-Ghouti & Al-Degs, 2011). Study done by Bhakta et al., showed that fluoride adsorption by activated carbon was limited. The activated carbon needed further surface modification to improve its adsorptive capacity. Treatment with aluminium hydroxide showed the best results with fluoride removal of 99% being achieved (Bakhta et al., 2022). It is therefore clear that activated carbon on its own has poor affinity for fluoride in water unless modified. This is because the physical interactions between the carbon adsorbent and fluoride ions in the water are weak and this limits its adsorption capacity (Pang et al., 2020). Other than this, the cost of activated carbon makes it a less priority in the choice for use in defluoridation. Activated carbon is noted to be very costly in comparison to other adsorbents such as diatomite, with diatomite being cheaper in the order of 500 times the cost of activated carbon (Erdem et al., 2005; Wu et al., 2005).

2.8.3.2 Bone Char

Bone char is a product of technical pyrolysis process on the animal bones (Zimmer et al., 2018). The adsorption capacity of bone char is very high in comparison to some of the commercial adsorbents. Medellin and coworkers found that bone char adsorption capacity for fluoride is 2.8 and 36 times that of activated alumina and activated carbon respectively (Medellin-Castillo et al., 2007). Similarly, bone char has been identified as an environmentally friendly and cost-effective adsorbent for fluoride removal (Alkurdi et al., 2019).

Despite the high and promising capacity for fluoride removal, bone char is noted to have several resistances in its application in water treatment for drinking water. One such hindrance is the customs and religious beliefs in various parts of the world. Hindus for example do not accept char produced from cow bones while the use of bone char sourced from pigs is not acceptable in the Muslim faith (Alkurdi et al., 2019). Moreover, the bad taste associated with the water treated using bone char is a key factor that has decreased the application of bone char for water treatment as a cheap alternative adsorbent (Cheung et al., 2001; Tolkou et al., 2021).

2.8.3.3 Calcium-Based Minerals

Calcium based materials are among the substances that have found great application in water treatment. Several studies have detailed their application in the removal of various contaminants, for example in phosphorus (Bing et al., 2022), fluoride (Ting et al., 2022) and ammonium (Yin & Kong, 2014), among others. A key calcium-based mineral that has found great application in water treatment is hydroxyapatite (HAp). HAp is a calcium phosphate material with very high resemblance to the bone in its composition (Amenaghawon et al., 2022). It represents 65 – 70 % of the mineral composition in a natural bone (Sobczak et al., 2012).

The application of HAp in fluoride removal has further gained interest due to the high removal capacity of fluoride in water. Mourabet and coworkers found HAp to remove up to 86.34 % of fluoride at optimum conditions (Mourabet et al., 2015). Bishnupriya et al., also achieved a maximum removal capacity of fluoride by eggshell derived HAp to be 95 % (Bishnupriya et al., 2017). Despite this success, the shortcomings of HAp have been identified. Among these drawbacks is less surface area. HAp porosity is mainly due to macropores rather than micropores and there is a challenge of handling during water treatment due to poor mechanical properties. Additionally, HAp causes difficulty in separating it from the treated water due to its particulate properties and high-pressure drop-in column setups (Nayak & Bhushan, 2021).

2.8.3.4 Diatomite

Diatomite is chalk-like (white and yellowish in color), delicate and exceptionally fine-grained siliceous sedimentary stone (Zahajská et al., 2020). It is an algal diatom-derived, porous, light, and loose sedimentary rock. It is associated with the large category of algae that can move around freely in lake and ocean waters, referred to as the diatoms (Bakr, 2010). Most of the diatoms are tiny, measuring 0.75 mm or less, with few varieties reaching 2mm in length (Mehmedi & Koç, 2012).

About 40–70 million diatoms are present in each cubic inch of diatomite (Mehmedi & Koç, 2012). Diatomaceous earth (diatomite) often contains silica because it comes from the sedimentary rocks that include fossilized diatom skeletons (Lin et al., 2012;Sandhya et al., 2018). The silica surface is made of silanol groups spread over the matrix, as shown in Figure 2.3 (Al-Ghouti & Al-Degs, 2011). The silanol groups on the surface of diatomite determine the chemical characteristics, particularly the ability of diatomite to adsorb the organic compounds. The terminators in the diatomite surface are the hydroxyl groups and the oxygen bridges. These act as the adsorption sites in diatomite (Al-Ghouti & Al-Degs, 2011). The OH groups act as the adsorption sites by forming hydrogen bonds with the adsorbates (Zhuravlev, 2000). The siloxane bridges -Si-O-Si, in addition to the -OH groups may also act as the adsorption sites in diatomite. This explains the good adsorption properties of diatomite (Al-Ghouti & Al-Degs, 2011).

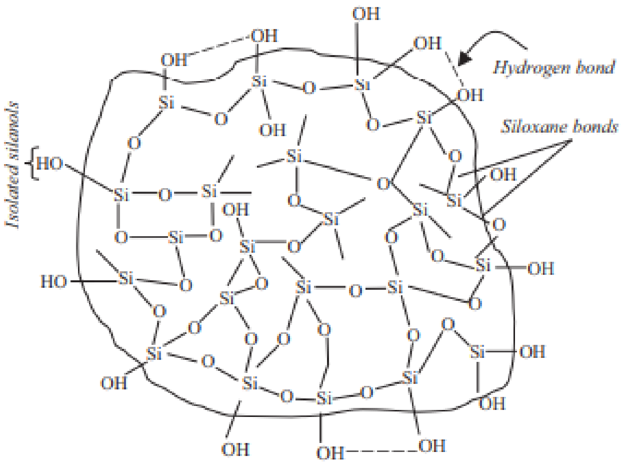

Figure 2.3: Structure of silica silanol groups, the siloxane bonds, and the hydrogen bonds (Al-Ghouti & Al-Degs, 2011).

Other than silica, diatomite contains trace amounts of other substances such as sodium, magnesium, iron, titanium, and aluminum oxides (Lin et al., 2012; Sandhya et al., 2018). This chemical composition dictates majority of both the physical and chemical properties of diatomite (Ivanov & Belyakov, 2008; Zahajská, 2020).

The common physical properties include high abrasiveness, insulating properties, inertness, low density, high porosity, high absorptive capacity, and high surface area. These properties make this material highly valuable for a wide range of applications (Ivanov & Belyakov, 2008; Zahajská et al., 2020).

Diatomite also has a high level of stability and particle structure that is unmatched by other silica-containing materials. The special properties such as low abrasiveness, low density, and high surface area make it useful as a filler and filter (Benkacem et al., 2016; Liguang et al., 2020). The effective density of diatomite typically ranges from 0.12 to 0.25g/cm^3 (Ivanov & Belyakov, 2008; Sun et al., 2013). Chemically, diatomite is noted to be inert although sometimes it can be affected by strong acids and alkali, for example hydrofluoric acid (Tsai et al., 2006).

2.8.3.4.1 Diatomite Deposits in Kenya

Diatomite is one of the key minerals that have been identified in Kenya (Ottichilo, 2015). The mining of diatomite in Kenya is one of the main mineral extraction activities (Davies & Osano, 2005). The deposits are spread along the Rift Valley region of Kenya.

Research have shown that the Olorgesailie pre-historic site in southern part of Kenya have diatomite deposits in addition to the alluvial and volcanic deposits formed over a million years ago (Behrensmeyer et al., 2002). Similarly, Kariandusi, near Lake Elementaita is associated with thick deposits of diatomite (Durkee & Brown, 2014). The deposit in this area has quality diatomite estimated at 6 million tons of diatomite deposits (Ottichilo, 2015).

The Lake Naivasha region has also shown evidence of diatomite deposits, with three diatomite beds exposed at Ol Njorowa Gorge, in the southern part of Lake Naivasha (Bergner & Trauth, 2004). The sedimentation patterns in the Baringo basin have also indicated the presence of several minerals with the sequence including diatomite deposits (Durkee & Brown, 2014). In addition to this, the county government of Baringo has identified diatomite as one of its potential minerals that the county can mine (Baringo County, 2014). Diatomite deposits in the Tiaty sub-county and Baringo

North sub-county borders have been identified as one of the minerals under conflict of resources for the communities living in the area (Kandagor & Moindi, 2019). It is therefore evident that Kenya has large quantities of diatomite in its mineral deposits.

2.8.3.4.2 Diatomite Extraction and Processing

In most of the countries where diatomite is mined, extraction is done by the open pit method, using combination of several machines such scraper-carriers, power shovels, bulldozers and trucks which remove the excavated materials (Namor & El-Gamouz, 2012). Open cast is the main extraction technique for diatomite because the deposits are located near the surface of the earth. Other than this, some diatomite deposits are found in freshwater and do not require open cast mining method (Namor & El-Gamouz, 2012; Zahradnik et al., 2019). The Africa Diatomite Industries Limited (ADIL) in Kenya, exploits quality diatomite deposits by this method at Kariadusi near Gilgil (Ottichilo, 2015).

After extraction, the mineral frustules are ferried by trucks for processing. The processing involves size reduction by hammer crushers. The crushing utilizes mild hammering due to the less dense property of the diatoms. Finally, the small sized diatomite particles are subjected to attrition scrubbing to further reduce the size (Ibrahim & Selim, 2010). The main reason for this process is to remove surface impurities from the diatomite through internal collision between the particles. The attrition scrubbing precedes the sieve classification by use of 74-micro sieve to remove most of the silt packing on the surface (Ibrahim & Selim, 2011; Sun et al., 2013).

Drying and calcination are also part of the process which the diatomite undergoes for its quality improvement. Typically, crude diatomite contains 40-60 % moisture content, and this requires reduction to lower values through drying (Aksakal et al., 2012). The calcination process is achieved by the use of heat treatment gas or fuel oil fired calciners (Ibrahim & Selim, 2010). The final process subjects the diatomite product further to a set of sequential equipment such as fans, cyclones and separators designed to perform various operations including removal of impurities, separation of powder particles into various sizes and expulsion of the absorbed water (Namor & El-Gamouz, 2012; Liguang et al., 2020). The final product is then packaged for its diverse applications (Bakr, 2010).

2.8.3.4.3 Applications of Diatomite

Filtration

Diatomite has numerous applications in filtration due to its special properties. This ranges from filtration of water, chemicals, pharmaceuticals, agro-food intermediates, and sugars in various industries. This is mainly due to the small size and high porosity of the diatomite particles (Bakr, 2010; Akafu et al., 2019; Ghobara et al., 2019). The numerous pores within the diatomite structure enable it to trap clay particles and any suspended particles during purification.

Most of the water treatment plants, breweries, chemical plants, and swimming pools have designs which allow the fluids to pass through diatomite-based structures. This helps to block and filter any impurities such as solid particles. This is because these particles cannot pass through the small pores in diatomite-based filter media (Postolachi et al., 2018; Reka et al., 2021).

Materials Improvement

Diatomite application spans the materials industry as well. It is used in the rubber industry for improvement of the tensile strength of rubber. This is attributed to the high absorption capacity and porosity contribution by diatomite (Lin et al., 2012;Liu & Li, 2020). Diatomite also improves adhesion resistance in rubber products (Shukry et al., 2017).

The cement industry utilizes raw materials rich in silicon dioxide. Diatomite being rich in silica content, find use as an additive in the cement industry to boost the silica content in cement (Guatame-Garcia & Buxton, 2018; Hasanzadeh & Sun, 2018). The silica content in diatomite is as high as 80%. (Hasanzadeh & Sun, 2018). Diatomite also facilitates ease in the grinding of the clinker during the cement manufacturing process (Wang et al., 2009).

Diatomite is also used as filler agent in manufacturing products such as paint, polishes, and toothpaste (Kietzman & Rodier, 1984). This is because of the inert and lightweight properties of diatomite. In the paint industry, diatomite acts as an extender or whitening agent (Dobrosielska et al., 2020). In polish, it is capable of cleaning surfaces through rubbing by facial scrubs or metal polishers (Shukry et al., 2017). The mildly abrasive property of diatomite is also beneficial on toothpaste (Deniz, 2011). The low thermal conductivity characteristics also make diatomite ideal in the manufacture of heat-insulating materials (Ivanov & Belyakov, 2008).

Adsorption and Absorption

The characteristic high porosity, large surface area, high permeability, low density, small particle size, thermal resistance and chemical stability makes diatomite a good adsorbent and absorbent material (Xu et al., 2015). It has therefore found application in various processes in which adsorption and absorption are involved.

