SORPTION OF FLUORIDE IONS FROM AQUEOUS SOLUTIONS USING KENYAN KISII SOAPSTONE AND CALCIUM BENTONITE CLAY

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I56/CE/25344/2014

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE IN APPLIED ANALYTICAL CHEMISTRY IN THE SCHOOL OF PURE AND APPLIED SCIENCE OF KENYATTA UNIVERSITY

JUNE, 2025

DECLARATION

This thesis is my original work, and it has not been presented for a degree in any other University or for any other award.

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DEDICATION

This thesis is dedicated to my wife Florence, my daughters Stacey and Macey, my mother Winnie Omolo, my late brother Geoffrey, my late sister Lilian and my sister Kandi.

ACKNOWLEDGEMENTS

I am grateful to the Almighty God for giving me strength to carry out this research work.

My sincere gratitude goes to my supervisors Prof. Damaris N. Mbui and Prof. Ruth N. Wanjau for their support, guidance and invaluable suggestions I received from them throughout the research period. I would also like to express my gratitude to the laboratory technicians from Kenyatta University department of chemistry for their support in analysis, and my classmates and colleagues who offered technical and social support.

My appreciation also goes to Kenyatta University for arming me with the necessary skills to carry out this research, Kenya Bureau of Standards and Department of Mines and Geology where most of the work was done, Prof. Austin O. Aluoch for his technical support and Dr. Gerald W. Mbugua who came in handy by directing the flow of this work.

Finally, to Kandi Omolo, for proofreading the work.

May God bless you all.

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ABBREVIATIONS, SYMBOLS AND ACRONYMS

Ca-bent	- Calcium bentonite
CDN	- Catholic Diocese of Nakuru
EDX	- Energy Dispersive X-Ray
FTIR	- Fourier Transform Infrared Spectroscopy
GPS	- Global Position Sensing
ISE	- Ion Selective Electrode
PET	- Polyethylene Terephthalate check font!!!
PTFE	- Polytetrafluoro-ethylene
WHO	- World Health Organisation
XRD	- X-Ray Diffraction
XRF	- X-Ray Fluoresence
RPM	- revolutions per minute
SEM	- Scanning Electron Microscope
TEM	- Transmission Electron Microscopy
TGA	- Thermogravimetric Analysis
TISAB	- Total Ionic Strength Adjustment Buffer

ABSTRACT

Safe drinking water is scarce and has been established to be the leading source of dietary fluoride intake by humans. The amount of fluoride absorbed by humans can either be beneficial or detrimental and for that reason there is a need to control its level in water. Various methods have been applied to remove excess fluorides from water including the use of adsorption techniques, electrocoagulation and membrane filtration but they have been proved to be neither cost effective nor sustainable for low-income communities. It has also been established that the adsorption method offers the comparatively cheaper and most effective method for the defluoridation of water. Some of the adsorbents that have been used in the removal of fluorides include bone char and alum. In this study soapstone and calcium bentonite capability of offering a cheap and effective method for removal of fluorides from aqueous solutions was explored. The study was anchored on borrowed conceptual theory of structure activity relationship given the presence of hydroxides and aluminum in both minerals. The soapstone was obtained from Tabaka, Sub County in Kisii County while the bentonite clay origin was Mount Kenya National Park. The composition, heat pre-treatment and adsorption capacities of Kisii soapstone and calcium bentonite for removal of excess fluoride in water was determined. Synthetic samples tested with the adsorbents had pH values held at 5.8. Varying the temperature of heat treatment from 100 ^{o}C to 500 ^{o}C resulted in a decline in adsorption capacity of both adsorbents from 34% to 25.5% and 31.0% to 15.3% for soapstone and calcium bentonite respectively, soapstone exhibiting better heat stability. Addition of 2.5 mgL^{-1}, 5.0 mgL^{-1} and 7.5 mgL^{-1} chlorides into the fluoridated water resulted in reduced percentage adsorption of fluorides steadily from 32% to 16 % and 28% to 16% for soapstone and calcium bentonite respectively. However, adjusting the pH downwards improved the adsorption capacity of both adsorbents where both reached their peaks at pH of 3.6 while increasing the pH upwards to 11.6 reduced the adsorption ability of both adsorbents quite significantly from 29.41% to levels below the instruments limit of detection for calcium bentonite and 27.46% to 4.55% for soapstone. The water samples used were drawn from Kiamunyeki area, a suburb of Nakuru town and they were found to have fluorides values of between 2.9 mgL^{-1} to 6.2 mgL^{-1} which is high with respect to the WHO and (KS EAS 12, 2018) maximum allowed limit for drinking water of 1.5 mgL^{-1}. The test performed on these water samples indicated that the adsorbents under investigation had the capacity to remove fluorides from the water. The highest removal rate of soapstone was found to be 0.02 mgg^{-1} while that of calcium bentonite was found to be 0.05 mg/g both at room temperature and at the samples pH values which varied from 7.3 to 8.5. Calcium bentonite also displayed a higher fluoride adsorption capability in laboratory model water samples with 0.21 mgg^{-1} while soapstone had adsorption capacity was established as 0.08 mgg^{-1}. The results obtained from adsorption of fluorides from ground water sample indicated a fluoride level of 3.0 mgL^{-1} was reduced to 1.3 mgL^{-1} and 1.5 mgL^{-1} using 8 g and 1.5 g of soapstone and calcium bentonite respectively in 50 mL of the water sample. The ability to adsorb fluorides was confirmed by Fourier Transform Infrared Spectroscopy spectrum that revealed abundance of hydroxyl groups in bentonite as compared to soapstone and SEM images also depicted higher porosity of the bentonite mineral allowing more absorption of the fluoride ions in its matrix. This study therefore concludes that, Kisii soapstone and calcium bentonite can reduce fluorides from water.

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

According to the World Health Organization (WHO), fluoride is one of the water contaminants that can lead to serious health issues when consumed (World Health Organization, 2017). Numerous minerals, including fluospar, cryollite, horneblende, mica, rock phosphate, and apatite, among others, contain significant amounts of fluorides (Singh and Singh, 2015). As per Edmunds and Smedley's (1996) findings, ground waters with a high cationic exchange of sodium for calcium may also have high fluoride concentrations, depriving the system of its natural fluoride precipitant.

Application of the geographic random forest model to the datasets used as predictors, found that there is probability that Africa is in more danger than all other continents for fluorides where 15% of Africa's land area and more than one out of every two cases have groundwater fluoride values more than 1.5 mgL^{-1} followed by Australia and South America (1 in every 12 cases for each), then 1 in every 50 cases in Asia and North America whereas only less than 10 in every 1000 cases for Europe (Less than1%) (Podgorski and Berg, 2022) . The high fluoride concentration in water is linked to the naturally occurring rocks that originated from previous volcanic activities (García and Borgnino, 2015).

The maximum allowable fluoride concentration in drinking water according to WHO is 1.5 mgL^{-1}, since higher levels cause dental fluorosis and even higher levels lead to crippling skeletal fluorosis (WHO, 2017). The low to high concentrations of fluoride ions are dependent largely on the presence of soluble calcium in water that allows the fluorides to precipitate as calcium fluoride (CaF_2) reducing its concentration and the absence of soluble calcium in the presence of fluoride bearing minerals around the water body leading to elevated fluoride levels in water (Farwell *et al.*, 2006).

Kenya has high fluoride levels especially in Nakuru County which is along the Rift Valley where volcanic activities were experienced (Ochieng, 2013). The ground water has been observed to have fluoride concentrations of up to 4.7 mgL^{-1} which are much higher than the 1.5 mgL^{-1}, the allowable levels recommended by WHO for drinking water (Ochieng, 2013).

A variety of adsorbents can remove fluorides from aqueous systems and have been used. Some include the calcium-based adsorbents, iron-based adsorbents, alumina and aluminum, modified activated alumina, carbon-based sorbents, metal oxides, bio adsorbents and some natural materials due to their low availability cost (Tomar and Kumar, 2013). All these adsorbents have specific components that allow them to adsorb fluorides from aqueous solution. This can be because of the adsorbent's surface's electrostatic attraction, exchange of ions between the anions in the adsorbent and F^-, reaction complexation of cations with F^- ligates and ion surface precipitates and hydrogen bonds with OH^- in the minerals lattice as practicable among others.

The methods have various advantages and disadvantages, and some are even very effective. However, these adsorbents today are not readily available in the market, some are costly to manufacture while others present disposal problems and others involve further steps of removal of undesirable excesses resulting from the materials used.

This study used soapstone and calcium bentonite in removing fluoride from water that is unsafe to drink. The minerals are largely found in varied deposits in Kenya. Soapstone is largely mined in Kisii County, Nyabigege area of Tabaka Sub County while calcium bentonite clay has large deposits in Mt. Kenya area.

Therefore, in this study, soapstone and calcium bentonite were explored for the removal of fluoride from unsafe drinking water, given that both minerals in their matrices have hydroxyl ions, that are known exchange with fluorides in aqueous solutions, and they also have aluminum ion that has a strong positive charge that can attract fluorides onto their matrices, and these adsorbents are readily available and usable in their natural forms.

1.2 Statement of the Problem

Studies on the potential negative effects of consuming fluoridated water over an extended period of time have shown that fluorides have negative effects on the skeletal tissues of teeth and bones (WHO, 2017). Research conducted in China and India revealed that consuming 14 mg of fluoride daily increases the risk of developing debilitating skeletal fluorosis (WHO, 2017). It has been reported that 19 million Kenyans have fluorosis, which affects the teeth and/or skeleton, according to a report in a local daily (Mwangi, 2019). Many methods have been tried to remove excess fluoride from water, but they have not been very successful because of problems with cost and material availability. Consequently, cheaper methods are needed especially in the low-income countries like Kenya if successful universal water defluoridation is to be achieved.

Soapstone has been characterized and found to contain talc ($Mg_3Si_4O_{10}(OH)_2$) and chlorite ($H_4(Mg,Fe)_2Al_2SiO_{11}$), which constitutes more than 90% of soapstone's total mineral content. The main mineral in calcium bentonite (ca-bent) clay is montmorillonite which has the chemical formula of [$Ca (Al, Fe,Zn)_2 (Al,Si)_4O_{10} (OH)_2 nH_2O$] (Ravindra, 2017). The presence of OH^- and Al^{3+} is the basis by which the two minerals are chosen as suitable adsorbents. Therefore, we explored the use of soapstone and calcium bentonite in removal of fluoride ions in water.

This study aimed at removing excess fluorides from aqueous solutions using Kenyan Kisii soapstone and calcium bentonite clay obtained from Mt. Kenya National Park area in Kenya.

1.3 Justification of the Study

In order to address the objectives of the Sustainable Development Goals (SDGs), particularly SDG 3 (Good Health and Well-Being) and SDG 6 (Clean Water and Sanitation), this study highlights the crucial role that fluorides in water play as a key indicator imperative.

Fluoride is commonly present in water sources, with elevated levels typically found in regions where underground water interacts with fluoride-rich minerals.Along the Rift Valley from the Jordan river to southern Africa, the waters have high concentration of fluorides. Outside Africa, in almost 177 districts across 20 states and the Telangana region of India, there is an excessive amount of fluoride present in the ground water (Narsimha and Sudarshan, 2016).

Significant levels of fluoride have also been found in ground water in Kenya's Rift Valley. For example, Nakuru, which is situated along the rift valley, has fluoride levels that are higher than those advised by the WHO (Njagi *et al.*, 2022). Many studies have been conducted to determine how to remove excess fluoride (which ranges from 0.1 to much above 1.5 mgL^{-1}) so that the general public can drink safe water (Jorgend and Ingemar, 2005). One of the commonly used techniques is adsorption, and bone char is one type of adsorbent. Nevertheless, setting up a bone char generator is rather costly, producing bone char requires expertise, is labor-intensive, and some religions, like Islam, do not advocate for its use (Catholic Diocese of Nakuru, 2007).

Therefore, in order to remove excess fluoride from water, alternative materials that may be more broadly appealing natural minerals like soapstone and calcium bentonite should be explored. The western region of Kenya, specifically Kisii County, is rich in soapstone, which the locals use to sculpt and make ornaments (Akama and Onyambu, 2020). Thus, the purpose of this study was to examine how these minerals might be used to remove fluoride from water. No comparable research has been found despite a comprehensive analysis of the literature on soapstone's application in fluoride removal. On the other hand, fluoride adsorption studies have been conducted on calcium bentonite obtained from different sources.

1.4 Hypothesis

Soapstone and calcium bentonite clay can reduce excess fluorides in fluoride contaminated water.

1.5 Objectives

1.5.1 General Objective

To investigate sorption of fluorides from aqueous solutions using Kisii soapstone and calcium bentonite clay.

1.5.2 Specific Objectives

i. To determine the chemical composition of Kenyan Kisii soapstone and calcium bentonite clay using X-ray Fluorescence spectrometer.

ii. To determine the Fourier Transform Infrared Spectroscopy properties and microstructure of Kenyan Kisii soapstone and calcium bentonite.

iii. To determine the optimum conditions associated with Kenyan Kisii soapstone and calcium bentonite clay for effective removal of fluorides in water.

To determine the adsorption capacity of Kenyan Kisii soapstone and calcium bentonite for fluoride removal in bore water

1.6 Significance of the Study

This research will offer local and available solutions for removal of excess fluorides from water. Collection of Kisii soapstone and calcium bentonite will create employment and act as a source of income. This study will further open ways to further studies of the reaction mechanisms and kinetics in relation to the adsorption using the two minerals. The findings will also assist in bridging the knowledge gap on removal of fluorides and by extension removal of other excesses of anions by soapstone and calcium bentonite based on their multi-mineral component nature.

1.7 Scope and Limitations of the Study

This study was designed to test the efficacy of soapstone and ca-bent clay as adsorbents for fluoride removal in water. It focused its activities on determination of the defluoridation ability of soapstone from the Tabaka quarries of soapstone in Kisii County and ca-bent clay originating from Mt. Kenya National Park area. The study only focused on experimentation in batches. The contaminants in the soapstone and calcium bentonite clay were not considered. The water sample generation points were deliberately from a predetermined location generated by applying a systematic sampling technique with fixed interval of two. The effect of particle size of the adsorbents was not considered in this study although size reduction was performed, and final soapstone ground material was approximately 40 µm to 80 µm. Chlorides were the only ions considered in matrix effect studies.

CHAPTER TWO

LITERATURE REVIEW

2.1 Water Scarcity

Kenya is classified among the most water scarce countries in the world (Ondigo *et al.*, 2018). It has been reported that about 43% of people living in Kenya had no access to safe water (Marshall, 2011). The main challenges that have led to the scarcity of water include global warming, population development, expansion of towns, inadequate management of water resources, water contamination and pollution (Mulwa *et al*., 2021).

2.2 Water Pollution

Water pollution aggravates water shortage since it limits water use by consumers and levies a greater cost for remediation (Yongguan *et al*., 2001). Natural routes leading to alterations in water quality comprise weathering of rocks, evapotranspiration, wind depositions, soil leaching, run-offs, and biological progressions among others, while anthropogenic factors include impacts due to farming, use of fertilizers, manures and pesticides, animal farming activities, poor irrigation practices, deforestation, aquaculture, industrial effluents and domestic dirt, quarrying, and recreational activities (Khatri and Tyagi, 2015).