In agriculture, it is used as an absorbent to hold water during soil treatment process. It also has a high absorption capacity with the purified diatomite being able to absorb as high as 145% of its weight (Lin et al., 2012; Nguyen & Dang, 2020). This makes it useful in absorbing liquids and semi-liquids such as oils, water, grease, anti-freeze solutions, syrups, and other acids (ElSayed, 2018).

The silanol groups in diatomite are very active and can react with many contaminants in water by forming hydrogen bonds, a property which makes it very relevant in water treatment (Xu et al. 2015). Recent research work has shown that diatomite can remove fluoride, with its capacity being improved highly through surface modification (Akafu et al., 2019).

Insect and Pest Control

Diatomite has been used as an alternative to original synthetic pesticides and insecticides in its powder form (Korunić, 2013). It absorbs moisture which is contained in the outer thin layer covering the surfaces of insects and pests. The dusts stick on insect’s body and destroys the protective layer resulting to death of the insects and pests. It therefore effective in insects and pests’ control (Korunić, 2013; Tu & Satoh, 2001).

2.8.3.4.4 Diatomite Modification

Depending on its application, diatomite may require modification. Modification could be through acid or base treatment or other techniques, including calcination. This helps to modify the structure of diatomite (Ibrahim & Selim, 2010). During the treatment process, for example, in calcination, the temperature ranges from 125 – 900 °C and the sample of treated diatomite is dissolved in a solution of 2 % sodium bicarbonate (Ibrahim & Selim, 2010). This results in small changes in the internal structure of diatomite (Lin et al., 2012; Costa et al., 2018).

2.8.3.4.5 Modification with Al $(OH)_3$

Aluminium hydroxide (Al $(OH)_3$) has an interaction with fluoride in a similar manner as in Nalgonda technique. In this case, the alum dissociates to a final product which has aluminium hydroxide. The aluminium hydroxide reacts with the fluoride ions to form Al-F complex which precipitates out of the water (Karunanithi et al., 2019).

2.8.3.4.6 Diatomite in Water Treatment

Diatomite application in water treatment dates to the period after the World War II (Fulton, 2000). Since then, it has been adopted in the United States as one of the Environmental Protection Agency’s (EPA) approved technology for treatment of surface water to meet the Surface Water Treatment Rule (SWTR) for drinking purposes (Xia et al., 2017). The earlier application and development of diatomite filters for water treatment was due to the need by the American army for light weight and portable water filter with the capability of removing entamoeba histolytica cysts. The use of diatomite made this possible with later research showing that the filter removed giardia and cryptosporidium cysts as well (Fulton, 2000).

Diatomite has also been applied in the removal of heavy metals in water in its raw and modified form (De et al., 2012; ElSayed, 2018; Zhao et al., 2019). It has also found application in oily water treatment (Zhang et al., 2018). In addition, diatomite has shown potential in fluoride removal in water (Akafu et al., 2019; Yitbarek et al., 2019). Modified forms of the diatomite have been found to have improved fluoride removal (Akafu et al., 2019; Xiang et al., 2023).

2.8.3.5 Brick

Bricks are obtained from clay with high temperature kiln firing or from the ordinary Portland cement concrete (Zhang, 2013). The production process for brick dates back the period over 7000 BCE when it was used in the form of sun-dried mud blocks (Murmu & Patel, 2018). Its use has come a long way and of age in its application. Clay has aluminium and iron oxides. Both aluminium and iron binds to the fluoride and hence its use in the removal of fluoride by clays and brick (Kariuki et al., 2015). Some clays for example, the montmorillonite clay is known for the high cation exchange capacity which can contribute to improved adsorption capabilities when used in water treatment (Ihekweme et al., 2020).

Brick has found use as a cheap sorbent in wastewater treatment including removal of heavy metals in the water. This is attributed to the negative charge on the surface which gives it the ability to attract the cations on its surface (Priyantha & Bandaranayaka, 2011; Mhawesh & Ali, 2020).

One of the advantages of using brick is its ability to be produced from waste materials. The shortage of the natural sources of materials for brick in various parts of the world production has led to research which has supported the potential of production from waste materials such as demolition waste, limestone powder and cement kiln dust among others (Lianyang, 2013). Other than this, brick does not require impregnation or activation in its preparation as an adsorbent. The accessibility in rural areas as well reduces its cost in comparison to other adsorbents such as commercial activated charcoal (Yadav et al., 2006).

2.8.3.5.1 Fluoride Removal by Brick

Several studies have tested the removal of fluoride by brick in water (Padmasiri & Dissanayake, 1995; Chidambaram et al., 2003; Ahamad et al., 2019; Abd Ali & Ismail, 2021). Results have indicated that brick has medium capability for fluoride removal (Padmasiri & Dissanayake, 1995). The removal of fluoride by brick has been found to be good at low concentrations of fluoride up to 5 mg/l (Ahamad et al., 2018) ,with bricks of size 6.3 - 4.75 mm having good fluoride removal capacity of up to 90.33% for an initial concentration of 3 mg/l of fluoride (Manjunath et al., 2014). Despite this, little has been done to shed light on the effect of mixing brick with other adsorbents in removal of fluoride. This still offers a great opportunity for more research to mixing brick with other adsorbents in removal of fluoride.

2.9 Diatomite and Brick in View of Cost

Fluoride removal using diverse adsorbents have been considered by several studies and compared in terms of their economic feasibility (Ayalew, 2020). Adane and co-workers conclude that clay minerals are low-cost adsorbents. This includes fired clays (brick) (Fernandes, 2019). Similarly, diatomite (diatomiceous earth) has been classified under low as cost adsorbents (Gomoro et al., 2012). When compared to the commonly used adsorbents including activated carbon and activated alumina, diatomite emerges as a cheap adsorbent, with activated carbon doubling up as expensive due to the need for pH adjustments when used for fluoride removal (Ingle et al., 2014). The process involved in the application of activated alumina for fluoride removal is also expensive (Agarwal et al., 1999).

Among the factors considered in accessing the cost of an adsorbent is the cost of precursor collection (Mukherjee et al., 2018). The availability of both diatomite and bricks in Kenya reduces the cost of access. Bricks are locally made in Kenya (Oteng'i & Neyole, 2007; Zhang et al., 2017). Similarly, diatomite is readily availabe in Kenya with the current mining in Kariandusi and with upto Ksh. 200 million diatomite mine to be set up in Baringo (Kipsanai, 2017). Diatomite and brick are therefore promising low-cost adsorbents for consideration in fluoride removal in Kenya.

2.10 Summary and Research Gap Identification

Diatomite is a locally available material in Kenya and deposits have been identified in Baringo in addition to the currently exploited deposits at Kariandusi, Nakuru County. It is a cheaper option compared to activated commercial carbon but equally effective as activated carbon in filtration process (Akafu et al., 2019). The effectiveness of diatomite in defluoridation is low but is improved by surface modification (Akafu et al., 2019). Bricks have also been found to remove fluoride due to the presence of iron and aluminum oxides (Swarnakar et al., 2007). A filter media formulated from surface modified diatomite and brick could be more effective and easily customizable to household level for defluoridation. Previous studies have not considered mixing surface modified diatomite and brick.

This study bridges this research gap by determining the optimum mixture of surface modified diatomite and brick for fluoride removal. The optimization of the defluoridation media was achieved through the response surface methodology by means of the Box-Wilson central composite design using the design expert software. The study is important because it evaluates the potential of low cost and locally available materials in fluoride removal.

CHAPTER THREE: MATERIALS AND METHODS

3.1 Materials and Equipment

Several materials and equipment were used in this research. They included: aluminium chloride (analytical grade), diatomite, distilled water, photometer, Fluoride AP179 reagents, pH meter, magnetic stirrer, Edwards Sputter Coater S150B (England) and Scanning Electron Microscope with energy disperse x-ray capability (CamScan 44 and CamScan 24). The photometer used was ELE International Paqualab^{TM} Photometer (England). On the other hand, SensION pH meter (Germany) was used for pH measurements. Some of the major equipment used is given in Figure 3.1.

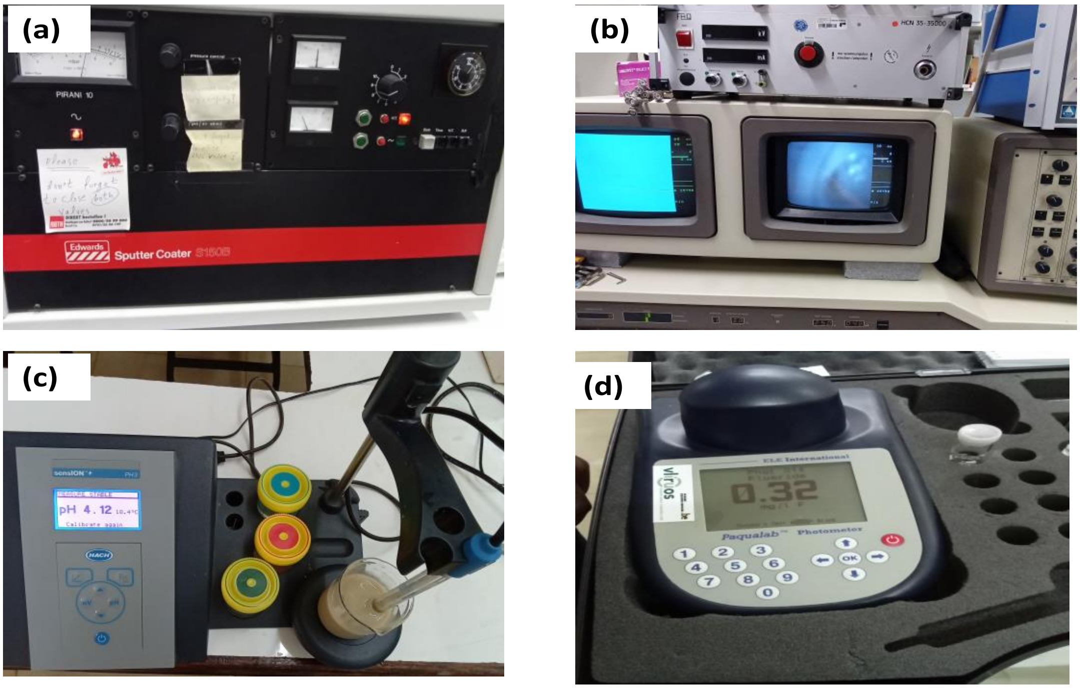

Figure 3.1: Major equipment used. (a) Sputter Coater (S150B), (b) CamScan 24 SEM (c) SensION pH meter (d) ELE Paqualab^{TM} Photometer.

3.2 Methods

3.2.1 Study Area

Lake Baringo is located between the longitudes 36o00’ E and 36o10’ E and the latitudes 0o 30’N and 0o45’ N (Ondiba et al., 2018). It is at 105 Km south of Nakuru, and 60km north of the equator (Renaut et al., 2023). It is the largest Kenyan freshwater rift valley lake, with a surface area of upto 108 km2, and is the source of water for domestic use and livestock consumption for the communities in the lake basin (Onyando et al., 2005).

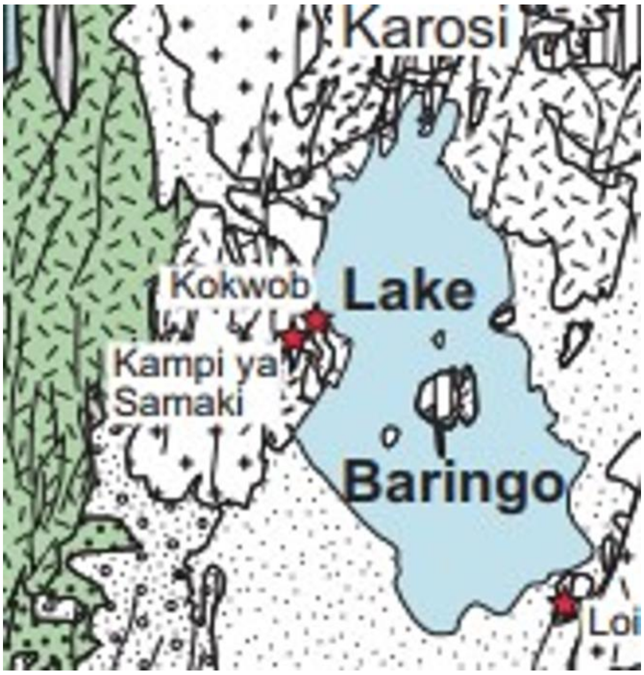

Figure 3.2: Map of Lake Baringo (Renaut et al., 2023).

Kampi ya Samaki is the main village on the shore of the lake (Näslund & Snell, 2005; Deichsel, 2019). It is located on the north-west shoreline of the lake as shown on Figure 3.2. The shore at Kampi ya Samaki was selected for sample collection owing to its large population and the busy town on the shore of the lake, which depends on the water for drinking and domestic use (Onyando et al., 2005).