2.3 Fluoride and its Sources

Fluorine is the most electronegative element and is found in the environment as fluoride (Kanduti *et al*., 2016). Fluorides are found at appreciable quantities in a large range of minerals including, apatite, fluorspar, rock phosphate, mica and hornblende among others (Singh and Singh, 2015). Fluoride is also commonly associated with other rock mineral sources (Dharmagunawardhane and Malaviarachchi, 2016). The East African Rift Valley from the Jordan Valley is an area documented to be associated with volcanic activity and hence high fluoride levels (García and Borgnino, 2015). Many of the lakes along the Rift Valley have extremely high fluoride concentrations close to 200 mgL^{-1} (Wambu and Muthakia, 2011; Addison *et al.*, 2020).

2.4 Health Effects of Fluoride

Fluoride is beneficial to human beings in various ways. It is beneficial to teeth at low concentrations (García and Borgnino, 2015). It is also the key agent in reducing dental carries through remineralization of early damage to enamel, improving the chemical structure of the enamel and thus increasing its resistance to acid attack and lowering of plaque bacteria to produce acid (Sheila, 2005; Anil *et al.,* 2022). Fluoride interacts with hydroxyapatite to form fluorapatite, which is less susceptible to erosion by acid-producing oral bacteria (Peckham and Awofeso, 2014. Fluoride lowers pH, requiring more energy from the bacteria to maintain a neutral pH. As a result, the bacteria have less energy to grow, reproduce, and produce undesirable acids and polysaccharides (Aoun *et al.,* 2018). Additionally, it has been demonstrated that fluoride inhibits cariogenic bacteria, which causes tooth decay or encourages its development.

This is postulated to occur mainly through inhibition of enzyme mediated glycolysis in cariogenic microorganisms such as *Streptococcus mutants* (Peckham and Awofeso, 2014).

However, excessive exposure to fluorides has the potential to cause adverse health effects from mild dental fluorosis to crippling skeletal fluorosis which is a cause of morbidity

(Farwell *et al*., 2006). This fact established several years ago has led to extensive research on how to remove fluorides from drinking water (Unde *et al*., 2018).

Excessive fluoride has been shown to disrupt the thyroid gland. Fluoride has the ability to raise thyroid stimulating hormone (TSH) and lower thyroxine (T4) and triiodothyronine (T3) hormone concentrations. This can cause hypothyroidism in certain populations, which can have detrimental effects, including a decrease in learning and memory abilities (Dey and Giri, 2016).

As Mg^{2+} is the activator of over 300 enzymes in humans, it has been accepted that fluoride toxicity generally results from competition between fluoride and Mg^{2+} inhibiting the process. For example, fluorides can disrupt the pathway that leads to the formation of a complex with magnesium and phosphates that binds to the enzyme's active site and prevents 2-phosphoglycerate, the substrate for the ninth step of glycolysis, from binding to Enolase, a dimeric metal-activated enzyme that is responsible for glycolysis. This eventually prevents glucose from being used to produce energy (Strunecka and Strunecky, 2020).

2.5 Global Distribution of Fluorides

Research shows that more than 260 million people drank water from sources with unusually high fluoride concentrations across the globe (Amini *et al*., 2008). While Mexico is only moderately affected, countries with high groundwater fluoride levels, such as China, Ethiopia, Kenya, India, and Argentina, are cause for serious concern. According to Ali *et al*. (2016), all the states in South Asia—including India, Pakistan, and Sri Lanka have high levels of fluoride contamination in their groundwater. Nearly all of

India's states have fluoride contamination in their water supplies. Topical estimates suggest that 200 million people worldwide, from 25 different countries, face the terrible threat of fluorosis because of consuming excessive amounts of fluoride in China and India, the two most populous nations.

2.6 Distribution of Fluoride in Kenya

In countries like Tanzania, Kenya, and Ethiopia where part of the East African Rift Valley crosses, the levels of fluoride in groundwater are extremely high. According to Thole (2013), the ground waters of the volcanic regions of Nairobi, the Rift Valley, and the Central Provinces in Kenya had the highest concentrations known. Lake Nakuru in Kenya has so far reported the highest fluoride concentration of 2800 mgL^{-1} (Demelash *et al.,* 2019). The Lake Victoria basin area in Kenya has also been found to have levels of fluoride reaching 5.44 mgL^{-1} with the fluoride's levels in the ground waters next to the lake decreasing with increasing distance from the lake suggesting possible hydro-geologically translocation of fluorides into the location from geochemical origins beyond the area (Wambu *et al.,* 2014). In Turkana County, a study of ground water observed that fluoride values were in the ranges of 0.15–5.87 mgL^{-1} (Rusiniak *et al.*, 2021).

2.7 Techniques Applied in Defluoridation of Water

As covered in the subsequent subsections, coagulation, precipitation, membrane filtration, reverse osmosis, ion exchange technology, and adsorption techniques are some of the frequently used techniques for fluoride removal (Loganathan *et al.*, 2013).

2.7.1 Coagulation

Coagulation is a process that results from nonexistence of repulsion between ions in aqueous phase and can be due to the introduction or modification of a species in the media (for example, by neutralization of the surface charge). The intermolecular forces of attraction would then cause particles to stick to each other, forming big aggregates which settle out from solution (Bobadilla *et al.*, 2019). The advantage of this method is that it is effective in fluoride removal, but some matrices may also present other contaminants and their elimination involves further processes (Crini and Lichtfouse, 2019).

2.7.2 Precipitation

Chemical precipitation, which is used in water and wastewater treatment to remove ionic constituents from water by adding counter-ions to reduce their solubility, is the transformation of materials dissolved in water into solid particles (Vaccari *et al.*, 2005). Calcium containing compounds have been studied due to the potentiality of the metal for the F^- ion (Turner *et al*., 2005). The addition of lime to precipitate fluorides in grossly fluoride laden water, has the potential to lower the F^- concentration to about 1 mgL^{-1} but increases the pH of water in the process. However, the fluoride concentration following precipitation is typically 7–15 mgL^{-1}, higher than the allowable limits, because of specific solubility and kinetic effects (Kedar Oke, 2011). These can be eliminated by using a selective ion exchange resin or by adsorption on activated alumina.

2.7.3 Membrane Filtration

Membrane filtration processes are defined by membrane separation processes using membranes with a pore size of approximately 0.01 up to 0.0001 microns under extreme filtration pressure (Shon *et al.,* 2013). Although these techniques eliminate the use of additives, they are subject to fouling, have high set-up costs and are only applicable where there is electrical energy and as a result their application in developing countries is reserved (Ayoob *et al*., 2008).

2.7.3.1 Reverse Osmosis, Microfiltration and Nanofiltration

Techniques for membrane filtration include reverse osmosis, microfiltration, and nanofiltration. These physical processes generate incredibly clean water by forcing incoming water through a semi-permeable membrane under pressure to remove impurities (Litza *et al.*, 2015). However, in membrane filtration processes, fouling is a critical challenge (Obotey and Rathilal, 2020). The ensuing subsections cover these methods in detail.

2.7.3.1.1 Reverse Osmosis

By forcing feed water through a semi-permeable membrane under pressure, reverse osmosis (RO) is a physical process that removes impurities and tends to produce incredibly pure water (Litza *et al.*, 2015). In RO systems, incoming water is separated into two streams, one with a high salinity and the other with little to no salinity. The low salinity stream is called permeate, which is the product water; the high salinity stream is called concentrate, brine, or reject. The permeability and differential pressure of the feed-permeate membrane surface area determines how much water can pass through a membrane (Gray, 2016). RO needs to be able to push past the membrane's osmotic pressure to function. The pressure required to stop water from flowing inward through a semi-permeable membrane is known as osmotic pressure (Voet, 2017).

The approach has been used in developed nations and has been demonstrated to remove up to 95% of F-ions (Arora *et al.,* 2004), so the results have been encouraging. These techniques cannot be fully implemented in developing nations due to their high setup, maintenance, and operating skill requirements (Litza *et al.,* 2015). Reddy (2017) found in another study that at various water fluoride concentrations, reverse osmosis water purifiers could significantly lower the fluoride ion concentration to the ideal range (0.7–1.2 mgL^{-1}).

2.7.3.1.2 Nanofiltration

Nano filtration (NF) can hold on to low molecular weight organics and ions due to its pore size of 1-4 nm. It functions at a lower pressure and has a much higher water permeability than RO membrane (Sewerin *et al.,* 2021). It has the properties of both reverse osmosis and ultrafiltration but requires less energy and it has high charge in aqueous state making it suitable for charged ions removal (Yang *et al.,* 2019). When compared to Reverse Osmosis membrane separation, which rejects 99% of the salt present in the water and encourages the disposal of every fluoride ion, the Nanofiltration membrane separation process results in only partial defluoridation of the water; however, by adjusting the operating conditions, the ideal fluoride concentration in the water can be achieved (Sanghratna and Arfin, 2015). Using NF membranes in pre-treatment unit operations in thermal and membrane seawater desalination processes, pre-treatment chemicals have been used less frequently, energy consumption has decreased, and water production costs have decreased, leading to the development of enhanced ecologically sustainable procedures (Izadpanah and Javidnia, 2012).

The limitation of this method is that the process is expensive and complicated (Sanghratna and Arfin, 2015) on a community level scale.

2.7.4 Ion Exchange Technology

According to Kansara *et al.* (2016), ion exchange technology is an adsorption technique that involves the exchange of ions from adsorbate to adsorbent and is dependent on the concentration and composition of the solid and aqueous phases. However, there is a lack of specificity, and lower efficiency could result from the presence of other ions. Temperature and pH have an impact as well, so managing these factors is crucial (Singh *et al.,* 2013). In developing nations, this adsorption technique has been widely used (Litza *et al.,* 2015). Recently, there has been a lot of interest in metallic-based adsorbents because of their great efficacy. However, because of their high cost, they are not widely used (Litza *et al.,* 2015).

2.7.5 Adsorption Techniques

Adsorption methods are thought to be more widely accepted and offer many advantages. This can be attributed to their affordability and environmental impact, as well as their effectiveness and ease of design (Swarnaka *et al.,* 2016; Dar and Kurella, 2023), as will be covered in the ensuing subsections.

2.7.5.1 Biosorption

Based on several processes, such as ion exchange, surface complexation, adsorption, absorption, and precipitation, *biosorption* is a physico-chemical and metabolically distinct operation (Formina and Gadd, 2014). Due to their higher attraction for the opposite charges of fluoride ions owing to their magnesium and calcium contents, fungal biosorbents are effective at adsorbing fluoride (Mukherjee and Halder, 2018). *Biosorption* is therefore useful, but it has drawbacks such as choosing the appropriate biosorbent, being easily obtainable, and being difficult to use, which makes it inappropriate for use only by those lacking the necessary scientific knowledge and resources.

2.7.5.2 Bone Char Adsorption Method

The adsorption technique using bone char—which is made by burning bones to ash at a reduced oxygen supply—has been widely used in low- to middle-income countries (Fung *et al.,* 2021). Hydroxyapatite, a substance found in bone char, is what allows fluorides to be removed from water by means of ligand exchange between fluoride and the hydroxyl ion (Medellin-Castillo *et al.,* 2014).

The defluoridation company of the Catholic Diocese of Nakuru (CDN) eliminates fluorides from drinking water using bone char-based filters (Korir *et al.,* 2009; Sawangjang *et al.,* 2021). Contact precipitation, which incorporates calcium and phosphate pellets into the bone char filter material, was developed as a result of additional research on bone char to enhance its adsorption properties and has been implemented in Ethiopia with support from CDN (Johnson *et al.,* 2011).

2.8 Soapstone and Ca-bent

Two major minerals and other minor minerals make up the naturally occurring mineral known as soapstone. Talc ($Mg_3Si_4O_{10}(OH)_{2)}$ and chlorite ($H_4(Mg,Fe)_2Al_2SiO_{11}$) are the two main minerals that make up over 90% of the total mineral content of soapstone. Montmorillonite, whose chemical formula is [$Ca\ (Al,\ Fe,Zn)_2\ (Al,Si)_4O_{10}\ (OH)_2\ nH_2O$], is the primary mineral in ca-bent clay (Ravindra, 2017). The two major minerals have OH^- and Al^{3+} in their matrices.

It was anticipated that talc and montmorillonite would exchange hydroxyls with fluorides in water, similar to what happens in the hydroxyapatite found in bone char, based on the phenomenon of structure activity relationship. Patel *et al.* (2011) asserts that talc's hydroxyl groups are typically found inside the magnesium layer and are only exposed to water at the silicate sheet's edges. Since hydroxyl groups in mineral crystal matrices exchange with fluorides, a thorough size reduction of the soapstone was required in order to expose as much of the active sites as possible and achieve the maximum and most effective adsorption surface. Chlorite ($H_4(Mg,Fe)_2Al_2SiO_{11}$), the main mineral present in soapstone and montmorillonite in ca-bent [$Ca\ (Al, Fe,Zn)_2\ (Al,Si)_4O_{10}\ (OH)_2\ nH_2O$], just like alum ($KAl(SO_4)_2 \cdot 12H_2O$) used in Nalgonda technique (Vardhan and Karthikeyan, 2011) are minerals that contain aluminum, an atom with high positive charge density was thus were postulated to have the capability of removing fluorides through adsorption of the highly electronegative fluoride ion. Since both ions (Al^{2+} capable of adsorbing F^- due to its high charge density and OH^- capable of displacement of F^- in the mineral matrix) are present in soapstone and ca-bent, this study supposes that they are responsible for their effectiveness in the removal of fluoride in water.

2.9 Characterization and Chemical Composition Determination

Numerous methods have been employed for the quantitative mineral analysis and characterization of different natural minerals using different techniques such as Fourier transform infrared spectroscopy (FTIR) (Jozanikohan and Abarghooei, 2022), energy dispersive X-ray spectroscopy (EDX) (Obiajunwa, 2001), X-ray fluorescence spectroscopy (XRF) (Mengue *et al.*, 2022), X-ray diffraction spectrometry (XRD) (El Kasmi *et al.*, 2016), scanning electron microscopy (SEM) (Cook, 2000) Transmission electron microscopy (TEM), thermogravimetric analysis (TGA) (Abdullahi and Audu, 2017) among others. The XRF depicts the chemical compositions of clays and other minerals displaying results such silica oxide and aluminum oxide and thus suitable for compositional analysis (Nayak and Singh, 2007). This study used FTIR to identify the functional groups, SEM to check the surface porosity and XRF to find out the chemical composition.

2.10 Sorption Parameters

2.10.1 pH of Aqueous Solution

The adsorbent determines the pH range at which fluorides can be adsorbed. It is acknowledged, nevertheless, that at low pH levels, hydrogen ions and fluoride combine to form hydrogen fluoride. Furthermore, a high pH prevents fluoride ions from diffusing because hydroxide ions are abundant there (Anusha and Raja, 2014). According to a test of the pH dependence of fluoride adsorption, little fluoride was removed at neutral pH of 7.0 and efficacy was only observed at pH values lower than 3.0 (Vardhan and Karthikeyan, 2011).

Fluoride ion removal from aqueous solutions using aluminum-impregnated chitosan biopolymer was found to be less effective in studies where the pH of the medium was raised further. Conversely, in acidic media, the formation of weak hydrofluoric acid frequently affected the amount of fluoride adsorption by the adsorbent material (Swain *et al.*, 2009).

2.10.2 Contact Time

Contact time depends on the properties of the adsorbents (Sivarajasekar *et al*., 2017) and therefore varies for different adsorbents. Increased contact time with the adsorbent results in enhanced adsorption, according to variation studies on contact time. This is explained by the assumption that at the beginning, all adsorbent sites are available for the anion coordination and that the primary solute concentration gradient is also high. Once adsorption site saturation is reached, the rate of fluoride adsorption remains nearly constant because there are fewer unoccupied sites on the adsorbent and fewer fluoride ions left in the solution. (Korir *et al.*, 2009; Elkhaleefa *et al.*, 2021).

2.10.3 Dosage of Adsorbent

An increase in the fluoride adsorption sites occurs in tandem with the adsorbent dosage. As a result, adding more adsorbent dose to an aqueous fluoride-contaminated water increases its ability to remove fluoride. F^- removal was found to be enhanced as the chitosan dosage increased in a study by Akbari *et al.* (2018) on the evaluation kinetics of fluoride adsorption in aqueous solutions on chitosan adsorbent.

2.10.4 Adsorbate Concentration

To ascertain the impact of the initial fluoride concentration on the adsorption process, an experiment was conducted with a fluoride solution volume of 100 mL, a contact period of 40 minutes, an adsorbent dose of 7.0 gL^{-1}, and a concentration range of 1–10 mgL^{-1}. It was reported that the percentage of fluoride removed decreased as the initial fluoride concentration increased. This was explained by the fact that when fluoride concentration rises, the adsorbent's binding capacity approaches saturation value, which lowers the removal percentage overall (Ayinde *et al.,* 2022). The Langmuir adsorption isotherm model was used to confirm this adsorption process.

2.10.5 Existence of Co-ions

Groundwater containing fluoride contains a number of other ions that can also participate in the adsorption process with fluoride. It was found that bicarbonate, carbonate, chloride, sulfate, and nitrate were adversely affecting fluoride adsorption, indicating the impact of coexisting ions on fluoride removal. The presence of bicarbonate and carbonate resulted in almost no fluoride removal in a study of the adsorption capacity of modified chitosan-based adsorbent (Jagtap, 2009). Another related study on chitosan derivatives and composites' ability to remove fluoride from water confirmed the findings of the previously cited study. It found that ions such as sulfate, bicarbonate, and chloride have a significant impact on the uptake of fluoride by adsorbents in drinking water, thereby competing with fluoride sorption (Miretzky and Cirelli, 2011).

2.11 Methods of Analysis

2.11.1 Fluoride Ion Selective Electrode (ISE)

The activity of a particular ion in a solution can be converted by an ion selective electrode (ISE) sensor into a potential that can be measured using an Ion meter or mV (Ionode, 2019). The fluoride ion electrode's sensing membrane, according to Kandil *et al.* (2016), is made of single crystal lanthanum fluoride (LaF_3). To increase the conductivity, europium is doped into the crystal. The formation of LaF^{2+} at the membrane-solution interface is the equilibrium that results in the membrane surface gaining a charge. For a solution with a lower F^{-}concentration, the equilibrium moves to the right, increasing the potential with respect to the membrane's other side. The LaF_3 crystal membrane experiences a potential difference as a result, which is measured and translated into F^{-} concentration. Even though the fluoride ion selective electrode is incredibly selective to F^{-} ions, at pH values higher than 8, OH^{-} ions, which have almost the same diameter as F^{-} ions, can cause interference. The basis for the ion-selective electrode's operation is the linear proportionality between the electrical potential across the membrane and either the effective concentration of the solution or the logarithm of the ions' activity in the solution, as determined by Nernst equation 2.1.

$$E = Eo + \left(2.303 * \frac{RT}{nF}\right) log(a) \qquad \text{Equation 2.1}$$

where E is the measured electrode potential (mV),

E_0 is the standard electrode potential for the ion selective fluoride (mV),

R is the gas constant (8.314 J/K/mol),

T is the absolute temperature (K),

F is the Faraday constant (9.648×10^4 Coulomb/mol),

a is the activity of the fluoride ion,

n is the charge on the ion (-1 for fluoride)

2.11.2 X-Ray Fluorescence Spectroscopy (XRF)

According to Young *et al.* (2016), XRF spectroscopy is a widely utilized method that provides diagnostic compositional data on geological samples. Its working principle is to subject a sample to a stream of intense X photons, which interact with an electron in its inner shell. An electron is expelled from the newly formed vacancy and is followed by an electron from any of the outer shells that occupy it because the energy of the incoming photon is much greater than the binding energy of the shell. If the process is followed by an excess of electron energy, the elements that make up the sample are typical of the x-ray that is released (Bouh, 2020). With wavelengths ranging from roughly 10 nm to 10^{-4} nm, X-rays are defined as radiation with energies between those of gamma and ultraviolet light. They are a subset of the electromagnetic spectrum.

Figure 2.1 typically illustrates the XRF setup, showing the incident X-ray beam striking the sample at a specific angle, the emitted fluorescent X-rays leaving the sample at the take-off angle, and the detector positioned to capture these emissions

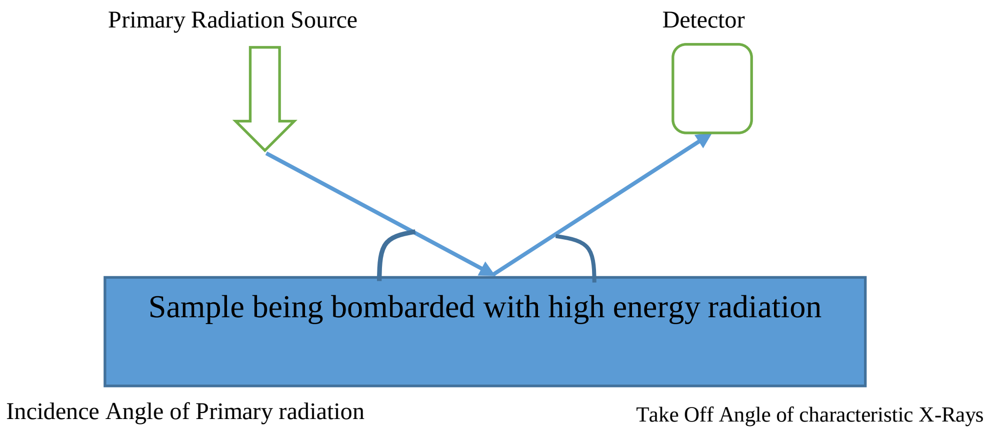


Figure 2.1 An illustration of the parameters of XRF analysis

2.11.3 Scanning Electron Microscopy (SEM)

Using an electron beam, scanning electron microscopes (SEMs) are spectrophotometric instruments that image materials at nanoscale resolutions. In the electron source, the electrons are released from a filament and collimated into a beam. A series of lenses in the electron column then focus the beam onto the surface of the sample (Hidayanti and Harnovan, 2020). Many electron and X-ray signals are produced when high energy electrons from this concentrated beam strike the sample. Electrons that are scattered out of the sample and only slightly lose energy are known as backscattered electrons. They have a strong interaction with the sample and come from a few microns below the surface. They offer compositional details with lower resolution images. Following elastic interactions between the beam and the sample, backscattered electrons are reflected (Kejzlar *et al.,* 2014).

The secondary electrons that are released from the sample within a few nanometers of its surface due to inelastic interactions between the electron beam and the sample have less energy than the electrons that are backscattered. They offer topographic information and are highly sensitive to surface structure (Hidayanti and Harnovan, 2020). When electrons strike the sample surface, characteristic X-rays are also generated. They provide details regarding the sample's elemental composition (Kejzlar *et al.,* 2014).

Owing to these qualities, SEM was the preferred technique for figuring out the sample's internal and external morphology.

2.11.4 Fourier Transform Infrared Spectroscopy (FTIR)

The word "spectroscopy" refers to a broad category of chemical analytical methods that focus on the interaction of light and matter. A spectrum is created when matter absorbs radiant energy and goes through excitation and de-excitation (Sasikala *et al.*, 2021). The fundamental idea is that every substance has a specific range of wavelengths over which it can either transmit or absorb light.

Infrared spectroscopy with Fourier transform explores the resonant frequencies of molecules. A molecule can be distinguished by grouping all its functional groups together, as each functional group vibrates and has a distinctive vibrational energy (Duygut *et al.*, 2009). Because of this characteristic, FTIR microscopy can be used for particle analysis, multilayer film characterization, and sample determination.

As seen in Figure 2.2, the FTIRs spectrum is composed of various regions that correspond to unique energy (E), frequency (v), and wavelength (λ) ranges. The inverse correlation between wavelength and frequency generates the wavenumber (cm^{-1}) as the unit for infrared (Verma, 2022).

$$\text{Energy}(\text{E}) = \text{hv} = \text{C}/\lambda \qquad \text{Equation 2.2}$$

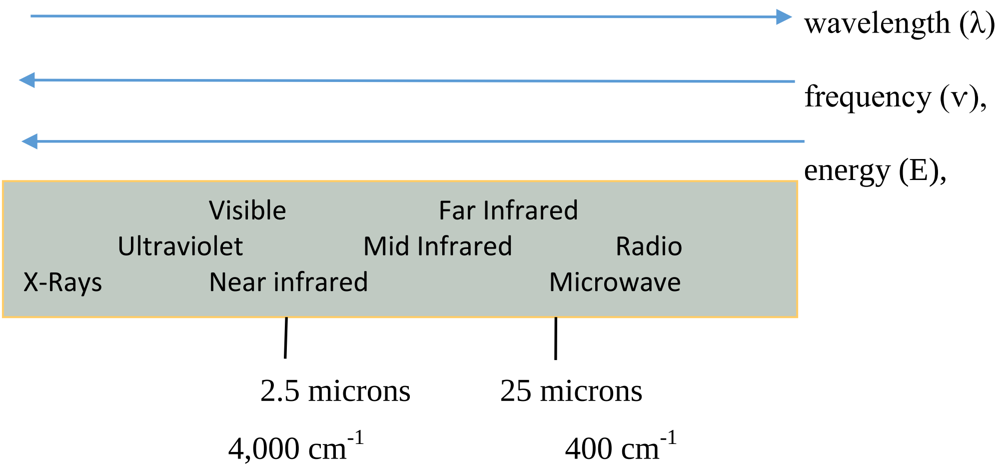


Figure 2.2 An Illustration of the electromagnetic Spectrum

The basis of FTIR spectroscopy is the way in which infrared light modifies the dipole moments in molecules, which corresponds to specific vibrational energy.

2.11.5 Freundlich and Langmuir Equilibrium Adsorption Isotherms

Models such as the Freundlich and Langmuir isotherms have been found to be helpful in explaining the adsorption process by different adsorbents. The Langmuir model presupposes uniform adsorption energies onto the surface and no adsorbate transmigration in the surface plane, whereas the Freundlich model pertains to a heterogeneous adsorbent surface (Gatchev *et al.*, 2014).

The equilibrium between the adsorbate and adsorbent system is described by the Langmuir adsorption isotherm, where it is assumed that the adsorbate adsorption is restricted to a single molecular layer at a relative pressure of one. According to Lingling *et al.* (2019), the Langmuir further assumes that the adsorption-desorption rates at equilibrium are equal and that the fraction of surface coverage is directly proportional to the rate of desorption from the surface. Equations 2.3 and 2.4 represent the linear equation for the Freundlich and Langmuir isotherm models:

Freundlich isotherm: $log\ qe = log\ KF + (1 / n)\ log\ Ce$ Equation 2.3

Langmuir isotherm: $(Ce / qe) = (1 / qaKL) + (Ce / qa)$ Equation 2.4

Where KF (mgg $^{-1}$) is the Freundlich constant and ‘n’ the Freundlich exponent, qe (mgg $^{-1}$) is the adsorbed amount of F^- at equilibrium, Ce (mgL^{-1}) is the equilibrium concentration of F^- qa (mgg $^{-1}$) and KL (L mg^{-1}) are Langmuir constants related to adsorption capacity and energy of adsorption.

2.11.6 pH Measurement

A reference electrode, a temperature element that provides a temperature signal to the pH analyzer, and a hydrogen ion potential sensitive electrode are the three main components of pH measurement.

The pH electrode generates a potential in the form of voltage proportional to the hydrogen ions in the solution by placing a specially formed, pH-sensitive glass in contact with the solution. Completing the pH measuring circuit inside the solution, the reference electrode sustains a steady potential that serves as a reference potential.

A millivolt signal proportional to pH is produced by the potential difference between the pH and reference electrodes. The –Log concentration of H ions in the solution is the expression for pH. This makes it possible to express pH as a whole number because measured concentrations are typically expressed to multiple decimal places.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Research Design

The water was examined using an electrochemical technique that used a pH meter and a selective electrode for fluoride ions, both before and after treatment. This is premised on the fact that fluoride ion activity is dependent on fluoride ion complexes, pH, and the total ionic strength of the solution. By adding Total Ionic Strength Adjustment Buffer (TISAB), the electrode was able to accurately measure the fluorides because it produced a relatively uniform ionic strength background, controlled pH, and dissociated any fluoride complexes (Farwell *et al.,* 2006). The analytical grade ammonium fluoride reagent was used to calibrate the fluoride meter properly using a range of fluoride standards that corresponded to the expected concentration range. To zero meters, distilled water devoid of fluoride was utilized. The flow chart of the process is depicted in the illustration in figure 3.1.

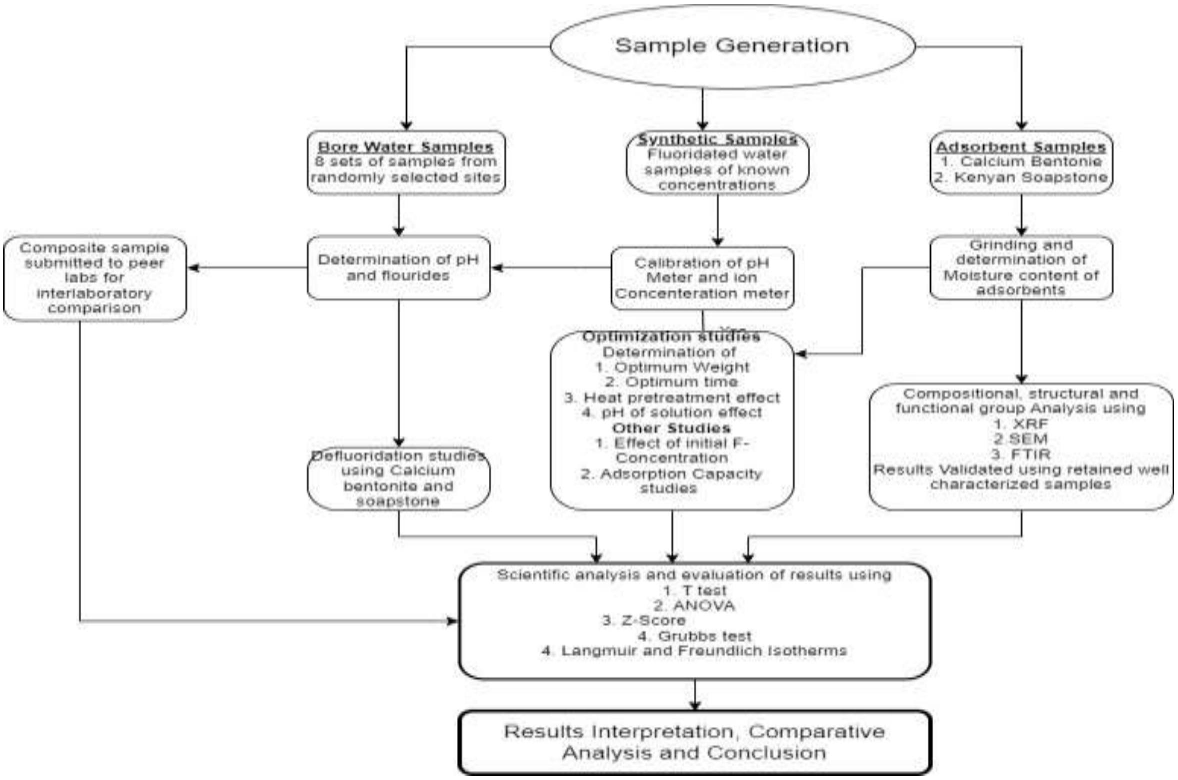


Figure 3. 1 Research Methodology Flow Chart

3.2 Chemicals and Reagents

In this study, analytical grade sodium chloride crystals (99.5% purity), 0.1 M sodium ammonium hydroxide (99.5% purity with expanded uncertainty of ± 0.005 mgL^{-1}), 100.0 mgL^{-1} of 99.5% purity with expanded uncertainty of ± 0.4 mgL^{-1} ammonium fluoride solution, and 99.5% pure citric acid crystals were used. The source of these reagents was Romil Pure Chemistry in the United Kingdom.