3.2.2 Sample Collection

Four samples were picked from four different sections of the lake at Kampi ya Samaki where the residents draw the water for drinking and cooking. The four samples were identified as KYS.M, KYS.A1, KYS.A2 and Soi.M. KYS. M was a sample collected at the busiest section of the shore at Kampi ya Samaki. This is the section too where many fetched the water for drinking and domestic use. Similarly, KYS.A1 and A2 also registered beehive of activities including fish scale removal and water fetching as well. Soi .M was on the northern side of the town, and was a less busy section of the shore, marked mainly by water fetching by the locals.

The sample picking and collection was as guided by the Standard Methods for the Examination of Water and Wastewater (Baird et al., 2021). The samples of water were picked in 5 litre polyethylene bottles and transported to the lab for analysis.

3.2.3 Water Sample Characterization

The samples were characterized for fluoride content using the ELE International Paqualab ^{TM} palintest photometer (England) shown in Figure 3.3(a). The Fluoride AP179 reagent used in the analysis with the photometer was obtained from DLA Scientific Ltd (Kenya). All samples prepared were diluted to values equal to or less than 1.5 mg/l of fluoride ions. This is the concentration which is within the range of the photometer reading. Dilution was done with the use of distilled water. 10 ml of the diluted sample was placed in the photometer tube and Tablet No1 reagent added. The tablet was crushed with agitation to full dissolution. After dissolution, Tablet No 2 reagent was added and crushed with agitation until fully dissolved and the solution turned red to pink in colour. The solution was left to stand for 5 minutes. After 5 minutes, the equipment was blanked with distilled water then the fluoride content from the prepared sample was read. The readings were multiplied by a factor of 10 to get the actual fluoride content. Figure 3.3 (b) shows the blank and a sample treated with the palintest reagents ready for reading in the palintest photometer.

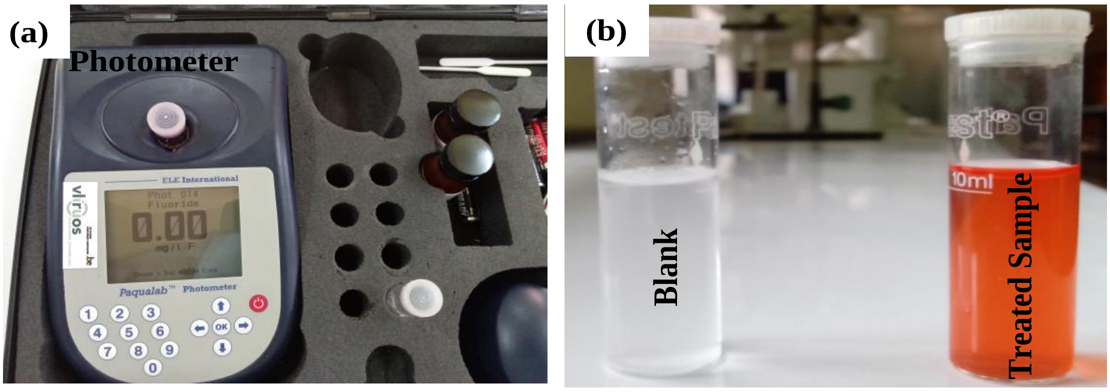

Figure 3.3: Palintest photometer kit and the samples. (a) Palintest photometer kit (b) Blank and treated sample: pink colour is an indicator of the presence of fluoride in the sample treated with the palintest fluoride test reagents.

3.2.4 Surface Modification of Diatomite

The diatomite collected from ADIL company (Kenya) was subjected to surface modification based on the procedure employed by Akafu et al., with some little modifications introduced (Akafu et al., 2019). One hundred grams of the sample were weighed and washed with distilled water to remove dirt. The washed sample was then transferred to a 1litre glass beaker and 400ml of 1 M aluminium chloride solution was added. After the addition of the aluminium chloride solution, an equal amount of 3M sodium hydroxide was immediately added to the mixture as guided by equation 3.1. The mixture was then stirred at 200 rpm for 4 hours. After 4 hours, the mixture was acidified to a pH of 2 using 1M hydrochloric acid and then stirred for 30 minutes. The solid was then washed again with distilled water with the aid of a vacuum filter until the pH of the supernatant was 6. The solid was then dried in an oven at 80 °C for 12 hours. After the drying process, the dried solid was removed, covered with aluminium foil, and left to cool to room temperature. The dried modified diatomite was then crushed and sieved through a 280 µm sieve to obtain fine powder. The powder was placed in a plastic container tightly closed with a cork and kept ready for use.

$$\mathrm{AlCl_{3\,(aq)}} + \mathrm{3NaOH_{(aq)}} \rightarrow \mathrm{Al(OH)_{3\,(aq)}} + \mathrm{3NaCl_{(aq)}} \tag{3.1}$$

3.2.5 Brick Preparation Process

Red bricks were obtained from Kesses, near Moi University. The bricks were crushed using heavy weights at the mechanical engineering department of Moi University to reduce particle sizes. The crushed bricks were then sieved through 280 µm sieve in the Chemical Engineering laboratory to obtain fine powder. The fine powder was kept in a sealed polythene bag ready for use.

3.2.6 Surface Morphology Studies

The surface morphology of the adsorbents were studied using the scanning electron microscope following the procedure used by Suárez-Peña et al., in his study of filter substrate (Suárez-Peña et al., 2016). Approximately 1cm^2 sample was flat mounted on the aluminium SEM stubs using a two-sided adhesive film to adhere the sample to the stub. The sample was then sputtered with a thin coating of gold layer using the Pirani 10 sputter coater at chemistry department, University of Siegen Germany. The microscopic observation was then made by means of SEM equipped with secondary electrons (SE) and backscattered electrons (BE) detectors. This provided detailed information on the morphological characteristics and texture of the surface of the sample as well as the particulate composition of the samples as obtained from the micrographs.

Figure 3.4: Sample preparation for SEM analysis. (a)Gold sputtering in the Pirani 10 sputter coater, (b) Gold sputtered sample in the SEM machine sample holder (c) prepared sample in the sample storage box.

3.2.7 Adsorbent Mixture Formulation Process

The adsorbent mixture formulation process was carried out in several steps. Initially simulated water was prepared in the laboratory using sodium fluoride. The fluoride contamination was made up of 10 mg/l of fluoride. The optimum amount of surface modified diatomite required to remove fluoride to a residual level of 1.5 mg/l from 10 mg/l was determined. The determination was done by dosing varied masses of the surface modified diatomite to 1 L of the fluoride contaminated water. Stirring was carried out for 1 hour in a batch process and the residual fluoride in the water was measured using a photometer. This process was repeated for brick dosage to determine the optimum brick required to reduce the fluoride content to the WHO standard of 1.5 mg/l. The mass ratios of the adsorbents (surface modified diatomite and brick) were then optimized through experimental design.

The design of the experiment was done using Box-Wilson central composite design (CCD) of the Response Surface Methodology, using design expert software, version 13.0. The masses of surface modified diatomite and brick were used as the input variables and residual fluoride as the response variable in the design. Five levels and two factors were used, which yielded a total of 13 experiments with 5 replications at the center points. The optimum masses of surface modified diatomite and brick, required to reduce the fluoride in water to 1.5 mg/l, as obtained in the preceding experiments, were used as the maximum limits in the design of experiment.

The choice of CCD was based on its ability to predict optimized conditions accurately with a minimum number of runs (Dhawane et al., 2018). Table 2.3 shows the independent variables and their levels for the experiment.

Table 2.3: Independent variables and their levels in CCD design. Codes: X1- Mass of modified diatomite (g), X2-Mass of brick (g).

	Variable Levels				
Variable	$-\alpha$: -1.414	-1	0	1	α: 1.414
X1	0.236544	5	16.5	28	32.7635
X2	10.2944	60	180	300	349.706

The optimized masses of surface modified diatomite and brick which resulted in the least residual fluoride in the water, from the DoE model, was used to constitute the mixed adsorbent media.

3.2.8 Isotherm Studies

3.2.8.1 Modified Diatomite

The studies on isotherms were carried out for the surface modified diatomite by dosing 2g of the surface modified diatomite to 125 ml samples of water with varied concentrations of fluoride ions. The fluoride ion concentrations ranged from 100 mg/l to 5 mg/l. The mixtures were stirred for a constant time of 30 minutes at a rate of 200 rpm, after which the equilibrium concentration of the F- ions was measured using the photometer and recorded for each sample. All studies were carried out at room temperature (20^{o}). The results were analyzed and fitted to both Langmuir and Freundlich isotherms.

3.2.8.2 Brick

The studies on isotherms were carried out for brick by dosing 20 g of powdered brick to 125 ml samples of water with varied concentrations of fluoride ions. The fluoride concentration was 100 mg/l to 10 mg/l. The mixtures were stirred for a constant time of 30 minutes at a rate of 200 rpm. The equilibrium concentration of the F- ions was then measured using the photometer and recorded for each sample. The experiments were conducted at room temperature (20^{o}). The results were analyzed and fitted to both Langmuir and Freundlich adsorption isotherms.

3.2.9 Kinetic Studies

3.2.9.1 Modified Diatomite

The kinetic studies for surface modified diatomite were carried out with the optimum mass of the surface modified diatomite. Mass of the adsorbent (3.5 g) was dosed in 125 ml of water samples containing 10 mg/l of F- ions. Each water sample was stirred at a rate of 200 rpm for varied periods of time of 0 - 150 minutes. Residual fluoride concentration was determined after every set of time and recorded. The data collected was analyzed and fitted to both pseudo first order and pseudo second order kinetic models.

3.2.9.2 Brick

The kinetic studies for brick were carried out with the optimum mass of powdered brick. Mass of the brick (37.5 g) was dosed on 125 ml of water samples containing 10 mg/l of F- ions. Each water sample was stirred at a rate of 200 rpm for varied periods of time of 0 - 135 minutes. Residual fluoride concentration was determined after every set of time and recorded. The data collected was analyzed and fitted to both pseudo first order and pseudo second order kinetic models.

3.2.9.3 Diatomite-Brick

The study of the kinetics for the diatomite and brick mixture was carried out with the optimized mixture of masses of brick and diatomite as obtained from the Design Expert software optimization. A total of 24.5 g of the mixture (22.2 g of brick and 2.3 g of surface modified diatomite) was dosed on 125 ml of water samples containing 10 mg/l of F- ions. Each water sample was stirred at a rate of 200 rpm for varied periods of time of 0 - 150 minutes. Residual fluoride concentration was determined after every period and recorded. The data collected was analyzed and fitted into both pseudo first order and pseudo second order kinetic models.

3.2.10 Breakthrough Studies

A mixture of the surface modified diatomite together with brick as optimized from the DoE model was made. The mixture was placed in a perforated plastic container with cotton wool at the base. The water sample was put on the container and constituted a total of 1 cm thickness. The water was allowed to trickle down through the adsorption media. The residual fluoride of the adsorbate was monitored with time to obtain the breakthrough curve results. Figure 3.5 shows a summary of the set up used in the breakthrough studies.

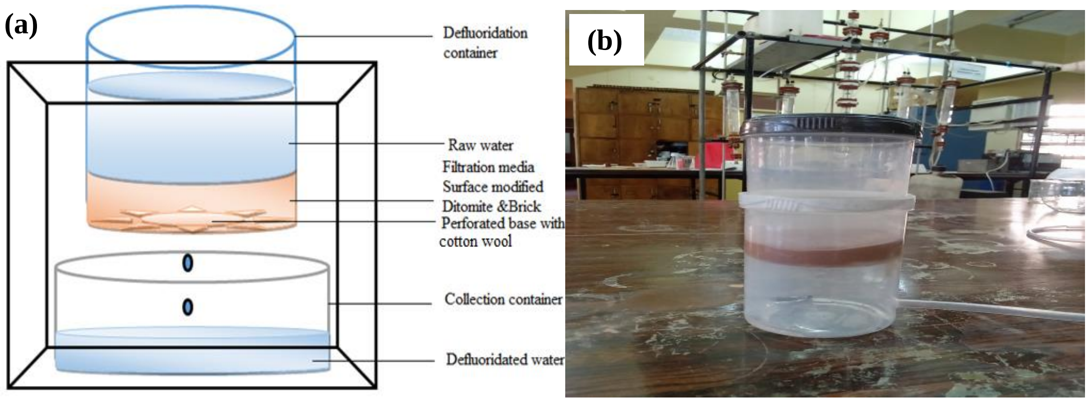

Figure 3.5: Set up of the column studies (a) Set up drawing (b) Actual set up.