3.2.1 Fluoride Standard Solution

The 100.0 mgL^{-1} fluoride standard solution which was obtained from Romil Ltd was accompanied by a calibration result in a certificate of analysis indicating 100.0 mgL^{-1} @20 ^{o}C. The traceability of the calibration was done using Ag primary reference material. The certificate of analysis indicated that it was prepared from NH_4F into water matrix and that it was meant for Ion Selective Electrode calibration making it fit for purpose.

3.2.2 Total Ionic Strength Adjustment Buffer (TISAB)

This TISAB was packaged by the manufacturer with a certificate of analysis. According to the instructions, 2 mL of TISAB needed to be added for every 50 mL of water sample.

3.2.3 The pH Buffer Solutions

The pH buffer used were from Romil Ltd. Buffers used had pH values of 4.01, 7.01 and 10.00.

3.2.3.1 The pH Adjustment Solutions

Citric acid and sodium hydroxide were used for adjustment of pH of the test samples. They were obtained from Romil Ltd and were accompanied by certificates of analysis.

3.3 Instrumentation

3. 3.1 Fluoride Ion Concentration Meter

Using the fluoride ion selective electrode on the EDT direct ION DR359TX - Ion Concentration Meter, the fluoride content of the solutions was ascertained. To maintain a constant ionic strength, 2 mL of total ionic strength buffer (TISAB) was added to 50 mL of the sample for the test portion. NH_4F standard solutions with concentrations of 0.01, 0.1, 1.0, 5.0, and 10 mgL^{-1} were used to calibrate the ISE.

3.3.2 X Ray Fluorescence Spectrophotometer (XRF)

The Bruker S1 TITAN 800, a portable X-ray fluorescence (XRF) analyzer made for quick and precise elemental analysis, was used to perform compositional analysis. Its design is lightweight and sturdy, and it provides accurate and fast element detection ranging from magnesium (Mg) to uranium (U).

3.3.3 Scanning Electron Microscope (SEM)

The Schottky field-emission gun on the FEI Nova NanoSEM 230 microscope, which enables visualization of samples at high (HV) and low (LV) vacuum (< 200 Pa), at variable potential (50 V to 30 kV), and with the option to decelerate the electron beam, was used to generate the SEM images.

3.3.4 Multiparameter Meter with GPS Capabilities

For pH determination and GPS location Hanna Instruments Multiparameter Meter HI9829 was used. It is a versatile, waterproof multi-parameter portable meter designed for all-inclusive water quality testing equipped with GPS capabilities, allowing for precise location tracking of sampling sites, ensuring accurate geographical data integration with large storage module for data retention. This meter was also used to measure pH.

3.3.5 Orbital Shaker

The MRC Orbital Shaker was used for mixing the samples and ensuring adequate contact of adsorbent adsorbate in aqueous solution. It features digital controls for setting speed, time, and wide range of motions, ensuring uniform mixing of samples for consistent and reproducible results.

3.4 Samples Collection and Generation

Soapstone samples were obtained from Kisii County, Nyabigege Village in Tabaka Sub County where there are large deposits of the mineral. It was noted that they are basically in shades of cream and red. A 20 kgs sample of soapstone was drawn from three quarries in small portions of between 100 g and 500 g. They were placed in suitable polythene sampling bags and transported to the Eldoret, Kenya Bureau of Standards laboratories for experimentation. Powdered ca-bent clay was purchased from local supermarkets within Mombasa city. The origin of the clay was traced to Mt Kenya national park area.

Eight water samples were drawn at Kiamunyeki in Nakuru East Sub County, Nakuru County and these sample generation sites were randomly selected based on prior intelligence on sites with fluoridated water. The general location being guided by information obtained from the Catholic Diocese of Nakuru (CDN) water defluoridation company. Water samples were drawn using the discharge outlets into 1 L bottles. A total of 8 water samples were drawn of 2 L each from Nakuru County. The samples transported to the Eldoret, Kenya Bureau of Standards laboratories for experimentation.

3.5 Adsorption Experiments

With the help of the filtration system, the ion concentration meter, orbital shaker, optimization studies covered in the next section were performed by way of, batch adsorption tests were conducted.

3.6 Optimization Experiments

3.6.1 Contact Time

Plastic beakers were filled with 36, 50 mL portions of 10 mgL^{-1} fluoride solutions. Each sample received 0.5 g of ca-bent clay and soapstone, which were added and mixed at the same 150 rpm orbital shaker speed. At intervals of 0, 5, 10, 30, 45, and 60 minutes, samples were removed from the shaker and vacuum-filtered through Whatman® number

41 double filter paper with a porosity of 20–25 μm. The filtrate's fluoride ion content was then determined using an ISE.

3.6.2 Optimum Weight of Adsorbents

A number of 50 mL of the 10 mgL^{-1} anion solution (fluoride) were dispensed in replicates into plastic beakers. Samples of 0.10, 0.20, 0.30, 0.50, 0.75, 1.00 and 1.50 g of ca-bent and soapstone samples were added to the plastic beakers and put on an orbital shaker for optimum time informed by the results in part one, to obtain the optimal weight for adsorption.

3.6.3 Aqueous Solution Concentration

The optimal weight of adsorbent established in the previous experiment was weighed in replicates into plastic beakers and added into aqueous fluoride solutions of 0.05, 0.10, 0.20, 0.40, 0.50, 0.75 and 10.00 mgL^{-1} prepared from stock solution (3.2.1) to determine the adsorption capacities of adsorbents.

3.6.4 Optimum pH Determination

Using sodium hydroxide and citric acid solutions, the pH of the synthetic fluoride solutions was adjusted to 1.5, 2.0, 3.6, 4.2, 6.2, 10.9, and 11.6. The impact on fluoride removal was determined by comparing the outcomes using an ISE.

3.6.5 Heat Pretreatment of the Adsorbents

Powdered samples of the adsorbents each 50 g were placed into aluminum moisture dishes placed into an oven. The samples were placed into the oven in 3 batches at three different temperatures and held in the oven for 2 hours each time. and another batch also in the muffle furnace for the higher temperature. The operating temperatures were 100 °C, 210 °C, 300 °C and 510 °C in the furnace. The duration of heat treatment was two hours.

After cooling the adsorbent samples to room temperature, they were used in adsorption experiments to determine the adsorption profile, which considered the impact of pre-heating the adsorbents.

3.7 Effect of Chlorides in Aqueous Test Solution

Known concentrations of ultrapure sodium chloride solution were mixed with standard fluoride ion solutions to ascertain their impact as current competing ions on fluoride removal from aqueous solution. The samples were first subjected to adsorption experiments using soapstone and ca-bent, with final concentrations of 2.5 mgL^{-1}, 5 mgL$^{-1,}$ and 7.5 mgL^{-1} of chlorides having 10 mgL^{-1} of fluorides in each case. Weight of 4.0 g of soapstone and 0.75 g of ca-bent were separately added to 50 mL of synthetic fluoridated water samples spiked with chlorides. The contact time for the experiment was 45 minutes for ca-bent and 5 minutes for soapstone.

3.8. Analysis of Bore Water Samples

Ground water samples obtained from boreholes of Nakuru County, preserved in PET bottles, were used to determine the ability of soapstone and ca-bent to remove excess fluorides in real water samples. An ion concentration meter equipped with a fluoride ion selective electrode was used to measure the fluoride content of the water. 50 mL of bore water samples were combined with 4.0 g of soapstone and 0.75 g of ca-bent, which were added in separate portions. The mixtures were then agitated at 150 rpm to achieve the ideal contact time determined by the batch experiments. The mixtures were then filtered through a vacuum filtration apparatus into a vacuum flask, 50 mL portions transferred into separate beakers. TISAB was then added to the samples at a ratio of 2:50 to guarantee a relatively uniform ionic concentration between the samples and the standards and a fluoride ion selective electrode was used to determine the fluoride concentration.

3.9 Validation of the Method

Replicas of known volumes of buffered ground water samples that had previously been measured for F-concentration were combined with known concentrations of synthetic fluoride ion solutions to ascertain the effects of the sample matrices. The mixtures were buffered, and the fluoride content was ascertained after equilibration. The formula in equation 3.3 was used to determine the recovery percentage.

$$\frac{\text{Spiked Sample F}-\text{amount (mg) – Ground Water Sample F}-\text{amount (mg)}}{(\text{Amount of spiked F}-\text{ in mg})} \times 100 \qquad \text{equation 3.3}$$

Through the use of certified reference materials and available samples, we verified the results generated by the X-ray fluorescence spectrophotometer, the scanning electron microscope, and the Fourier transform infrared spectrometer.

3.10 Data Analysis

To ascertain the adsorption capacities, the experimental test results were fitted into Freundlich and Langmuir isotherms. Using an ANOVA one-way factor, the variations in response to modifications brought about by optimization studies using the two adsorbents were investigated.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

The findings of this study, which used ca-bent clay and soapstone that are readily available in nature, are presented in this chapter. The sections and subsections that follow provide discussions of the findings.

4.2 Method Validation

4.2.1 Validating Fluoride Ion Selective Electrode

Using standard F^-solutions and interlaboratory comparative testing, the linear working range, reproducibility, and detection limit of the fluoride ion selective electrode were determined. The results are shown in table 4.1.

Table 4. 1 Method Validation Results

Linearity test		Interpretation
Regression, R^2	0.999	0,1% of Y Explained by Random Error
Slope error	0.007	99.3% Precision
Standard error of y	0.006	99.4% Accuracy
Intercept error	0.03	3.0% Baseline Drift
Repeatability limit, r	0.09	95% CL Acceptance

From table 4.1, linearity gave an R^2 of 0.999 when standards of 0.0, 0.1, 0.5, 1.0, 5.0 and 10.0 mgL^{-1} of fluorides were used in calibration of the fluorides curve. The slope error was established to be 0.007, while the standard error of y as 0.006 and the y intercept error as 0.03.

4.2.2 Validating Accuracy, Repeatability and Reproducibility of Method

The test for accuracy, repeatability and reproducibility were combined in the recovery test as displayed on table 4.2.

Table 4. 2 Accuracy, Repeatability and Reproducibility Fluoride Results

Period	Day	Spiked (mg)	Sample (mg)	Total (mg)	Final (mg)	Difference	% Recovery	Average
Within day (Repeatability)	Day 1	2.5	2.1	4.6	4.4	0.2	92	94.4
	Day 1	2.5	2.1	4.6	4.5	0.1	96	
	Day 1	2.5	2.1	4.6	4.4	0.2	92	
	Day 1	2.5	2.1	4.6	4.5	0.1	96	
	Day 1	2.5	2.1	4.6	4.5	0.1	96	
Between days (Reproducibility)	Day 1	2.5	2.1	4.6	4.46	0.14	94.4	92.48
	Day 2	2.5	2.1	4.6	4.4	0.2	92	
	Day 3	2.5	2.1	4.6	4.5	0.1	96	
	Day 4	2.5	2.1	4.6	4.3	0.3	88	
	Day 5	2.5	2.1	4.6	4.4	2.3	92	
	Average	**STDV**	**RSD**	**P**	**α (95%CL)**			
Within day	94.4	2.19	2.32	0.44	0.05			
Between days	92.48	3.03	3.27					

A sample that had been verified to have 4.2 mgL^{-1} through consensus value of interlaboratory comparative testing of fluorides was mixed with equal volume of 5 mgL^{-1} of synthetic aqueous solution prepared in the lab. The expected fluoride level was thus calculated as 4.6 mgL^{-1}. As reported by Little (2016), method recovery acceptance criterion was set at between 90% and 110% of the nominal value which translated to 4.14 mgL^{-1} to 5.06 mgL^{-1}.

From table 4.2 the analysis shows that the within-day recovery has an average of 94.4% and for a period of five days of testing the recovery average is 92.48. The t test was done to determine whether quantification of fluorides on the sample over a period had significant difference compared to the same sample tested within a day returned a value of 0.44 at 95% CL or probability of 0.05. This means that the variation in the results from the two sets of data were not significantly different but were just because of random errors.

It was also confirmed that the relative standard deviation of repeatability for the constituted sample analysed on the same by the same analyst was 2.32 while the reproducibility relative standard deviation examined over a period of 5 days was found to be 3.27. Regression statistics on the same set of data returned a R^2 of 0.999, a slope error of 0.007 representing a bias of 0.07% of the average values of the data set equivalent to linearized calibration range accuracy of 99.93%.

4.2.3 Validating Suitability of XRF Instrument

Table 4.3 shows the results obtained using the Bruker Titan S1 XRF on a sufficiently characterized secondary reference material.

Table 4. 3 Validation Results of XRF Instrument Used for Compositional Analysis

Parameter	Al_2O_3	CaO	Fe_2O_3	MgO	Mn_2O_3	P_2O_5	SiO_2	TiO_2
Reference Value R %m/m	1.399	0.034	96.448	0.073	0.125	0.192	1.431	0.137
Uncertainty U_{RV}	0.043	0.010	0.334	0.020	0.005	0.007	0.034	0.007
Lab Results	1.386	0.033	96.306	0.077	0.129	0.186	1.438	0.128
Uncertainty U_L	0.012	0.003	0.020	0.004	0.002	0.003	0.004	0.004
Upper Value of Lab Results	1.398	0.036	96.326	0.081	0.131	0.189	1.442	0.132
Lower Value of Lab Results	1.374	0.030	96.286	0.073	0.127	0.183	1.434	0.124
Validity Statement for Equipment Results	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass

U_{Rv} and U_L refers to the uncertainties of the reference value and that of the laboratory results respectively.

All the results obtained are within the acceptable range based on assigned values obtained through inter laboratory test on a reference sample done in several different laboratories. The average of repeat laboratory results, when expanded by the uncertainty values still fall within the band of the reference value and its associated uncertainty. Systematic bias of the results was not detected as the results were with the band both on the upper and lower sides of the refence value, R. The band of reference value is the assigned value is expanded by the uncertainty factor associated with the particular result.

4.2.4 Validating FTIR Spectrum of Instrument Used

The FTIR instrument was validated using a reference mineral sample, and the peaks found during the instrument's validation were consistent with the sample's peak stored in the library. Vibration bands at 3615 cm^{-1} and 3406 cm^{-1}, which were identified in the FTIR spectrum of the bentonite was attributed to O-H stretching and both the intralayer and interlayer H-bonded O-H stretching. Additional bands that were picked were those in the 934 cm^{-1} and 490 cm^{-1} regions, which are linked to the Si-O group's bending and stretching vibrations.

4.3 Sorbent Analysis

4.3.1 The XRF Compositional Analysis of Adsorbents

Soapstone and calcium bentonite adsorbents were subjected to XRF analysis using handheld Bruker S1-Tinan model and the results presented in table 4.4.

Table 4. 4 XRF Compositional Analysis Results of Soapstone and Ca-Bent

Element	% m/m in Soapstone	% m/m in Ca-bent
Silica as SiO_2	50.74	63.17
Aluminum as Al_2O_3	34.74	18.44
Titanium as TiO	3.6	0.33
Potassium as K_2O	2.17	7.3
Calcium Oxides as CaO	0.96	1.06
Phosphorus as P_20_5	0.86	0.84
Iron as Fe_2O_3	0.35	8.04
Sulphur as S	0.13	0.12
Barium as Ba	0.09	0.08
Tin as Sn	0.07	ND
Rubidium as Rb	0.04	ND
Manganese as MnO_3	0.01	0.16
Chromium as Cr_2O_3	0.01	ND
Zichronium as Zr	ND	0.23
Zinc as Zn	ND	0.02

The results from table 4.4 show that the oxides that are most prevalent in both mineral samples are SiO_2 (50.74% m/m in soapstone and 63.17% m/m in ca-bent). It is also observed that Al_2O_3 in soapstone and ca-bent was 24.74%m/m and 18.44%m/m respectively. Presence of Aluminum (a Lewis acid electron acceptor) in the adsorbent is responsible for binding affinity with fluoride (a Lewis base electron donor) (Xiang *et al.*, 2023). However, after treatment, there is a high concentration of aluminum in the water because aluminum-based adsorbents have low magnetic properties. The presence of iron as iron oxide in the ca-bent (8.04% m/m) presumptively improves its magnetic property hence reducing the risk of aluminum deposits after treatment (Girma *et al.,* 2020).

Calcium oxide was found to be 0.96%m/m and 1.06%m/m in soapstone and ca-bent respectively. This mineral though in trace amount has the influence of precipitating fluorides from the solution especially in acidic environment (Ren *et al.,* 2016). Precipitation, however, was not the primary goal of this study but binding of fluorides to the mineral matrix of the adsorbents.

Titanium based compounds such as its oxide which was found present in soapstone and ca-bent 3.60% m/m and 0.33% m/m respectively have also the ability to reduce fluoride in aqueous solution through adsorption (Li *et al*., 2010). Potassium oxide is also present in both minerals in appreciable amounts of 2.17% m/m and 7.30% m/m in soapstone and ca-bent respectively. No known role in defluoridation would be authoritatively assigned to its presence as well as the other elements which were in trace amounts of less than 1% m/m. These findings are in good agreement with the findings of a study conducted by Folorunso *et al.* (2014) on the characterization and qualitative analysis of some clay that originated in Nigeria. The sample in question had a silica value of 63.35% m/m, followed by aluminum at 22.42% m/m and iron at 6.109% m/m. The ca-bent's analytical results also revealed that the Al_2O_3/SiO_2 ratio is roughly 1/3, which satisfies the basic structure of montmorillonite, the primary mineral on the ca-bent. This finding is consistent with a study carried out by Khan *et al.* (2017), which examined samples from seven distinct Pakistani sources of bentonite. and a comparative study of the chemical composition of bentonite clays from the Ashaka and Tango deposits in Gombe State, Nigeria, was carried out by Abdullahi and Audu (2017). They discovered that the Si, Al, and Fe orders corresponded to the three dominant species.

4.3.2 FTIR Analysis

Calcium adsorbent and soapstone were analyzed using FT-IR and the results presented in the following subsections.

4.3.2.1 FTIR Analysis of Soapstone

Figures 4.1 shows FT-IR spectrum for the adsorbent soapstone.

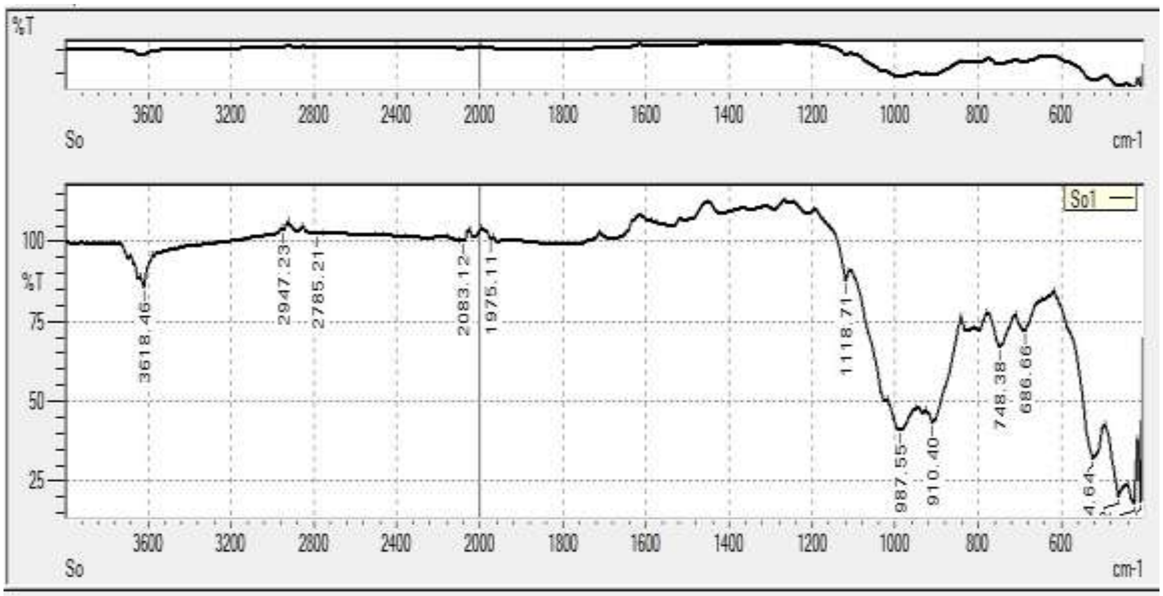


Figure 4.1 FTIR Spectrum for Soapstone

A band at 3618.46 cm^{-1} was observed in the spectra shown in figure 4.1, and this band is linked to the vibrations of isolated silanol groups (Si–OH). A possible correlation between the band at 3618.46 cm^{-1} and geminal silanol groups (Si(OH)$_2$) exists. The binding sites for fluoride sorption are created in the sample by the presence of (Si–OH) groups.

4.3.2.2 The FTIR Analysis of Ca-bent

Figure 4.2 displays the bentonite sample's FTIR spectrum, which was recorded between 4000 and 400 cm^{-1}.

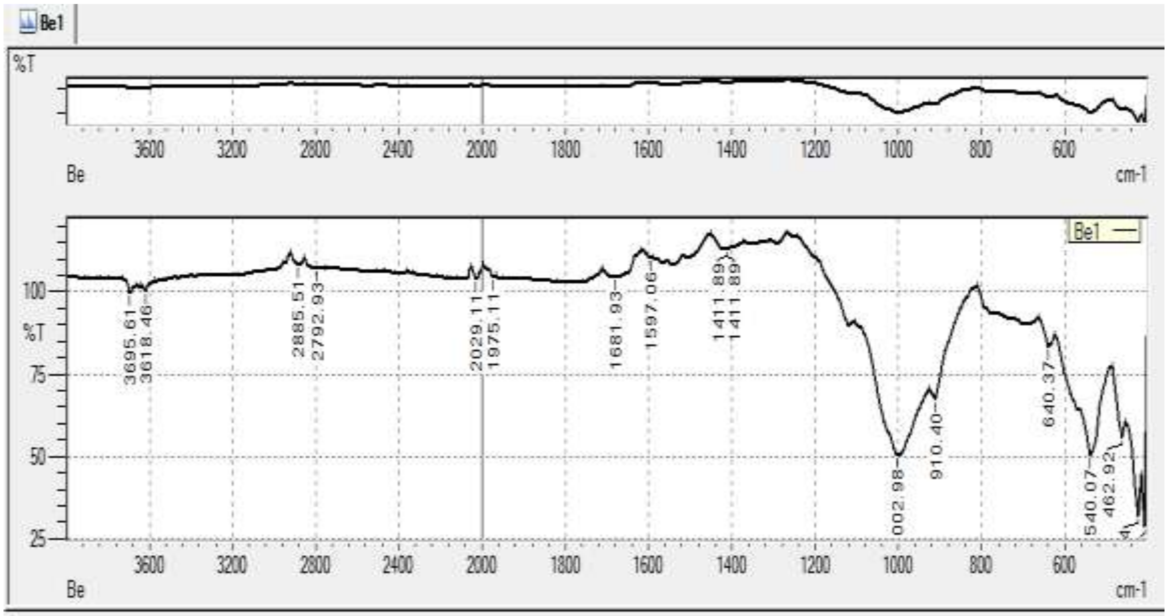


Figure 4. 2 The FTIR Spectrum for Ca-bent

Figure 4.2 shows that there is a band in the 950–1100 cm^{-1} region that corresponds to the Si–O group symmetric and asymmetric stretching vibrations. This band splits into a sharp band at 1002.98 cm^{-1}, and the shoulder at about 1100 cm^{-1} is thought to be caused by the Si–O group splitting perpendicularly (Xie e*t al.*, 2001). Al-OH-Al is linked to the sharp peaks at 3695.61 cm^{-1} and 3618.46 cm^{-1} in the mineral. According to Alemdar *et al*. (2005), the band seen at 910 cm^{-1} is attributed to the OH^{-}deformation mode of Al-Al-OH or Al-OH-Al.

More binding sites for the sorption of fluoride ions were indicated by the presence of more OH-peaks in calcium bentonite. The scanning electron microscopy (SEM) analysis, as covered in the subsection that follows, was used to confirm this.

4.3.3 The SEM Analysis

Figures 4.3(a) and 4.3(b) respectively show the results of an investigation into the surface morphology of soapstone and bentonite clay.

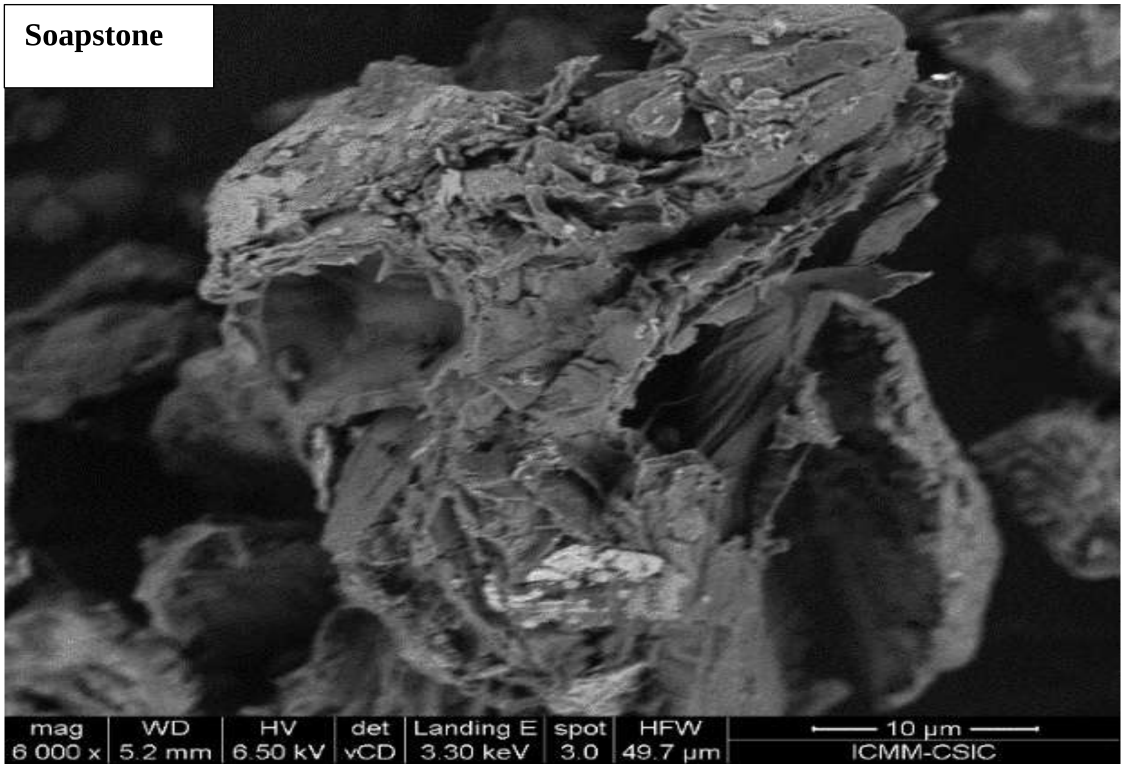


Figure 4.3.(a) SEM Image of Soapstone

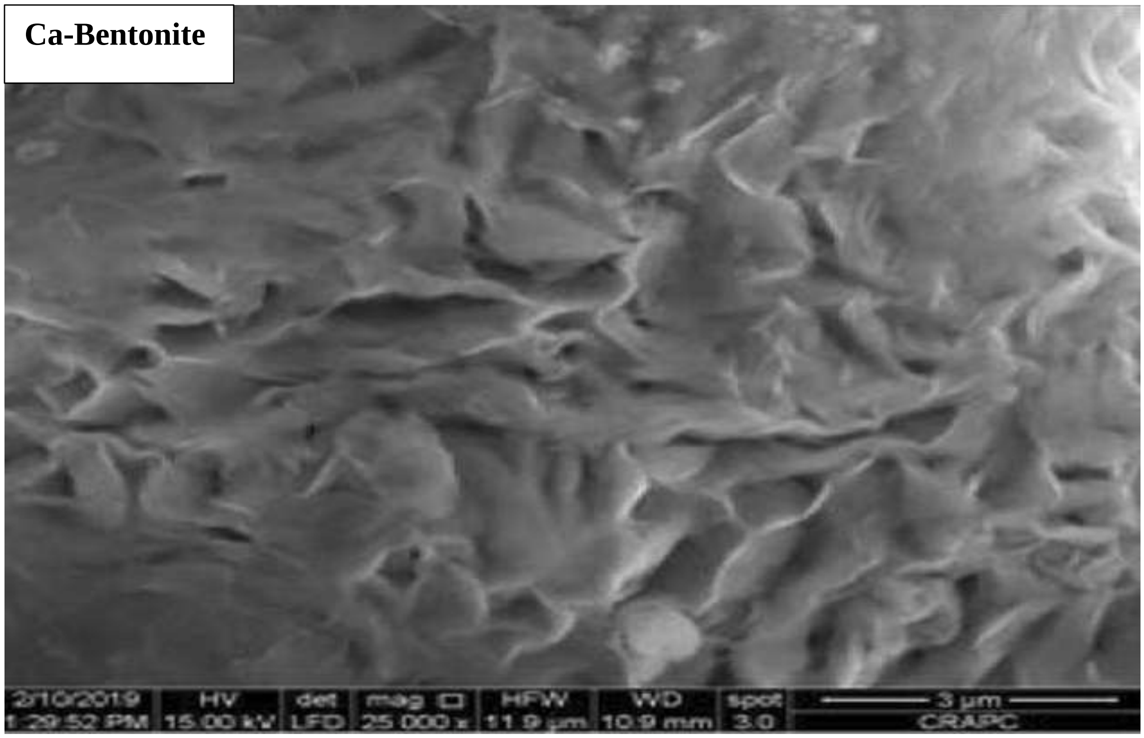


Figure 4.3 (b) SEM Image of Ca-bent

From images in figures 4.3 (a) and 4.3(b) it was observed that there was a higher number of pores in calcium bentonite than in soapstone. The high number of pores increases the surface area for sorption of fluoride ions in ca-bent as was found in an experiment for finding the impact of pore size on hydrocarbon adsorption in activated carbon fibers based on phenol (Mangun *et al.,* 1998). In addition, Idris *et al.* (2013) reported that higher porosity increases removal capacity. The large surface area of ca-bent likely contributed to its higher removal capacity in this study compared to soapstone. A bright crystallite solid that appears to be composed of free silica can be seen at the surface of the ca-bent (Marouf *et al.,* 2021).