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1 Introduction

This chapter presents the obtained results and its interpretation. The results are discussed in detail from the findings of the material characterization, the sample characterization to the outcome of the defluoridation process. The isotherms are discussed together with the kinetic models as well as the breakthrough analysis. The findings of each study are presented in subsections along with their interpretation.

4.2 Surface Morphology Analysis

4.2.1 Diatomite Morphology

The microstructural features of diatomite in its raw, modified and used form were obtained by the SEM imaging. The SEM micrographs of the raw diatomite samples are shown in Figure 4.1. The micrographs showed that the diatomite was majorly composed of centric diatom particles, but with presence of pinnate structures as well (Figure 4.1 (a)). Figure 4.1(a) also shows high void volume in the structure. A close view of the particles (Figure 4.1(b)) showed high porosity in the diatomite particles. This agrees with the work of others. Hong et al. observed diatomite samples obtained from China and found that the diatomite was mainly composed of centric diatom particles with two discs attached to each other by circular girdle. In addition, they observed numerous skeletal pores and inter-particle pores between the diatom particles which are akin to the high porosity of diatomite (Hong et al., 2006). Similarly, Izuagie and co-workers found pinnate structures on the diatomite sourced from Kariandusi mine in Kenya, with high porosity (Izuagie et al., 2016). The high porosity observed in the structure explains the good performance of diatomite in adsorption.

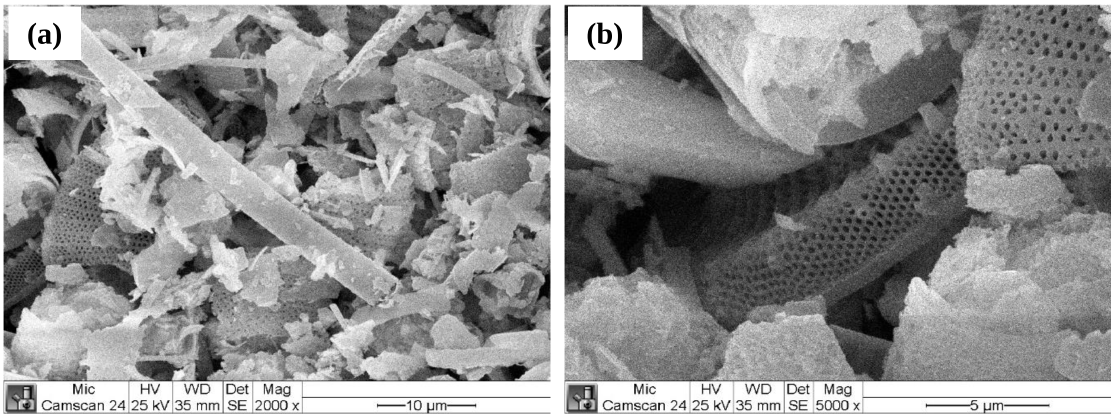

Figure 4.1: SEM Images of the raw diatomite. (a) The images show a diverse structure in the material (b) The material depicts high porosity

Figure 4.2 shows the diatomite after modification of the surface with $Al(OH)_3$ (Figure 4.2(a)) and after use in the defluoridation process (Figure 4.2 (b) and Figure 4.2 (c)). From Figure 4.2 (a), the surface of the diatomite was successfully modified. A new layer was observed to cover most of the pores on the diatomite surface and the pores which are still visible have been reduced in size due to the new layer of material introduced during the modification process. On the other hand, the used diatomite has the Al - layer used up and clear features of diatomite emerge again (Figure 4.2 (b)). In addition, regular shaped deposits are observable on the surface of the used diatomite as seen in Figure 4.2 (c). This could be deposits of AlF_3 in some metastable phase. Metastable phases of AlF_3, such as γ, t and ϵ exist, and may refer to the impure form or mixtures of beta phases (Alonso et al., 2000). These deposits are among the components that aid in the removal of fluoride by diatomite.

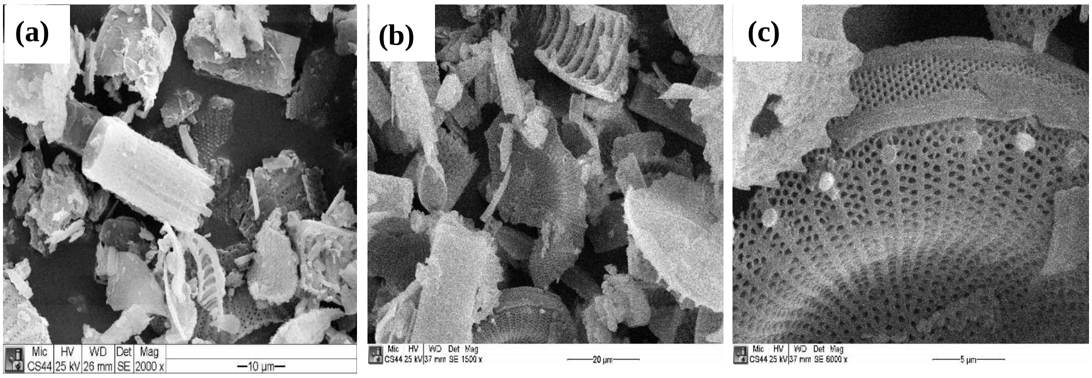

Figure 4.2: Surface Morphology of the modified and the used diatomite. (a) Surface modified diatomite, new layer has been attached to the surface and the pore sizes reduced after modification (b) Used diatomite (c) New features identifiable on the used diatomite.

4.2.2 Brick

Surface morphology of brick was studied using Scanning Electron Microscope to determine any unique features in its structure. The findings showed the presence of particulate matter distributed in its structure (Figure 4.3a). The presence of the space in between the particles is evidence of good porosity in brick. In addition to this, further focus on the structure of the particles in the brick revealed a structure like that of quartz (Figure 4.3b). This agreed with the findings of Ouyang et al. (Ouyang et al., 2021). Ouyang and co-workers compared the morphological structure of clay brick powder to that of commercial quartz and found out that there was not much difference in terms of morphological features between clay brick powder and quartz (Ouyang et al., 2021).

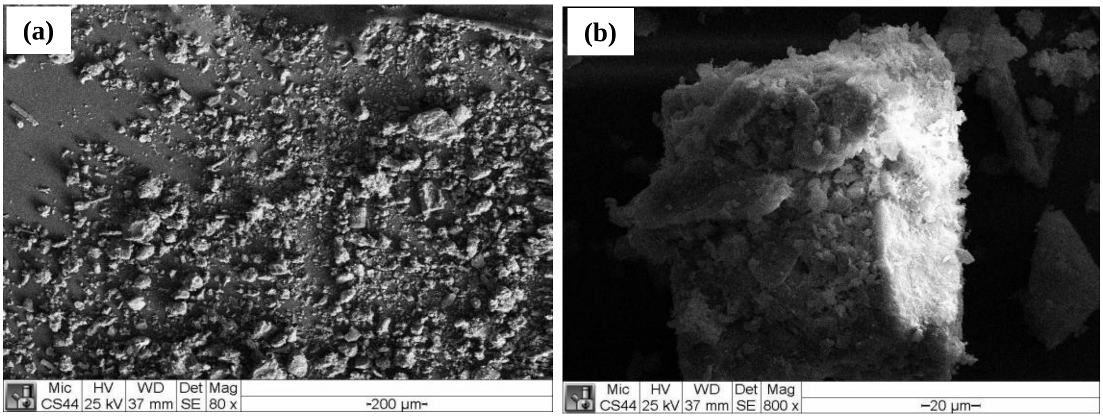

Figure 4.3: Morphology analysis of brick. (a) Brick is shown to have a structure with distribution of particulate matter depicting high porosity of the material (b) The structure of the particulate matter shows a similar structure to that of quartz crystals.

4.3 Energy Dispersive X-Ray Spectroscopy Analysis

4.3.1 Diatomite

An energy dispersive x-ray spectroscopy (EDS) analysis was carried out to determine the elemental composition of the diatomite samples before and after modification and after being used in the defluoridation process. Figure 4.3 shows the results of EDS analysis on the samples. From Figure 4.4, raw diatomite is shown to have silicon (Si), aluminium (Al), potassium (K), calcium (Ca), iron (Fe) and oxygen (O). Silicon had the highest counts in all the samples. This is because diatomite is mainly composed of silica ($SiO_2.\ n\,H_2O$) in its structure. Modification of the diatomite by Al $(OH)_3$ resulted in an increase in the count of oxygen and aluminium, reduction in silicon count and introduction of chlorine (Cl) in the sample. On the other hand, other elements including K, Ca and Fe were not detected after modification of the diatomite sample. Similarly, the oxygen count in the sample further increased after the defluoridation process. The Al count after the defluoridation process decreased. This can be attributed to part of the ions being used in the defluoridation process. The increase in the oxygen count after modification and after the defluoridation process could be attributed to the oxygen coming from the water molecules retained in the silica or the alumina matrix of the diatomite, during the modification process and the defluoridation process (Xu et al., 2015a). The absence of K, Ca and Fe after modification can be attributed to the ions of these elements being used up in the side reactions during the time of diatomite modification. Chloride ions in the modified diatomite are from the aluminium chloride and hydrochloric acid used in the modification process. Similarly, the reduction in the Si count after modification could be because of removal of Si ions by aluminium hydroxide and sodium hydroxide during the process of modification (Tokoro et al., 2014).

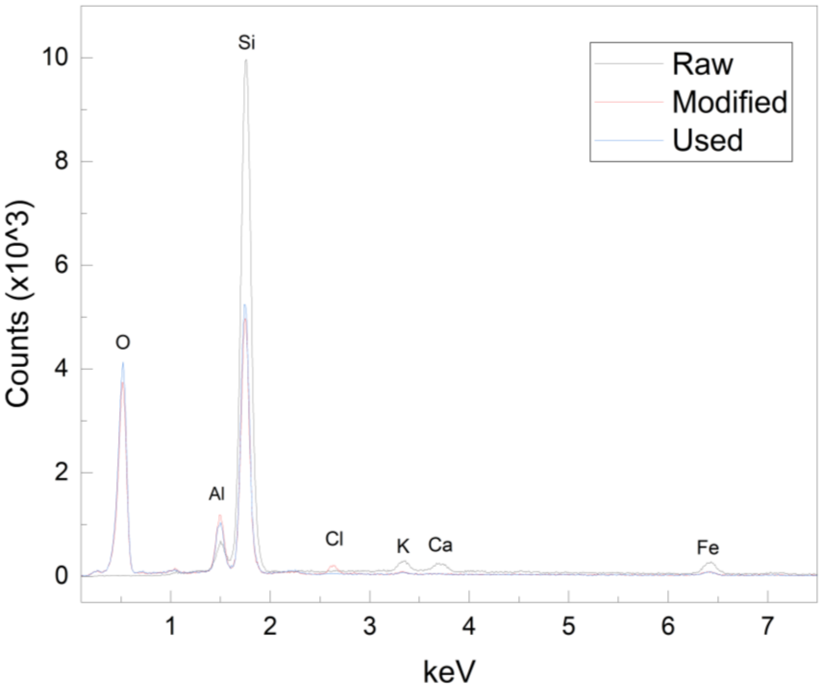

Figure 4.4: EDS analyses for Raw, Modified and Used diatomite samples. The Microanalyses shows a difference in elemental composition for the three samples.

4.3.2 Brick

The energy dispersive x-ray analysis of brick sample agreed with the findings of the SEM analysis. It is noted that a typical brick powder is a mixture of oxides of silicon, aluminium, iron, calcium, and magnesium (Yadav et al., 2006). On the other hand, quartz is composed of 98.8% silicon dioxide (Ouyang et al., 2021). The presence of highest counts of silicon and oxygen respectively in Figure 4.5a confirms the composition of brick to be mainly composed of quartz. It is however evident from Figure 4.5a, that brick has many other elements present in it including aluminium, titanium, selenium, potassium, and hafnium. Ouyang et al. found traces of calcium, magnesium, and sodium metals in addition to silicon dioxide in their clay brick powder (Ouyang et al., 2021). The difference in the elemental composition of brick as revealed by the microanalyses of brick in different studies can be attributed to the difference in the soil compositions of the areas from which the bricks were sourced. The defluoridation capacity of brick is aided by the presence of the metal oxides in the brick which interacts with the fluoride in the water (Yadav et al., 2006). The presence of iron in abundance in the brick was confirmed during the defluoridation process in which the magnetic stirrer used for stirring, had a lot of iron attached to it at the end of every experiment as shown in Figure 4.5 (b).The metallic iron present in abundance in brick explains the low fluoride uptake capacity by brick, since the defluoridation by brick is mainly aided by the metallic oxides present (Ihekweme et al., 2020).