To increase efficiency of sorbents, optimization of parameters was performed and discussed in the following sections.

4.4 Optimization Studies

4.4.1 Effect of pH on Removal of Fluorides in Water

One crucial parameter that controls the sorption process is the pH of the aqueous solution (Demirbas *et al.*, 2004; Hiremath and Theodore 2017; Collivignarelli *et al.*, 2020). Therefore, it is necessary to identify an appropriate pH range for an effective reaction. This study looked into how pH affected the fluoride removal in water, with the findings shown in figure 4.4.

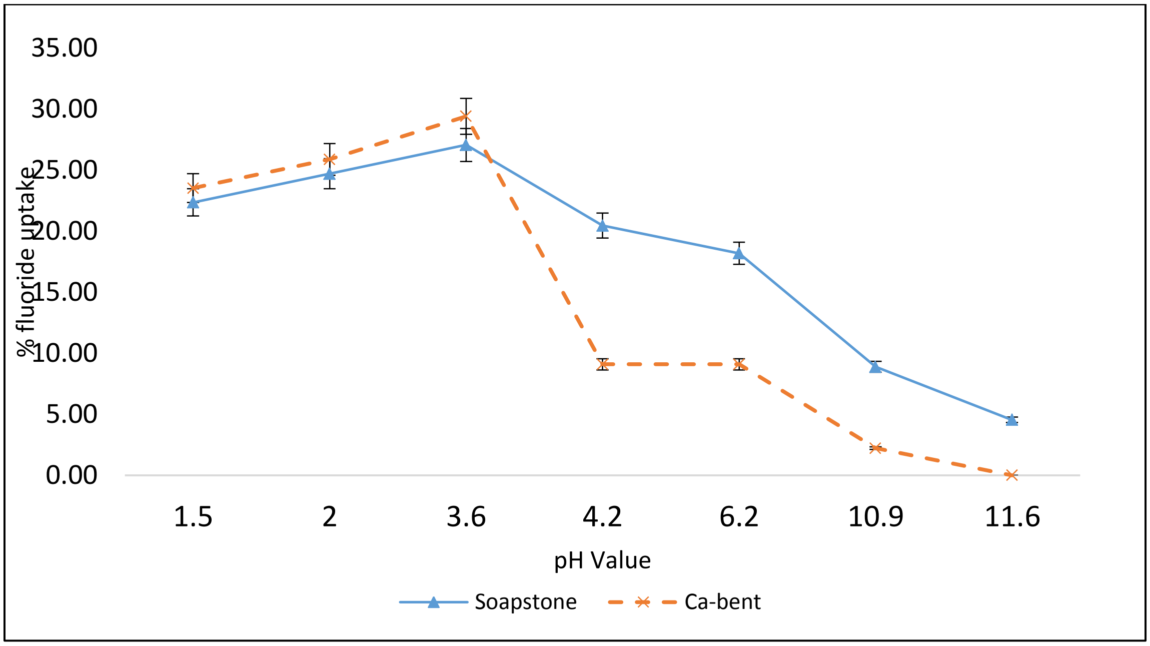


Figure 4.4 Effect of pH on Removal of Fluoride

(Temp of 24±1 ° C, Contact Time of 5 min /45 min and 0.75 g/1.0g of Soapstone Ca-bent)

From figure 4.4 the aqueous solution's pH dropped from 3.6 to 1.5, the uptake of fluoride in soapstone and ca-bent clay decreased from 27.06% to 22.35% and 29.41% to 23.53%, respectively. This may be because fluoride-soluble species, particularly HF, which forms preferentially at low pH values (Lashkenari *et al.*, 2012). The presence of optimally charged H+ ions on the adsorbent surface, as reported by Joshi *et al.* (2013), causes an increased sorption at pH values of 3.6, as this tends to neutralize oxides that form on the adsorbent surface in humid environments, as reported by Assaoui *et al.* (2020). This reduces the negative repulsion of ionic species, which in turn makes fluorides available for adsorption. The number of hydroxyl ions increases while the number of hydrogen ions decreases at higher pH values, from 3.6 to 11.6 (Fourest and Serre 1996; Pradhan *et al.*, 1998), leaving the adsorbent surface negatively charged. There may be increased competition between the hydroxyl and fluoride ions at these higher pH values, which could result in diffusion resistance (Tomar and Kumar, 2013). where OH^- displaces F^- from the adsorbent leading to decline in fluorides adsorbed from 27.05% to 4.55% for soapstone and 29.41 % to below detectable levels in ca-bent.

Since the pH of the solution can affect the surface properties of adsorbents, the observation generally agrees with that of Collivignarelli *et al.* (2020), who found that a relatively higher level of fluoride adsorption in water usually occurred at pH values of 3.6. More adsorptions occurs for both adsorbents as the pH drops from 11.6, which is basic, to neutral, which is acidic. Similar to these findings, a study showing that lower pH values favored fluoride adsorption was conducted to evaluate Bentonite/Chitosan beads for the adsorption of fluoride from aqueous solution (Zhang *et al.,* 2013).

Wambu and Kirui (2019) conducted a study to investigate the effects of pH and other solution parameters on fluoride adsorption onto soil adsorbents. Their findings showed that at pH values of 4 or lower, molecular HF predominated the aqueous fluorides, favoring their solubility and aqueous availability, while other fluorometallo complexes emerged at increasing pH values of 4 to 6, reducing the fluoride's aqueous availability and influencing its adsorption.

Schwertmannite is an iron-oxyhydroxysulfate mineral that is an effective adsorbent for fluoride removal between the pH range of 3 and 11; peak adsorption was at pH 3.6, according to a study by Eskandarpour *et al.* (2008).In a similar vein, a different investigation into the impact of pH on the adsorption of fluorides onto Cameroonian fired clay pots found that pH values between 4-5 were optimal for maximum adsorption (Kofa *et al.*, 2017). The outcomes also matched a study conducted by Kumar *et al.* (2017) on various adsorbents used to remove fluorides from ground water, which revealed that a higher percentage of fluoride adsorption occurred at acidic pH values, with a maximum absorption at that pH.

4.4.2 Effect of Contact Time

The effect of contact time was investigated by varying the contact time at intervals from 5 minutes, 10 minutes, 15 minutes, 30 minutes, 45 minutes and 60 minutes. Variation of contact time allows for determination of optimum time required for the anion to be adsorbed at the adsorbate sites and reach saturation. Figure 4.5 shows the effect of contact time on the adsorption of fluoride ions.

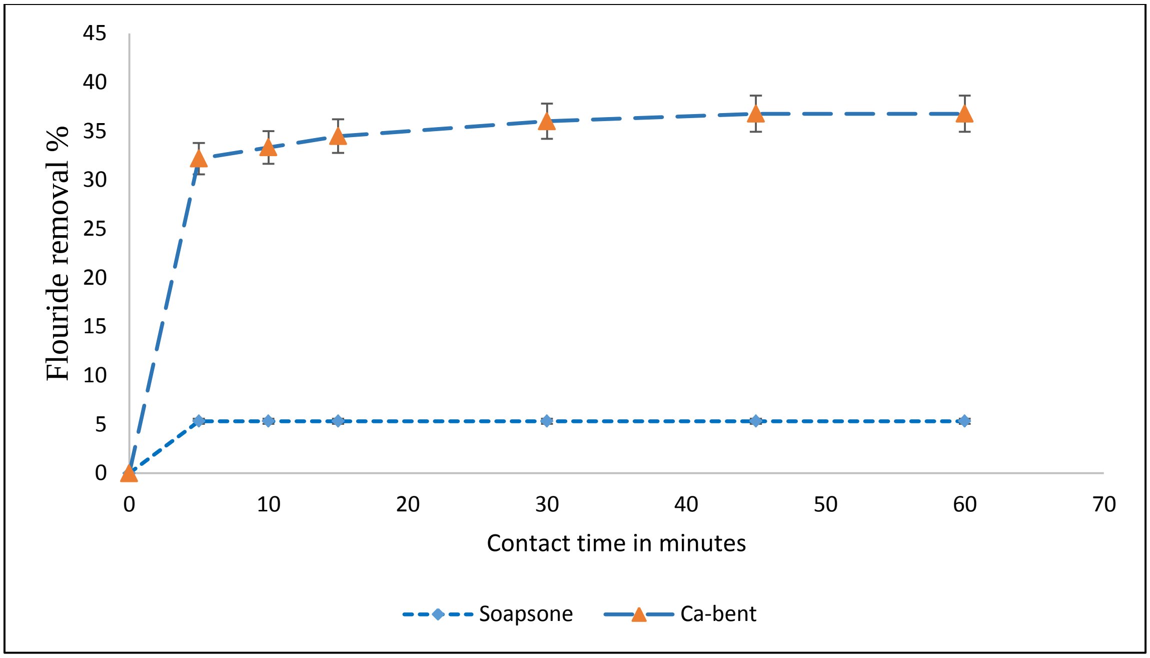


Figure 4.5 Effect of Contact Time on Defluoridation
(Temp of 24±1 ^{o}C 0.5 g of Soapstone and Ca-bent Respectively with 10 mgL^{-1} of Solution)

From figure 4.5 ca-bent was able to adsorb 32.18% m/m within the first 5 minutes while soapstone was able to adsorb 5.32% m/m. The amount adsorbed up to next 40 minutes for ca-bent is 36.78% m/m. The initial higher rate as compared to subsequent rate can be attributed to the fact that initially there were several adsorption sites on the surface of the adsorbent available for immediate adsorption then after 5 minutes as the sites became fewer, the probability of adsorption decreased. The plateau that can be observed after 45 minutes to 60 minutes of contact time of ca-bent and from 5 minutes for soapstone indicates that there are no further available sites for adsorption and the adsorbents are saturated.

Similar pattern of adsorption was reported in the study of adsorption of fluoride from water by Al^{3+} and Fe^{3+} pretreated natural Iranian zeolites by Rahmani *et al.* (2010). An experimental study on Nano graphene oxide coated bentonite as an adsorbent for removal of the basic dye methylene blue from solution also found that the optimum adsorption time was found to be 40 minutes as the graph plateaued after that time (Shaarawy *et al.*, 2020).

4.4.3 Effect of Concentration of Fluoride Ions on Adsorption of Fluoride Ions

Figure 4.6 highlights the findings of an investigation into the influence of fluoride concentration on fluoride ion adsorption.

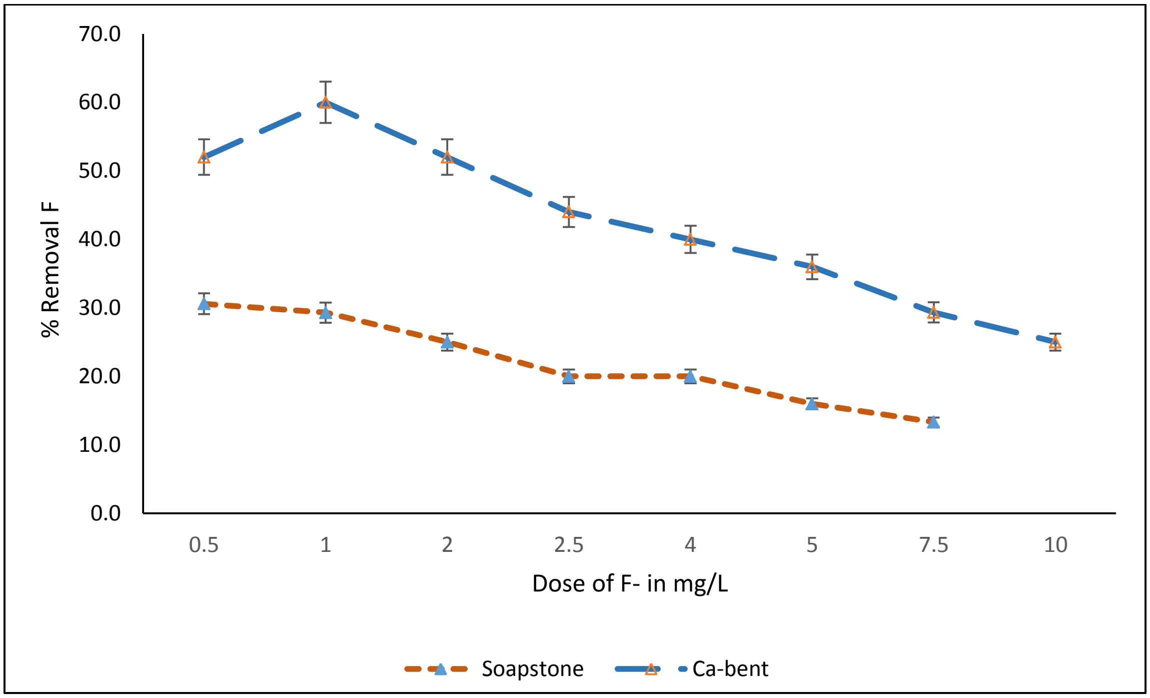


Figure 4.6 Effect of Initial Fluoride Concentration on Adsorption (Temp of 24±1 °C, time of 5 and 4.0 g/0.75 g of Soapstone/Ca-bent Respectively)

Figure 4.6 shows that increasing the adsorbate dose from 0.5 mgL^{-1} to 1.0 mgL^{-1}, ca-bent is able to adsorb additional available fluorides in the aqueous solution from increasing the removal from 50% m/m to 60% m/m. This increase can be attributed to the fact that the adsorbent still had available sites for adsorption till it reached its adsorption limit (Marouf *et al.,* 2021). On the other hand, the soapstone adsorbent curve reveals that at 0.5 mgL^{-1} of the adsorbate, the 4.0 g of the adsorbent used had attained its saturation limit having adsorbed 30.6% m/m of the fluorides. An increase in the dosage of the adsorbate to 0.1 mgL^{-1}, to 2.0 mg^{-1} and 2.5 mgL^{-1} relative to the fixed amount of the adsorbent decreases relative adsorption to 29.3% m/m through 25.0% m/m to 20.0% m/m. An increase in the dosage of the adsorbate to 0.1 mgL^{-1}, to 2.0 mg^{-1} and 2.5 mgL^{-1} relative to the fixed amount of the adsorbent decreases relative adsorption to 29.3% m/m through 25.0% m/m to 20.0% m/m. Raising the adsorbate dose gives the system a steady supply of F^-; conversely, decreasing the adsorbent to adsorbate ratio causes adsorption sites to become saturated, which lowers the removal percentage (Yu *et al.,* 2003).When the adsorbate dose is increased from 1.0 mgL^{-1} to 2.0 mgL^{-1}, 60% m/m to 52% m/m for ca-bent and 29.3% m/m to 25% m/m, it is evident that the rate of decrease in the relative percentage of m/m adsorbed is higher in ca-bent than in soapstone. This is because the ratio of adsorbent to adsorbate changes more slowly in ca-bent, which has a constant weight of 0.5 g, than it is in soapstone, which has a fixed weight of 4.0 g. Malakootian *et al. (2011)* found similar patterns when examining pumice's ability to effectively adsorb fluoride from aqueous solutions. The efficacy of adsorbate removal was found to decrease from 85.75 m/m to 64.14% m/m when the fluoride concentration was increased from 2 mgL^{-1} to 7 mgL^{-1} in that study.

4.4.4 Effect of Soapstone Dose on Removal of Fluoride

The effect of increase of soapstone adsorbent on defluoridation was also investigated and the results presented in figure 4.7.

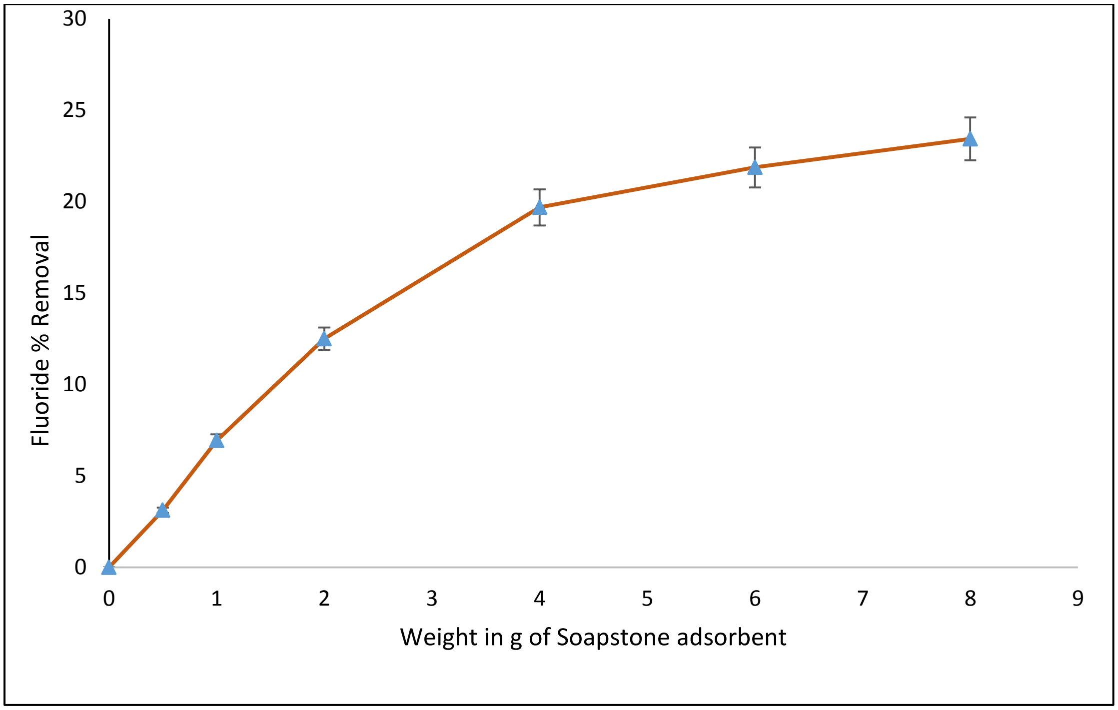


Figure 4.7 Effect of Increase of Soapstone in Adsorbent on Defluoridation (Temp of 24±1 ^{o}C, contact time of 5 min, dosage of 10 mgL^{-1} of fluorides)

As shown in Figure 4.7 the removal was 3.1% by mass when the soapstone dosage was 0.5 g/50 mL of 10 mgL^{-1} of aqueous solution. The amount of fluorides adsorbed gradually increased from 6.9%, 12.5%, 19.7%, 21.9%, and 23.5% with each increment of adsorbent, which was 2.0 g, 4.0 g, 6.0 g, and 8.0 g. This may be explained by the fact that there are more adsorption sites when the adsorbent dosage is increased (Nashine *et al.*, 2016). On the other hand, F-uptake was 19.7% at a dosage of 4.0 g and 21.9% at a dosage of 6.0 g of soapstone (a 2.2% difference). Conversely, an increase in adsorbent dosage from 2.0 g to 4.0 g resulted in an uptake of 12.5% to 19.7%, a 7.7% difference. This signaled the beginning of a decrease in the rate of adsorption, and the optimal adsorption weight was determined to be 4.0 g of soapstone. Similar findings were reported by Kanaujia *et al.* (2015) and Daouda *et al.* (2019), who found that raising the dosage of the adsorbent increased the uptake of fluoride and, subsequently, decreased the relative % adsorption of fluoride (Kardam *et al.*, 2014). The subsequent section delves into the findings of the investigation into the impact of other ions on fluoride sorption.

4.4.5 Effect of Ca-bent Dose on Removal of Fluoride

The effect of increase of ca-bent adsorbent on defluoridation was also examined and the results presented in figure 4. 8.

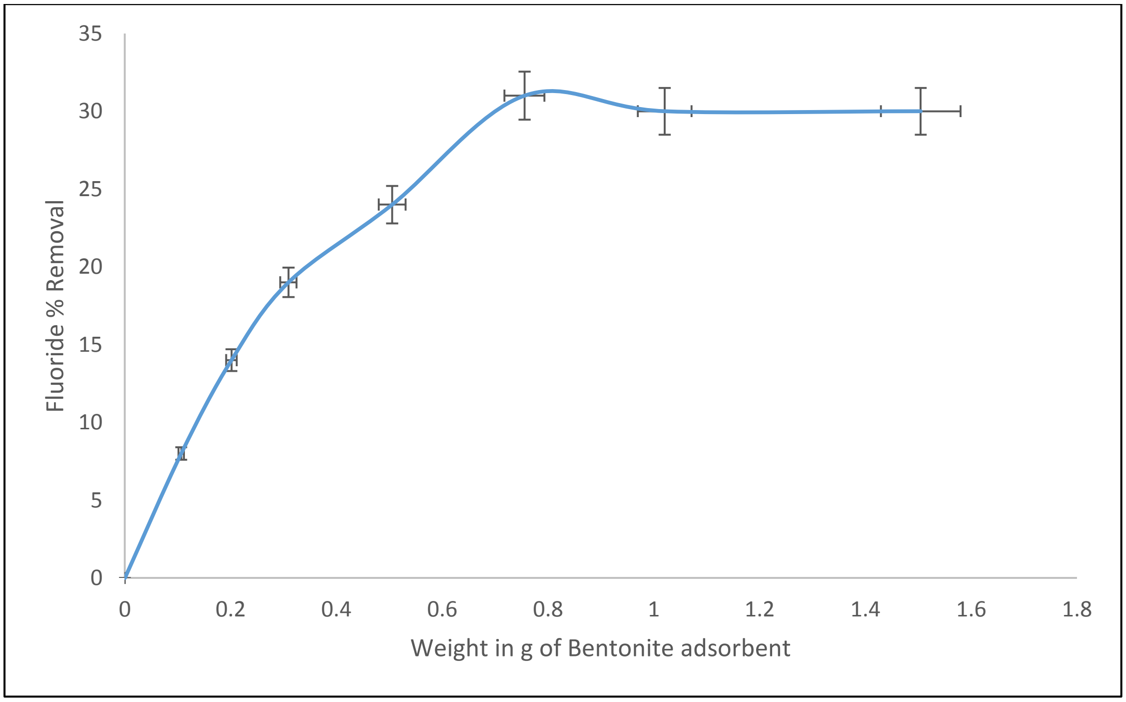
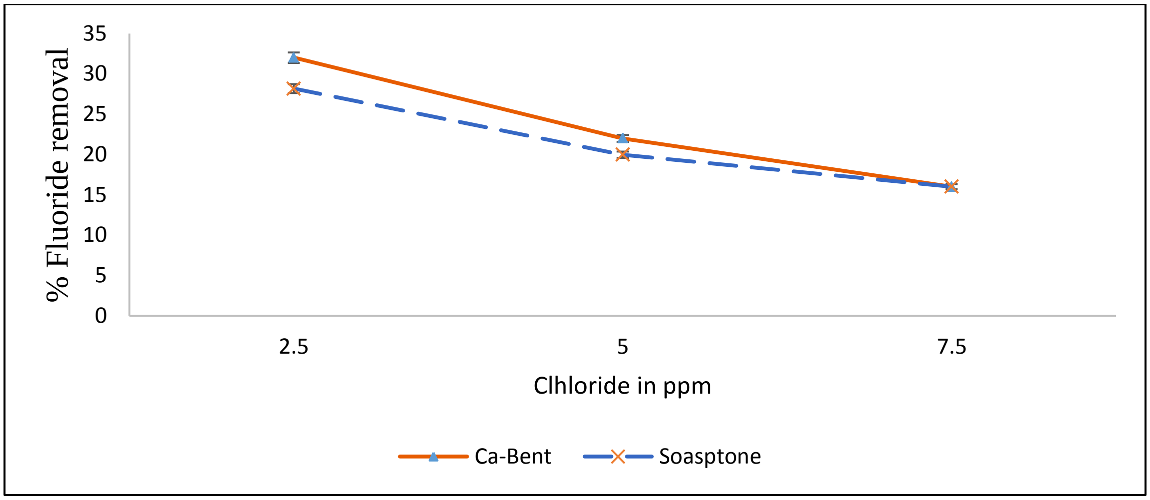


Figure 4.8 Effect of increase of ca-bent adsorbent on defluoridation (Temp of 24±1 ^{o}C, contact time of 5 min, dosage of 10 mgL^{-1} of fluorides)

The study on the impact of raising the dosage of ca-bent adsorbent on fluoride removal is shown graphically in figure 4.8 above. 50 mL of 10 mgL-1 synthetic fluoride ion solution was mixed with bentonite in increments of 0.10 g, 0.25 g, 0.50 g, 0.75 g, 1.00 g, 1.50 g, and 3.00 g. The first rate of adsorption peaked at 0.75 g and then plateaued at 30% m/m of fluoride adsorption as a result of the initial increase in adsorbate. According to Daouda *et al.* (2019), this suggests that the amount of adsorbate adsorbed per unit mass of adsorbent has a limit with the adsorbent dosage because of matter rate transfer at the absorbents' surface. This illustration is depicted in the graph on figure 4.8. Thus, 0.75 g was determined to be the adsorbent's ideal weight, and this weight was utilized in the experiments that followed. Similar findings were made by Kanaujia *et al.* (2015) and Daouda *et al.* (2019), who discovered that raising the dosage of the adsorbent increased the uptake of fluoride and, subsequently, decreased the relative adsorption of fluoride.

Thus, for soapstone and ca-bent, respectively, the ideal adsorbent weights for the ensuing investigations were determined to be 4.0 g and 0.75 g.



4.4.6 Effect of Presence of Chlorides on Fluorides Sorption

(Temp of 24±1 ^{o}C, time of 5 min /45 min and 0.75 g/4.0 g of soapstone/Ca-bent respectively)

Using soapstone and ca-bentonite, this study examined the impact of chlorides on defluoridation; the findings are shown in figure 4.9.

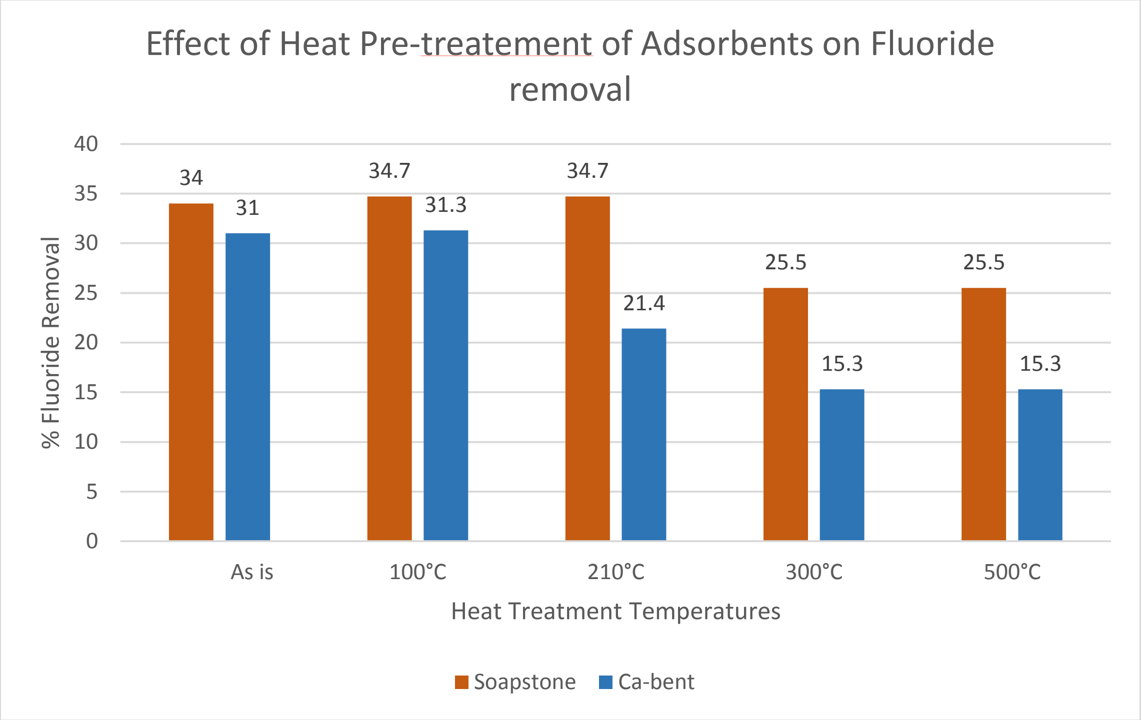


Figure 4.9 Effect of Chlorides Ions on Defluoridation

(Temp of 24±1 ^{o}C, time of 5 min /45 min and 0.75 g/4.0 g of soapstone/Ca-bent respectively)

The results in figure 4.9 showed that there was a general decreased uptake of fluoride ions with gradual increase of chlorides in the solution from 32% m/m and 28% m/m to approximately 22% m/m and 20% for ca-bent and soapstone respectively when chloride concentration was increased from 2.5 mgL^{-1} – 7.5 mgL^{-1}. This indicated that Chlorides compete with Fluorides for adsorption sites of both adsorbents (Nabizadeh *et al*., 2015) and it has higher diffusion coefficient and thus has more interaction to the adsorbents compared to fluorides (Nabizadeha *et al.*, 2015). Similarly in a study of carbonised *punica granatum* carbon for defluoridation of water selected competetion ions were studies and it was observed that fluoride adsorption amount diminished rapidly to 52% from 78.1% with the upsurge of competing ions primarily the bicarbonates concentration 0 mgL^{-1} - 500 mgL^{-1} which was explained by the ion race with fluoride ions at the active site of the adsorbent's surface.

4.4.7 Effect of Heat Treatment of the Adsorbent

By modifying the surface chemistry and increasing porosity and oxidation, heat has been utilized to enhance adsorbent and increase adsorption efficiency (Sáenz-Alanís *et al*., 2017). This study looked into how heat affected the sorption of fluoride by soapstone and calcium bentonite. Figure 4.10 presents the findings.