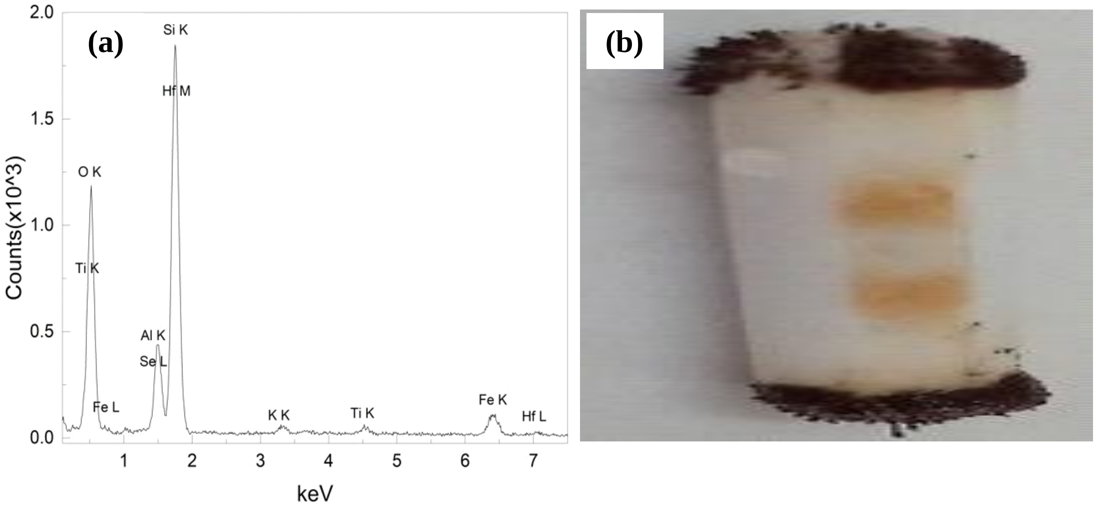

Figure 4.5: Elemental analysis of brick. (a) EDS microanalysis of brick (b) Iron on the magnetic bar after batch experiments involving magnetic stirring.

4.4 Characterization of Water Samples from Lake Baringo

The characterization of the water samples collected from the lake showed that the lake has excess fluoride, which is almost 5 times the level recommended by WHO. Table 4.1 provides a summary of characterization of the water samples from the lake. As seen from Table 4.1, all the sample points had fluoride concentration above 5 mg/l. Kampi ya Samaki main section sample (KYS.M) registered the highest concentration of fluoride in the water (7.4 mg/l), followed by the sample picked from Kampi ya Samaki section A1 and A2 respectively (6.1 mg/l and 6.0 mg/l). The sample picked from Kampi ya Samaki Soi section (Soi.M) registered the lowest concentration of fluoride (5.9 mg/l).

Table 4.1: Characterization results of the water from Lake Baringo.

Sample Code	F- Concentration (mg/l)/10			Average (mg/l)/10	Actual F- Conc (mg/l)	pH (at 20^{o}C)
	1st	**2nd**	**3rd**			
KYS. M	0.74	0.74	0.74	0.74	7.4	8.51
Soi. M	0.59	0.59	0.59	0.59	5.9	8.47
KYS.A1	0.59	0.60	0.63	0.61	6.1	8.44
KYS. A2	0.60	0.60	0.60	0.60	6.0	8.43
Average Lake water F-conc (mg/l)					**6.3**	**8.5**

The high level of fluoride recorded for the sample KYS.M**,** could be attributed to the activities in this section. The section (Kampi ya Samaki main) was marked with docking of boats, arrival of fishing and tourist boats, drawing of water for drinking and domestic use by the locals among many other activities. These activities are bound to cause disturbance and mixing of the water in this section. Given that the fluoride is originating from the rocks underneath the water (Chernet et al., 2001), the disturbance of the water could accelerate the leaching of the fluoride from the rocks into the lake water. Similarly, sections A1 and A2 had a myriad of activities ranging from clothes washing, water fetching, fish scale removal and cleaning of the caught fish among other activities. The many activities in these sections too can explain the high levels of fluoride recorded from the samples picked in the sections (KYS.A1 and KYS.A2). Soi section on the other hand was marked by quietness and few observable activities, mainly being fetching of drinking water by the locals. This can explain the recorded lower concentration of fluoride in comparison to the other sections of the lake sampling points. Despite this though, the fluoride level of 5.9 mg/l was still very high and indicates the overall high level of fluoride in the lake above the recommended limit of 1.5 mg/l in drinking water. Despite these detrimental levels of fluoride in the lake, the socio-economic data shows that the riparian community living around the lake depends on this same water for domestic purposes (Nyakeya et al., 2020).

The pH in the lake water was also found to be very high, with the average value being 8.5. This can be attributed to the positive alkalinity of the residual calcite in the water resulting in low concentration of the calcium ions in the water. The precipitation of the calcium ions in the form of calcium fluoride causes the alkaline properties of the water and hence the high pH (Chernet et al., 2001). On the other hand, the high pH promotes the fluoride leaching from the bed rocks into the water and explains the high fluoride level recorded (Srinivasamoorthy et al., 2012).

Previous studies on the characteristics of the Lake Baringo water found similar results. Gikunju et al. found fluoride level in the lake to be 5.4 mg/l (5.3 mg/l - 5.6 mg/l) with a pH value of 10.4 (10.1 - 10.7) (Gikunju et al., 1992). The Kenya Marine and Fisheries Research Institute (KMFRI) found the level of fluoride in the river tributaries supplying water to the lake to be in high levels greater than 1 mg/l (Nyakeya et al., 2020). Similarly, Walumona and co-workers found the levels of fluoride in the lake to be between 6.62 ± 5.20 mg/l to 7.59 ± 5.75 mg/l (Walumona et al., 2021). It is therefore clear from the fluoride concentration levels in Lake Baringo are way above the recommended limits and treatment is the appropriate measure required with a high level of urgency.

4.5 Removal of Fluoride by Diatomite and Brick

The removal of fluoride in water by diatomite and brick was studied to determine the optimum doses of the individual adsorbents that can remove the fluoride to the WHO standard of 1.5 mg/l. In addition, the raw and modified diatomite samples were compared to determine the impact of surface modification of diatomite on fluoride removal. Figure 4.6 shows the fluoride removal by both diatomite and brick. From Figure 4.6(a) fluoride removal by raw diatomite is low. For a litre of fluoride containing water, at initial concentration of 10 mg/l fluoride, 28 g of raw diatomite removes fluoride to a residual value of 9.5 mg/l in 1 hour. On the other hand, surface modified diatomite is very effective. A similar dose of the modified diatomite under the same conditions removes fluoride to 1.5 mg/l. This was the optimum dose for the modified diatomite for removal of fluoride in water. With similar initial concentration of fluoride of 10 mg/l, Akafu and coworkers found the optimum dosage of Al $(OH)_3$-surface modified diatomite to be 25 g/l (Akafu et al., 2019). The difference between the optimum values obtained by Akafu et al. and the present study could be due to the slight difference in diatomite modification procedures used. Figure 4.6(b), indicated low fluoride removal in water by brick. To achieve a residual fluoride content of 1.5 mg/l, a total of 300 g/l dosage of the brick powder is required. Despite this low capacity, the low cost of bricks, and its ease of accessibility makes it of interest in defluoridation (Yadav et al., 2006).

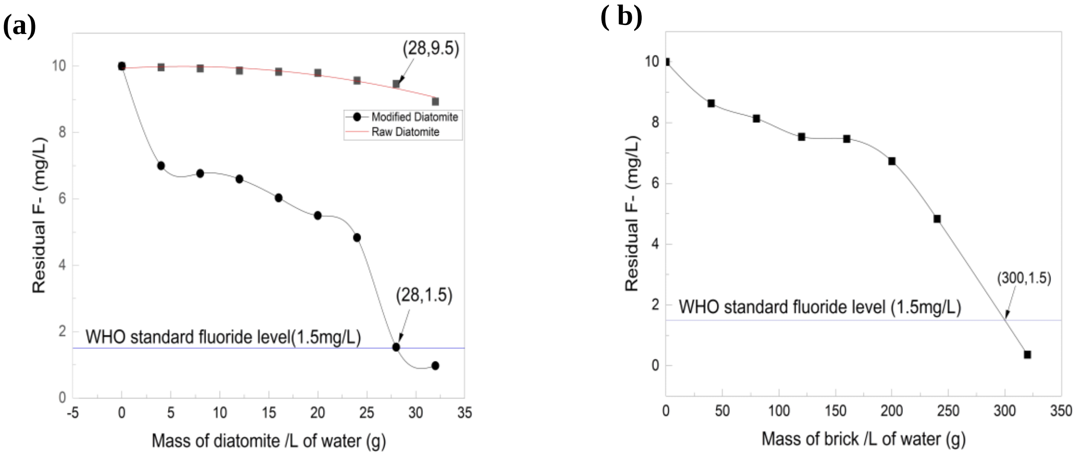

Figure 4.6: Fluoride removal by diatomite and brick samples (a) Raw and modified diatomite. Modification of the diatomite surface greatly improves its fluoride removal (b) Brick.

4.6 Adsorbent Mixture Optimization

The experimental outcome of the experimental design (DoE) together with the predicted outcome is presented in Table 4.2. The predicted outcome was with respect to the quadratic model presented in Equation 4.1. A test of the data presented in Table 4.2 for fit, with consideration of the linear, two-factor interaction (2FI), quadratic and cubic models showed the highest value of adjusted R^2 was with respect to the quadratic model. The adjusted R^2 for the quadratic model was 0.9466. With the consideration of the p-value and the predicted R^2 values, the quadratic model was suggested and chosen in the present study.

Table 4.2: CCD Matrix with Experimental and Predicted Residual Fluoride.

Run	X1: Diatomite (g)	X2: Brick (g)	Residual F-: Experimental (mg/l)	Residual F-: Predicted (mg/l)
1	0.236544	180	8.00	8.01
2	16.5	349.7	8.20	8.20
3	16.5	180	4.80	4.34
4	5	60	8.00	7.97
5	16.5	180	4.80	4.34
6	5	300	8.40	8.40
7	16.5	180	3.80	4.34
8	16.5	180	3.70	4.34
9	16.5	10.3	7.90	7.95
10	16.5	180	4.60	4.34
11	28	300	7.20	7.18
12	28	60	7.30	7.25
13	32.8	180	6.60	6.64

Table 4.3 shows the analysis of variance (ANOVA) for Response surface Quadratic model.

As seen in Table 4.3, the Model F-value of 43.54 implies that the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case X1, X12 and X22 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. Although (X1.X2) term was not significant, it cannot be dropped because it was part of the model hierarchy. The Lack of Fit also for the model was insignificant.

The Lack of Fit F-value of 0.0086 implies the Lack of Fit is not significant relative to the pure error. The p-value for the Lack of Fit > 0.05 indicates the absence of evidence that the model did not fit. There was a 99.87% chance that a Lack of Fit F-value of this magnitude could occur due to noise.

Table 4.3: ANOVA for Response surface Quadratic model for Residual Fluoride.

Analysis of variance: Partial sum of squares type III						
Source	Sum of Squares	df	Mean Square	F value	p value	
Model	37.31	5	7.46	43.54	< 0.0001	significant
X1: Diatomite	1.88	1	1.88	10.98	0.0129	
X2: Brick	0.0656	1	0.0656	0.3826	0.5558	
X1X2	0.0625	1	0.0625	0.3647	0.5650	
$X1^2$	15.50	1	15.50	90.41	< 0.0001	
$X2^2$	24.26	1	24.26	141.56	< 0.0001	
Residual	1.20	7	0.1714			
Lack of Fit	0.0077	3	0.0026	0.0086	0.9987	not significant
Pure Error	1.19	4	0.2980			
Cor Total	38.51	12				

Table 4.4 further highlights the summary of the Fit statistics of the model. The Predicted R^2 value of 0.9502 is in reasonable agreement with the adjusted R^2 of 0.9466. The difference is less than 0.2. On the other hand, the signal to noise ratio (Adeq precision) value of 14.437 indicates an adequate signal. A signal to noise ratio greater than 4 is desirable (Kumar et al., 2022). This model can therefore be used successfully to navigate the design space.

Table 4.4: Summary of the Fit statistics.

Std. Dev.	0.4140	R2	0.9688
Mean	6.41	Adjusted R2	0.9466
C.V. %	6.46	Predicted R2	0.9502
		Adeq Precision	14.4373

The model generated from this design is shown in Equation 4.1.

$$y = 11.9 - 3.98 \times 10^{-1}x_1 - 4.44 \times 10^{-2}x_2 - 9.06 \times 10^{-5}x_1x_2 + 1.13 \times 10^{-2}x_1^2 + 1.30 \times 10^{-4}x_2^2 \quad (4.1)$$

Equation 4.1 was used to plot the response surface and the contour shown in Figure 4.7 Figure 4.7 presents the interaction of the surface modified diatomite with brick in removing fluoride in water, with the response being the residual fluoride. The optimization in this case is a minimization problem, with optimum performance being achieved when the residual fluoride in the water is minimum. From Figure 4.7, the optima are shown to be obtained when the diatomite dose is close to 18.8 g and brick dose is about 180 g, for a litre of fluoride contaminated water. Analysis of the experimental data using design expert software with the goal being the minimization of the residual fluoride gave the optimum conditions with a desirability of 0.872 as 18.36 g diatomite, and 177.75 g of brick. This dosage gives a residual fluoride of 4.30 mg/l in 30 minutes of defluoridation as per the design software. This optimized mixture of surface modified diatomite and brick was experimentally tested for fluoride removal and was able to remove fluoride to a residual value of 1.5 mg/l in 1 hour, a value which meets the desired standard of fluoride in drinking water.

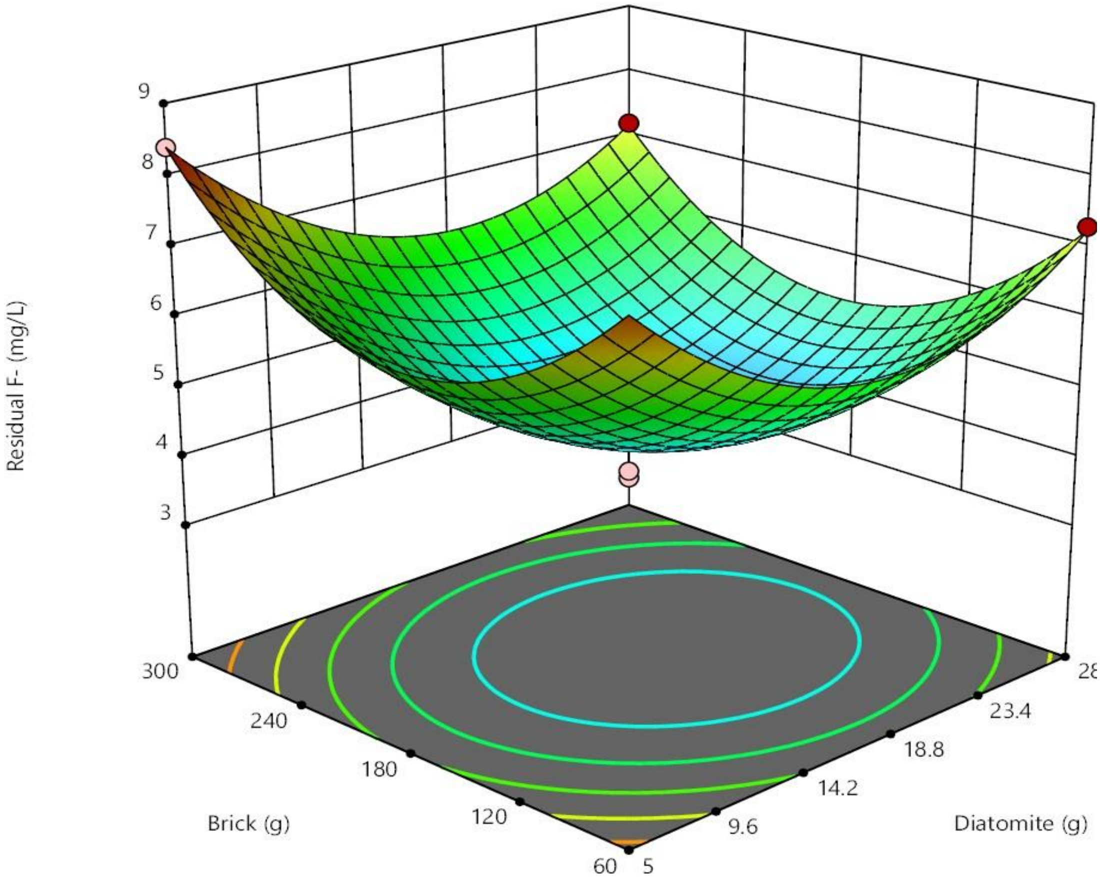

Figure 4.7: Response Surface plot. The effect of brick and surface modified diatomite on removal of fluoride in water (residual fluoride).

4.7 Adsorption Isotherms

The adsorption data was fitted to the adsorption models to understand the adsorption characteristics and the nature of adsorption involved in the individual adsorbents. Both Langmuir and Freundlich isotherms were used in the study, being useful in describing the adsorption for water and wastewater applications (Gomez et al., 2007; Kadirvelu et al., 2005). Figure 4.8 shows the Langmuir and Freundlich isotherms for the adsorption of fluoride from water by surface modified diatomite and brick. As shown in Figure 4.8, it was found that the adsorption by the surface modified diatomite is better explained by the Freundlich isotherm ($R^2 = 0.9753$). This agreed with previous studies, which found the adsorption of fluoride by aluminum hydroxide treated diatomite to involve a multilayer sorption mechanism (Akafu et al., 2019).

The adsorption by brick fit better to the Langmuir isotherm as shown in in Figure 4.8c, R^2 = 0.9804, in comparison to the Freundlich isotherm (Figure 4.8d, R^2 = 0.9372). The assumptions by Langmuir that each site is singly occupied by the adsorbate molecules and that there are no lateral interactions between the adsorbed species are applicable (Jain & Singh, 2014). The present study agreed with several of the previous studies. Priyantha and colleagues in their study of the adsorption behaviour of fluoride in normal brick found the highest regression coefficient on Langmuir isotherm (Priyantha et al., 2009). Similarly, Kooli and coworkers, while using waste brick to remove basic blue 41 from aqueous solution, found out that the removal conformed to the monolayer adsorption isotherm (Kooli et al., 2019).

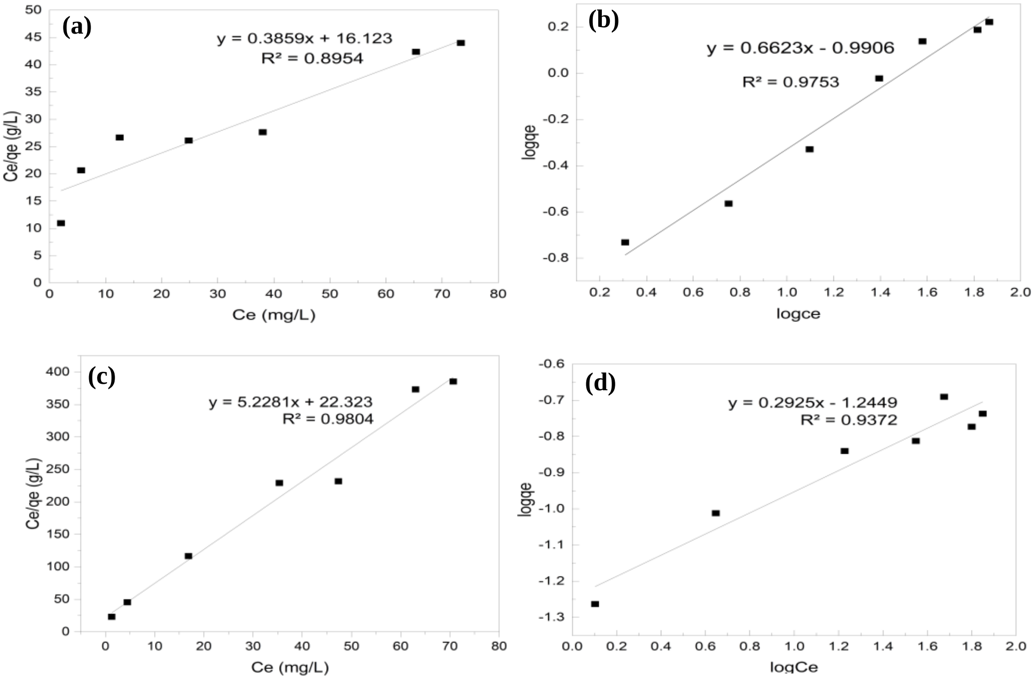

Figure 4.8: Isotherms for surface modified diatomite and brick, (a, b): Surface modified diatomite, (c, d): Brick, (a, c): Langmuir isotherms, (b, d): Freundlich isotherms.

Table 4.5 presents the summary of the parameters for both Langmuir and Freundlich isotherms for the surface modified diatomite and brick. From Table 4.5, the R_L values for both surface modified diatomite and brick indicate favorable sorption of fluoride by both surface modified diatomite and brick ($0 < R_L < 1$) (Akafu et al., 2019). It is also evident from the q_m values that the surface modified diatomite has very high adsorption capacity for fluoride. Its adsorption capacity is more than 10 times that of brick. This agrees with the values of K_F from the Freundlich isotherm, which also suggests high adsorption capacity by the surface modified diatomite as per its large value. The value of $1/n < 1$ is indicative of the existence of heterogeneous adsorption surfaces in both diatomite and brick (Akafu et al., 2019). On the other hand, the high value $1/n$ ($1/n=0.6623$) on the surface modified diatomite, as compared to that of brick ($1/n=0.2925$) suggests high bond strength between the adsorbent and the adsorbate for the case of the surface modified diatomite as opposed to brick (Proctor & Toro-Vazquez, 2009). The value of q_m obtained in this study for the surface modified diatomite (2.5913 mg/L) was higher than that obtained by Akafu and coworkers (1.67 mg/L) in their study (Akafu et al., 2019). This is evidence of the improved fluoride adsorption by surface modified diatomite in the present study in comparison to the previous studies. This can be attributed to the slight modification of the modification procedure used in the present in comparison to that used by Akafu and coworkers. Similarly, the value of q_m for the raw diatomite is very low (0.0011 mg/g). This confirms that surface modification of the diatomite greatly improves the ability of fluoride adsorption.

Table 4.5: Calculated Langmuir and Freundlich isotherm parameters.

	Langmuir Isotherm				Freundlich Isotherm		
	K_L	R_L	q_m	R^2	1/n	K_F	R^2
Modified Diatomite	0.0239	0.8071	2.5913	0.8954	0.6623	0.1022	0.9753
Brick	0.2342	0.2992	0.1913	0.9804	0.2925	0.0569	0.9372
Raw Diatomite (control)	-0.1138	-7.6923	0.0011	0.8604	0.8026	0.0957	0.9495

4.8 Adsorption Kinetics

To understand the adsorption mechanism involved in the adsorption of fluoride on to the surface of the modified diatomite and brick, the experimental data were fitted to both pseudo-first order and pseudo-second order kinetic models. Figure 4.9 provides the linear plots of both the pseudo-first order and pseudo-second order models. From Figure 4.9, it is observed that all the adsorbents followed the pseudo-second order kinetics in their removal of fluoride by adsorption. This is evident in the high values of the regression coefficients (0.9843,0.9754 and 0.9908) for the pseudo-second order model compared to the pseudo-first order model (0.9499,0.9393 and 0.9315) for the surface modified diatomite, brick and the optimized mixture of surface modified diatomite and brick respectively.

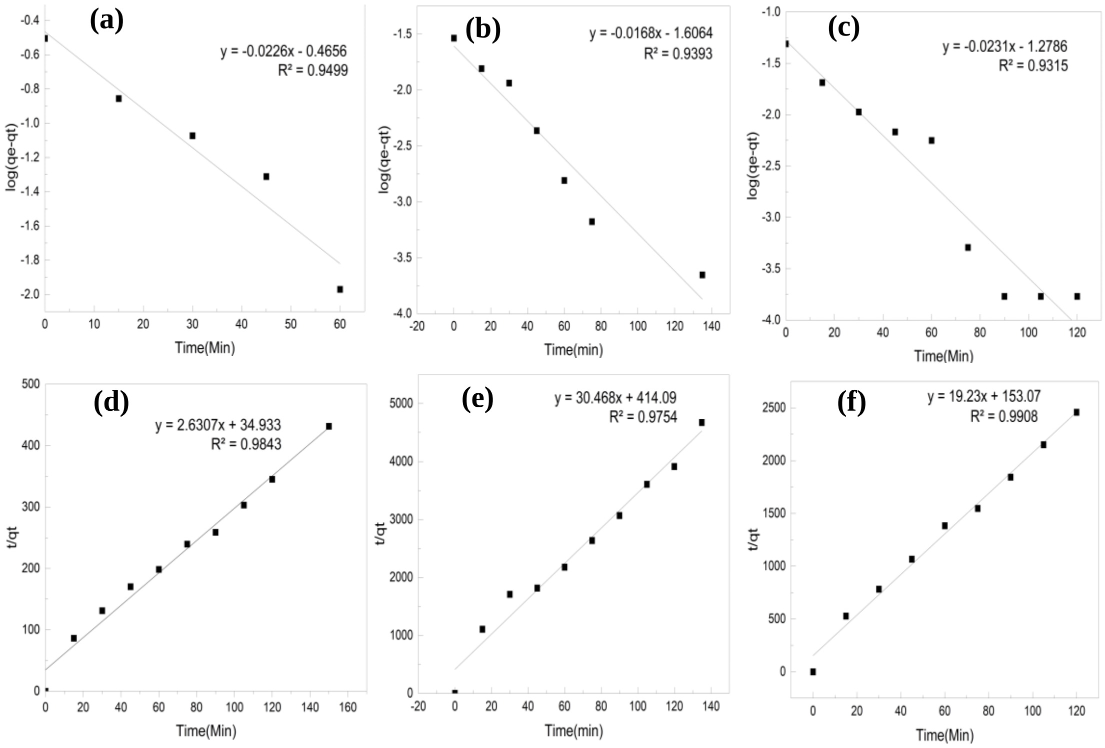

Figure 4.9: Adsorption kinetics. (a, b, c) Pseudo-first order kinetic models, (d, e, f) Pseudo-second order kinetic models, (a, d) Surface modified diatomite, (b, e) Brick, (c, f) Optimized surface modified diatomite-brick.

Table 4.6 presents the summary of the kinetic constants from the adsorption experiment. From table 4.6, the kinetic constants indicate the adsorption process by each category of the adsorbents followed the pseudo-second order kinetics. Other than the high regression coefficients for the pseudo second order kinetics, for each category of the adsorbents, the calculated equilibrium capacity of the adsorbents for the pseudo-second order model (q_{e2}) had minor deviation from the experimental equilibrium capacity ($q_{e\,exp}$) as compared to the calculated equilibrium capacity of the adsorbents in pseudo-first order kinetics (q_{e1}). The values of q_{e1} largely deviated from the experimental values. The large values of the rate constants K_2 support the fact that the adsorption process fit better to the pseudo-second order kinetic model. It is therefore clear that the adsorption process by both the brick and the surface modified diatomite involved chemisorption process, an assumption of the pseudo-second order kinetics (Alkan et al., 2007).

Table 4.6: Summary of the kinetic constants from the experiment.

Sample	Pseudo-first order			Pseudo-second order			
	K_1	q_{e1}	R^2_1	K_2	q_{e2}	R^2_2	q_{eexp}
Modified Diatomite	0.052	0.3423	0.9499	0.1981	0.3801	0.9843	0.3131
Brick	0.0387	0.0248	0.9393	2.2418	0.0328	0.9754	0.0291
Modified Diatomite + Brick	0.0532	0.0527	0.9315	2.416	0.052	0.9908	0.0490

4.9. Breakthrough Analysis

Breakthrough analysis is used to study the continuous adsorptive systems, as opposed to the batch studies which can mainly provide the useful parameters and data on the application of the adsorbents for contaminant removal (Bibiano-Cruz et al., 2016). Breakthrough analysis was carried out to determine the capacity of the optimized mixture of surface modified diatomite and brick in the removal of fluoride. As highlighted by Murutu and co-workers in their work, the design of a real system for practical applications should put more emphasis on the flowrate and the concentration of the influent water as opposed to the adsorbent height (Murutu et al., 2012). Figure 4.10 shows the breakthrough curve obtained for the test.

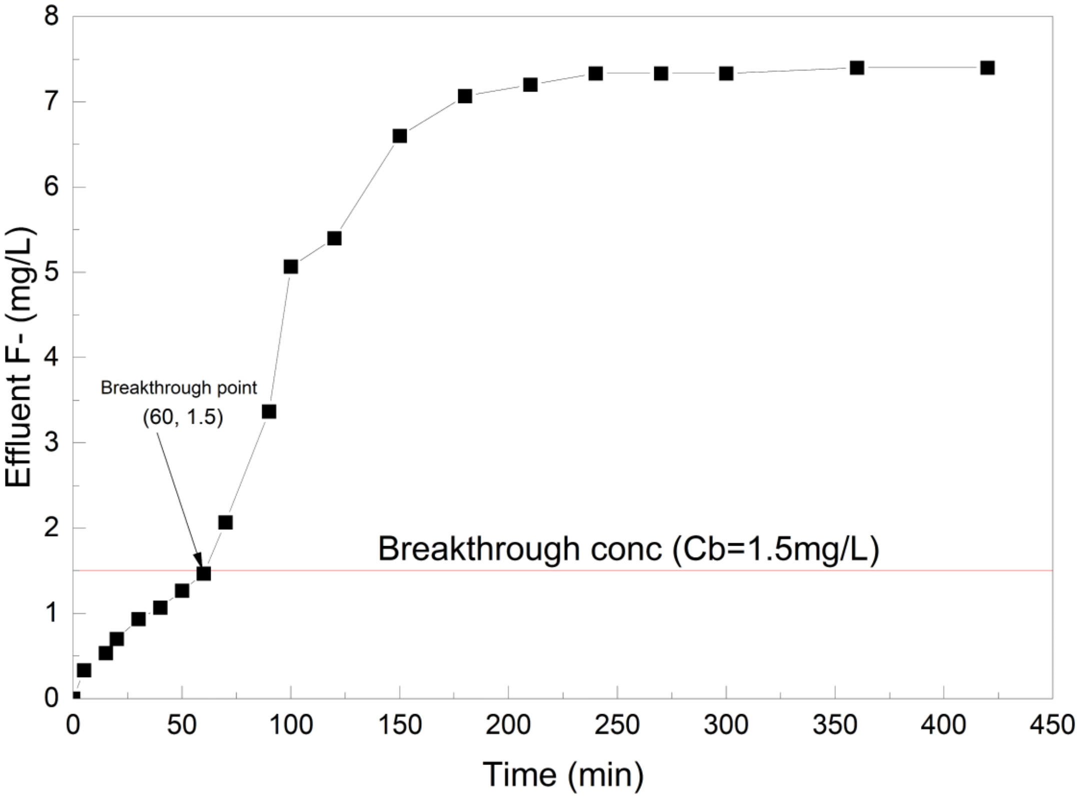

Figure 4.10: Breakthrough curve for sorption of fluoride onto optimized mixture of surface modified diatomite and brick. Mass of adsorbent=49g, Initial fluoride concentration=7.4 mg/l (sample from Lake Baringo), flowrate =1.67ml/min.

As it can be seen from Figure 4.10, the breakthrough was reached after 1 hour. The volume of water treated at breakthrough was 100.2 ml. The number of bed volumes was found to be 5 while the fluoride uptake capacity was 0.01 mg/g.

4.9.1 Thomas Kinetic Model

For successful design and application of fixed bed columns in an adsorption process, the concentration time profile (breakthrough curve) should be analysed. Thomas kinetic model is one of the simple kinetic models which can be applied to evaluate the possible prediction shape and position of breakthrough curves for some chosen conditions (Slavić et al., 2016). The model explains adsorption-desorption process where no axial dispersions are present (Chowdhury et al., 2015).

The column adsorption data in this study were fitted to Thomas model to determine if the adsorption of the optimized mixture of surface modified diatomite and brick can be predicted by the model. Figure 4.11 shows the data fitted to the linearized Thomas kinetic model.

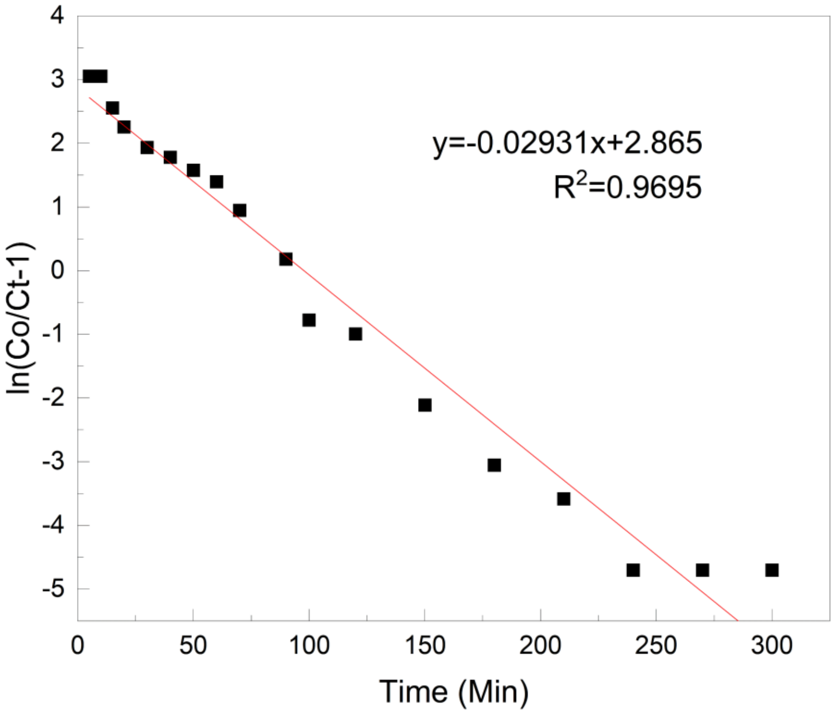

Figure 4.11: Column adsorption studies data fitted to linearized Thomas kinetic model.

From Figure 4.11, the data showed a good fit with high regression coefficient of 0. 9695 and therefore for design purposes of the adsorption columns, with the optimized mixture of surface modified diatomite and brick, Thomas kinetic model can be used to predict the adsorptive curve of breakthrough in the fixed mode. The maximum fluoride uptake capacity of the fixed bed (q_0) was found to be 0.02465 mg/g, while the Thomas rate constant k_{TH} was found to be 3.9606 $mlmg^{-1}min^{-1}$ which indicated good adsorption capacity of the mixed adsorbents for fluoride good adsorption rate as well.

CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS

5.1 Overview of the Research Objectives

The main objective of testing the application of surface modified diatomite and bricks as adsorbents for removal of fluoride contaminants from water was achieved. The optimum masses of the individual adsorbents that removed the fluoride to 1.5 mg/l were used in optimizing the adsorbent mixture. The optimization of the adsorbent mixture was done by means of response surface methodology, using the Box-Wilson central composite design.

Diatomite and bricks were successfully characterized for their physical features and chemical composition with the aid of scanning electron microscope and energy dispersive x-ray spectroscopy.

Furthermore, the study of the fluoride removal performance by the optimized mixture of surface modified diatomite and bricks were carried out through batch studies and evaluated by means of the adsorption isotherms and adsorption kinetics. The data obtained from the experiment were fitted to both Langmuir and the Freundlich adsorption isotherms. The isotherm constants obtained were used to evaluate the performance of the adsorbent media. Similarly, the kinetic performance was assessed by fitting the kinetic data to both the pseudo-first and pseudo-second order kinetic models. The results of the study indicated good performance by optimized mixture in removal of fluoride.

The last objective of determining the adsorption capacity of the optimized mixture of surface modified diatomite and brick in the removal of fluoride from water samples from Lake Baringo +in adsorption columns was achieved by means of breakthrough analysis. The optimized mixture of the aluminium hydroxide surface modified diatomite and brick was packed in a column equipment and the water sampled from Lake Baringo was passed through to assess the performance on fluoride removal from the lake water. The data from the column studies also fitted to the linearized Thomas kinetic model to determine the maximum fluoride uptake and Thomas constant for the column on fluoride adsorption. The study showed good capacity by the mixture for fluoride removal.

5.2 Key Findings

From the study, it was found out that raw diatomite has low fluoride adsorption capacity with 28 g of raw diatomite removing only 0.5 mg of fluoride in a litre of water containing 10 mg of fluoride, which is 5% fluoride removal from the water samples. On the other hand, it was found that surface modification of the diatomite with aluminium hydroxide greatly improved its fluoride uptake capacity. A dose of 28 g of the surface modified diatomite removed up to 8.5 mg of fluoride in one hour from a litre of water containing a total of 10 mg fluoride. This was 85% fluoride removal from the water samples.

Brick was found to have average fluoride removal capacity. The optimum dose of brick in a litre of water containing 10 mg fluoride was found to be 300 g for a contact time of 1 hour. This finding on average fluoride uptake capacity by brick agreed with the existing literature which indicate a medium fluoride adsorption capacity by brick. This can be attributed to the dominant negative charge on the surface of brick which reduces its uptake of the negatively charged fluoride ions in the water. The optimum mixture of the surface modified diatomite and brick was found to be 18.36 g and 177.75 g of surface modified diatomite and brick respectively, for a litre water containing 10 mg of fluoride.

The fluoride adsorption by brick fitted better to the Langmuir adsorption isotherm. However, the adsorption by the surface modified diatomite fit to Freundlich adsorption isotherm. On the other hand, the Al $(OH)_3$-surface modified diatomite, bricks, and the optimized mixture of the two had the fluoride adsorption process fitting to the pseudo-second order kinetic model. The adsorption process therefore was dominated by chemisorption.

The characterization of the Lake Baringo water showed that the water has excess fluoride and high pH value than the recommended levels. The average fluoride concentration was found to be 6.3 mg/l with the highest recorded value being 7.4 mg/l. The pH was found to be 8.5 on average. These values agreed with the previous research findings on the lake.

Column studies with the optimized mixture of surface modified diatomite and bricks showed that the breakthrough point of 1.5 mg/l residual fluoride was attained in 1 hour for the water sampled from Lake Baringo, having a concentration of 7.4 mg/l of fluoride. The bed volumes were 5 and a fluoride uptake capacity (FUC) of 0.01 mg/g. The Thomas model fit showed that the maximum fluoride uptake capacity was 0.02465 mg/g, and the Thomas rate constant was 3.9606 $mlmg^{-1}min^{-1}$. The model had a good fit with regression coefficient of 0.9695 and can be used to predict the adsorptive curve of the breakthrough in the fixed mode.

5.3 Conclusion

The findings of this study showed that the optimized mixture of brick and surface modified diatomite can be successfully used for fluoride removal in water. The optimization reduced the amount of the adsorbent required for both the surface modified diatomite and the brick to remove fluoride to the WHO standard for drinking water, with the brick still taking the largest portion in the mixture. From the findings, it is evident that the optimized mixture of bricks and diatomite whose surface has been modified by aluminium hydroxide can serve as adsorbents for fluoride removal in areas affected by high fluoride concentration in water.

The availability of diatomite deposits in Kenya and the ease of accessing bricks in the country and in the region affected by fluoride, makes the mixture surface modified diatomite and bricks viable and affordable technique for fluoride removal in water.

5.4 Recommendations

The diatomite and bricks mixture are easily available and affordable adsorbents and can be recommended for use in fluoride removal in drinking water in the areas affected, with surface modification of diatomite. Additionally, further research should be carried out on other affordable and locally available adsorbents for fluoride removal in water.

More research should also focus on methods of improving the fluoride uptake capacity of bricks to improve its effectiveness when combined with diatomite. The brick showed the presence of metallic iron in abundance. Attempt to convert the metallic iron to oxides can be done and the brick assessed further for the fluoride removal. The iron oxides could improve the fluoride uptake capacity of bricks because the process involved was shown to be dominated by chemisorption.

Thirdly, this research did not address the effects of the competing ions in the water. Future research work can investigate the contribution of the competing ions in the fluoride removal capacity of the aluminium hydroxide surface modified diatomite and bricks mixture. Furthermore, additional methods of surface modification of diatomite can be explored to find an easy and cheap alternative technique for its surface modification to enhance its fluoride uptake ability.

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APPENDICES

Appendix I: Experimental Data

This section provides the raw data obtained from the laboratory experiments.

Table A1: Surface modified diatomite fluoride adsorption isotherms studies data

Ci(mg/L)	Modified Diatomite Mass (g)	Volume (ml)	Residual Fluoride (Ce) (mg/L)			Average Ce (mg/L)	Actual Ce (mg/L)
			1st	2nd	3rd		
100.00	2.00	125	0.74	0.73	0.73	0.73	73.33
90.00	2.00	125	0.64	0.65	0.67	0.65	65.33
60.00	2.00	125	0.38	0.36	0.40	0.38	38.00
40.00	2.00	125	1.24	1.23	1.25	1.24	24.80
20.00	2.00	125	1.25	1.24	1.26	1.25	12.50
10.00	2.00	125	0.58	0.56	0.55	0.56	5.63
5.00	2.00	125	0.20	0.21	0.20	0.20	2.03

Table A2: Brick fluoride adsorption isotherms studies data

Ci(mg/L)	Brick Mass (g)	Volume (ml)	Residual F- {Ce}(mg/L)			Average(Ce) {mg/L}	Actual Ce(mg/L)
			1st	2nd	3rd		
100	20	125	0.69	0.71	0.72	0.71	70.67
90	20	125	0.62	0.63	0.64	0.63	63.00
80	20	125	0.46	0.47	0.49	0.47	47.33
60	20	125	0.36	0.36	0.34	0.35	35.33
40	20	125	0.83	0.86	0.84	0.84	16.87
20	20	125	0.43	0.46	0.44	0.44	4.43
10	20	125	0.15	0.12	0.11	0.13	1.27

Table A3: Surface modified diatomite fluoride adsorption kinetics studies data

Time (Min)	**Residual Fluoride(mg/L)**			**Average residual F-(mg/L)**	**Actual Residual F(mg/L)**
	1st	**2nd**	**3rd**		
0	1	1	1	1.0000	10.00
15	0.49	0.53	0.52	0.5133	5.13
30	0.36	0.38	0.34	0.3600	3.60
45	0.28	0.24	0.26	0.2600	2.60
60	0.16	0.15	0.15	0.1533	1.53
75	0.13	0.12	0.12	0.1233	1.23
90	0.03	0.03	0.02	0.0267	0.27
105	0.03	0.03	0.03	0.0300	0.30
120	0.03	0.02	0.03	0.0267	0.27
150	0.03	0.02	0.03	0.0267	0.27

Table A41: Surface modified diatomite fluoride adsorption kinetics studies data

Time	**Residual Fluoride(mg/L)**			**Average(mg/L)**	**Actual**
(min)	**1st**	**2nd**	**3rd**		**residual(mg/L)**
0	1	1	1	1.00	10.00
15	0.58	0.61	0.59	0.59	5.93
30	0.5	0.49	0.43	0.47	4.73
45	0.28	0.25	0.24	0.26	2.57
60	0.18	0.17	0.17	0.17	1.73
75	0.15	0.13	0.16	0.15	1.47
90	0.12	0.12	0.12	0.12	1.20
105	0.12	0.14	0.12	0.13	1.27
120	0.08	0.08	0.08	0.08	0.80
135	0.12	0.13	0.15	0.13	1.33

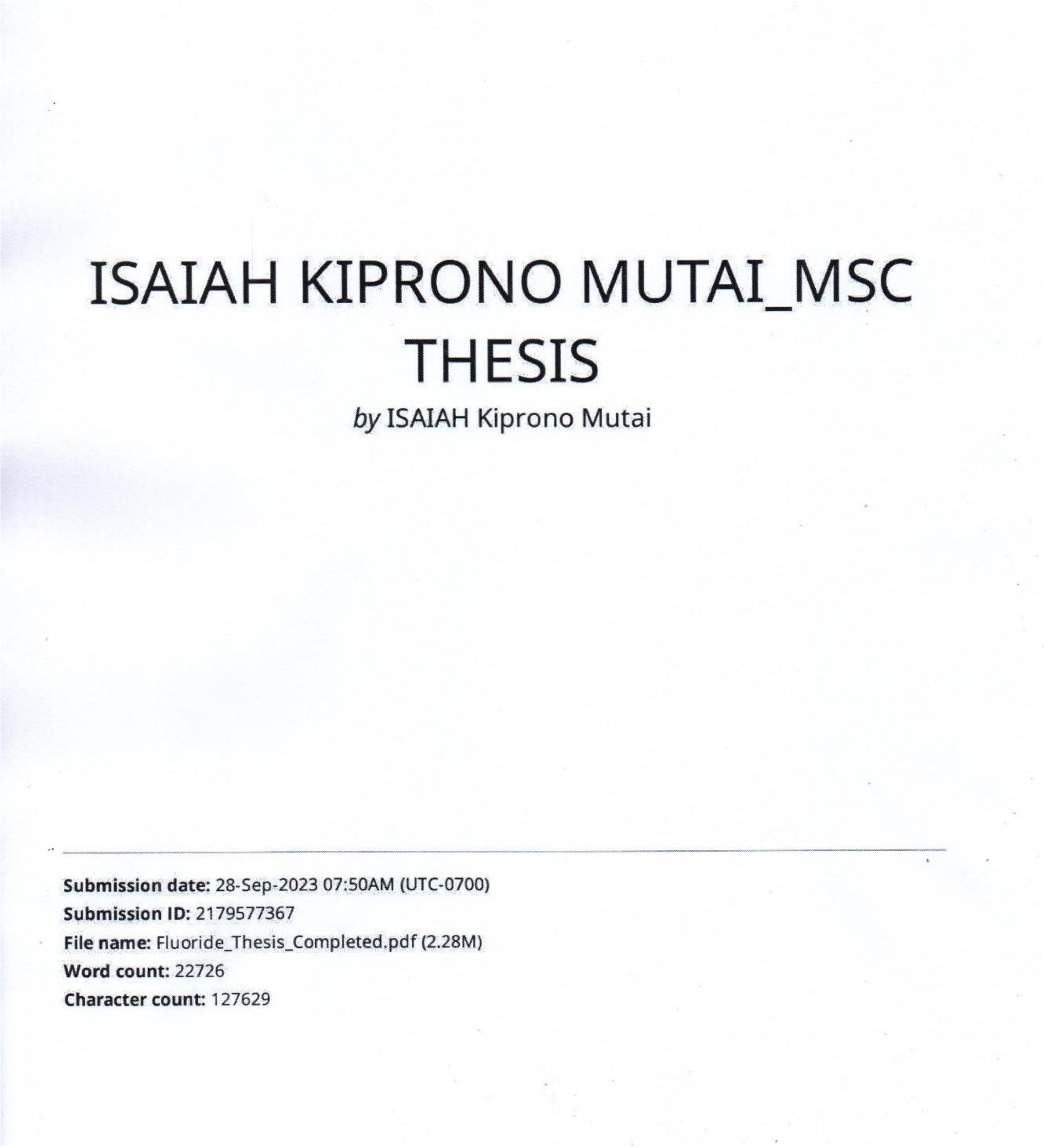
Table A5: Mixed surface modified diatomite and brick fluoride adsorption kinetics data

Time(Min)	**Residual F- (mg/L)**			**Avarage residual F- (mg/L)**
	1st	**2nd**	**3rd**	
0	10	10	10	10.00
15	4.6	4.5	4.2	4.43
30	2.75	2.5	2.2	2.48
45	1.8	1.7	1.7	1.73
60	1.6	1.5	1.4	1.50
75	0.5	0.8	0.2	0.50
90	0.5	0.4	0.4	0.43
105	0.4	0.5	0.4	0.43
120	0.4	0.4	0.5	0.43
135	0.3	0.5	0.4	0.40
150	0.4	0.4	0.4	0.40

Table A6: Breakthrough Analysis Data

Time (min)	Residual Fluoride (mg/L)			Average (mg/L)/10	Actual (mg/L)
	1st	2nd	3rd		
0	0.00	0.00	0.00	0.00	0.00
5	0.03	0.03	0.04	0.03	0.33
1o	0.03	0.03	0.04	0.03	0.33
15	0.04	0.06	0.06	0.05	0.53
20	0.07	0.07	0.07	0.07	0.70
30	0.09	0.09	0.1	0.09	0.93
40	0.1	0.11	0.11	0.11	1.07
50	0.12	0.13	0.13	0.13	1.27
60	0.14	0.14	0.16	0.15	1.47
70	0.21	0.2	0.21	0.21	2.07
90	0.34	0.34	0.33	0.34	3.37
100	0.5	0.5	0.52	0.51	5.07
120	0.53	0.53	0.56	0.54	5.40
150	0.66	0.66	0.66	0.66	6.60
180	0.7	0.71	0.71	0.71	7.07
210	0.72	0.72	0.72	0.72	7.20
240	0.73	0.73	0.74	0.73	7.33
270	0.73	0.74	0.73	0.73	7.33
300	0.74	0.73	0.73	0.73	7.33
360	0.74	0.74	0.74	0.74	7.40
420	0.74	0.74	0.74	0.74	7.40

Appendix II: Plagiarism Similarity Index



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