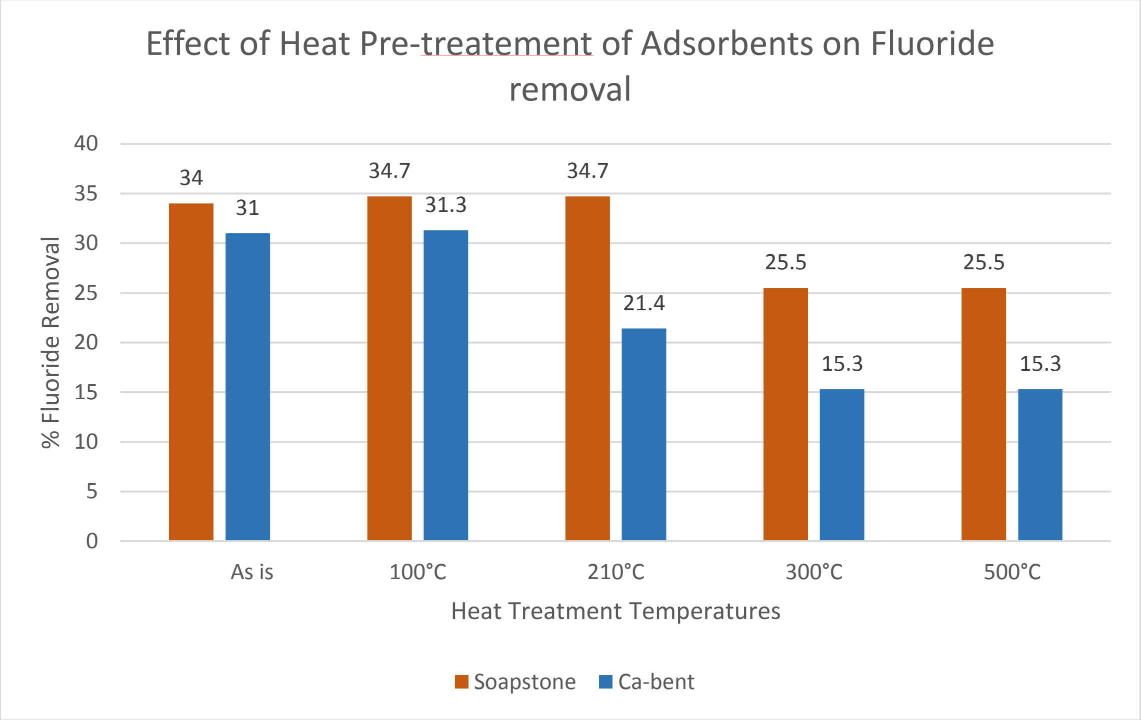


Figure 4.10 Effect of Heat Treatment of Adsorbents on Adsorption (Temp of 24±1 ^{o}C, time of 5 min /45 min and 0.75 g/4.0 g of soapstone/Ca-bent respectively)

From figure 4.10 it was observed that there is a slight fluoride uptake from 34.0% m/m and 31.0% m/m to 34.7% m/m and 31.3% m/m by soapstone and ca-bent respectively with initial heat treatment. This may be attributed to among others the fact that the drying led to moisture loss thus leading to relative increase of the net effective eight of the adsorbents. Soapstone appears to be more heat stable retaining its defluoridation efficacy up to 210 °C since the ability to adsorb starts dropping after 210 °C such that on further heat treatment up to 300 °C there is reduced fluoride adsorption ability going down from 34.7% m/m to 25.5% m/m then further heat treatment up to 500 °C yield not further change in defluoridation ability. In comparison, after 100 °C heat treatment of ca-bent there was a steady decline in its adsorption ability dropping from 31.3%m/m at 100 °C to 21.4% m/m when treated to 210 °C and finally to 15.3% m/m for heat treatment at 300 °C. Even after being heat pretreated to 500 °C, there was a plateau in the ca-bent percent F^- removal from 300 °C. Extreme heat may have distorted the adsorption site, which would explain the decrease in adsorption observed with increased heat treatment.

The outcomes were compared to a study conducted by Stagnaro e*t al.* (2012) on the impact of ca-bent treated to temperatures ranging from room temperature to 750 °C on Pb, Cd, and Zn adsorption in an aqueous solution. The study demonstrated that higher heat treatment decreased adsorption.

4.4.8 Statistical Evaluation of Differences

The sets of data obtained through experimentation using the two adsorbents subjected to ANOVA test returned the following tabulated results:

Table 4. 5 Results for ANOVA Evaluation of Specific Parameters

Summary of ANOVA Results at α=0.05		
Parameter under Test	**P-Value**	**Evaluation**
Effect of heat pretreatment of adsorbents	3.8×10^{-2}	Significantly different
Effect of Cl^- as co-ions on adsorbents	6.95×10^{-1}	Not significantly different
Effect of change in pH on adsorbents	6.90×10^{-1}	Not significantly different

The table 4.5 above compares the effect of changes on adsorption of fluorides resulting from deliberate introduction of specific conditions on adsorbate or adsorbent. In the first analysis above, the two adsorbents were heat pretreated at different temperatures and this affected the way they adsorb fluorides. From the ANOVA results above, there is a significant difference in fluoride adsorption by two adsorbents resulting from heat pretreatment. In general, where it is indicated that there is no significant difference it means the variations in ability to adsorb fluorides may be attributed to random errors associated with the experimentation but not resulting from the nature of the adsorbents. On the other hand, where it is concluded in the table that there is significant difference, the P value obtained statistically at 95% CL is lower than 0.05 suggesting that the nature of the adsorbent has significant effect on fluoride adsorption when the subjected to changes introduced. This therefore means that in the visual examination of figure 4.9 on the effect of heat pretreatment of adsorbents that seems to indicate that there is a significant difference in how this affects the adsorption capacity of the two adsorbents, is actually statistically confirmed as true.

4.5 Studies on Bore Water Samples

The following section discusses the levels of fluoride ions found in water samples taken from bore holes at various locations of Nakuru County.

4.5.1 Fluoride in Bore Water

Eight samples were purposively drawn from Nakuru East Sub County, Nakuru County for determination of fluoride levels and subsequent use in defluoridation studies. The samples were coded as Sample 1, Sample 2, Sample 3, Sample 4, Sample 5, Sample 6, Sample 7 and Sample 8. The fluoride levels in the samples were determined and the results are presented in figure 4.11.

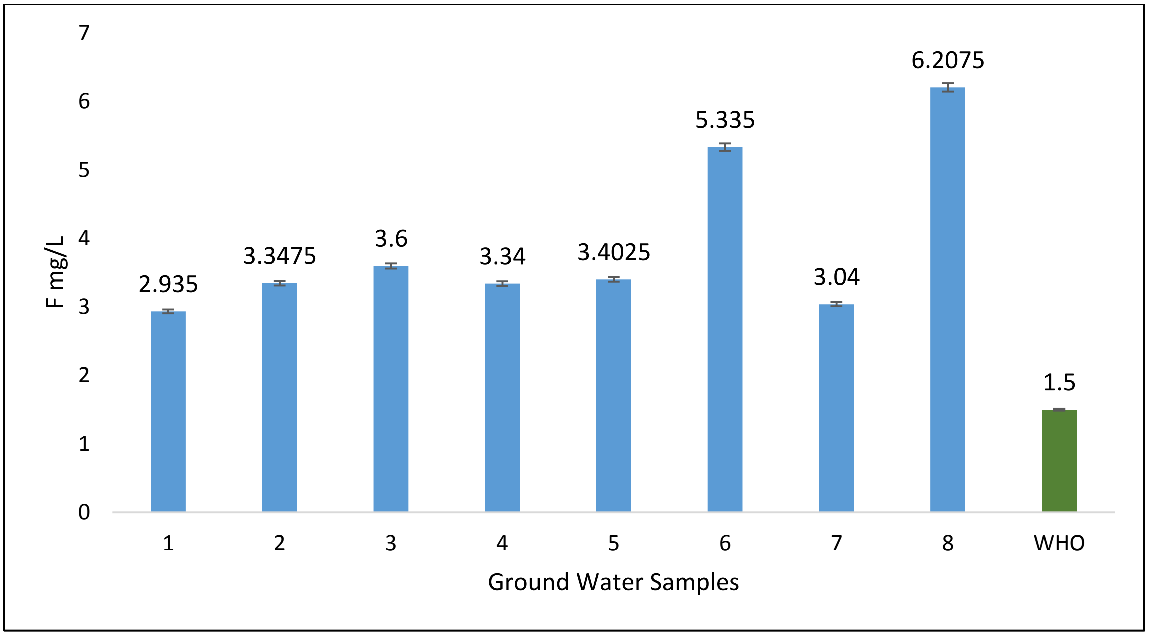


Figure 4.11 Concentrations of Fluorides in Bore Water
(Temp of 24±1 ^{o}C, at sample pH value)

As seen in figure 4.11 the levels of fluoride in water range from 2.94 mgL^{-1} to 6.21 mgL^{-1} with a mean of 3.90 mgL^{-1}. Sample 1 had 2.94±0.03 mgL^{-1}, Sample 2 had 3.35±0.07 mgL^{-1} Sample 3 had 3.6±0.02 mgL^{-1}, Sample 4 had 3.34±0.04 mgL^{-1} Sample 5 had 3.40±0.01 mgL^{-1} ' Sample 6 had 5.34±0.06 mgL^{-1} Sample 7 had 3.04±0.02 mgL^{-1}, and Sample 8 had 6.21±0.02 mgL^{-1}. The concentration of fluoride in all the boreholes sampled was higher than the recommended WHO, (2017) limit of 1.5 mgL^{-1}. The results were found to be comparable with the results obtained in a study commissioned by Nakuru County Government (Mwangi., 2024) where fluoride levels reported to range between 2.15 mgL^{-1} to as high as 6.5 mgL^{-1}.

4.5.2 Defluoridation of Studies of Bore Water Using Soapstone and Ca-bent

Various quantities of adsorbent were used in the experiment to determine the capability of soapstone and ca-bent clay defluoridation of water samples and the results presented in figure 4.12.

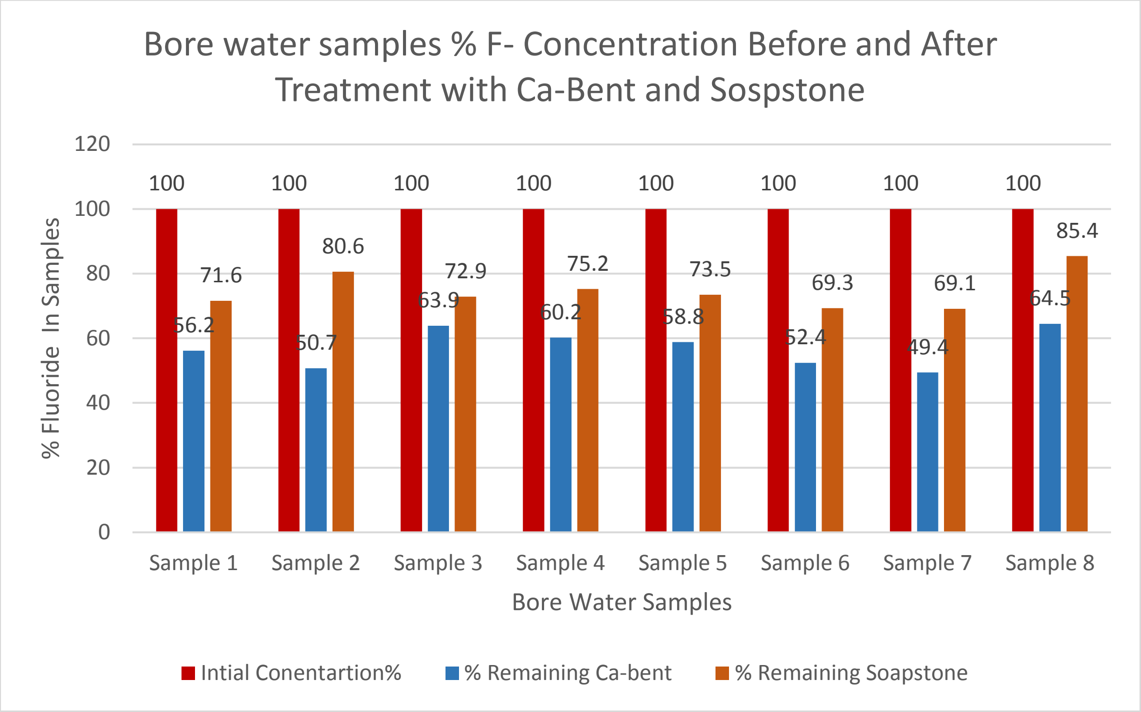


Figure 4.12 Change in F$^-$ Content of Bore Water Samples after Adsorption (Temp of 24±1 ^{o}C, time of 5 min /45 min and 0.75 g/4.0 g of soapstone/Ca-bent respectively)

Figure 4.12 above presents a comparative analysis of fluoride ion concentrations in eight borehole water samples before and after treatment using calcium bentonite (Ca-bent, 0.75 g) and soapstone (4.0 g) as adsorbents. The initial fluoride levels in all samples were normalized to 100% to allow for direct comparison, with the post-treatment residual fluoride values indicating the effectiveness of each adsorbent. Overall, calcium bentonite consistently outperformed soapstone, showing lower residual fluoride concentrations across all samples, with remaining fluoride levels ranging between 49.4% and 64.5%, translating to a fluoride removal efficiency of approximately 35.5% to 50.6%. In contrast, soapstone showed higher residual fluoride levels of 69.1% to 85.4%, indicating a significantly lower removal efficiency of 14.6% to 30.9%, despite being used in a higher mass. The superior performance of Ca-bent can be attributed to its high specific surface area, strong cation exchange capacity, and the presence of exchangeable Ca^{2+} ions that facilitate efficient fluoride adsorption. These results suggest that the mineralogical composition and surface chemistry of soapstone offer fewer active sites or lower affinity for fluoride ions. Notably, Sample 7 recorded the highest fluoride removal using Ca-bent, reducing fluoride from 100% to 49.4%, indicating a 50.6% removal efficiency and soapstone, reducing fluoride from 100% to 69.1%, indicating a 30.9% removal efficiency. This could be due to favorable water chemistry conditions in Sample 7, such as lower levels of competing anions, or reduced total dissolved solids, which enhance the adsorption interaction between fluoride ions and adsorbents. The figure thus underscores the greater suitability of calcium bentonite over soapstone in reducing fluoride levels in borehole water under the tested conditions.

Apart from the optimal weight, in this particular study no additional optimization of the adsorption parameters were applied in order to simulate conditions that would be used in a local setting.

4.6 Capacity and Mechanism of Adsorption of the Fluoride Ions on Adsorbents

The Langmuir adsorption isotherm equations were more appropriate, indicating that the adsorption process was a single-molecule adsorption process, even though both the Freundlich and Langmuir equations are suitable for fitting the adsorption process of F^- ions for both adsorbates (Mukitta *et al*., 2012; Zangi, 2024).

Thus, the experimental data were subjected to the Langmuir adsorption isotherms, resulting in the graphs in appendix 2, to ascertain the adsorption capacity and mechanism of the fluoride ions on ca-bent adsorbent.

Table 4. 6 Bentonite Adsorption Capacities

Average Wt in g of adsorbate	Average Co (mgL^{-1})	Average Ce (mgL^{-1})	qe mg/g	Ce/qe	% Removal
0.7519	0.5	0.24±0.002	0.017290	13.88	52±0.4
0.7500	1	0.4±0.004	0.040000	10.00	60±0.4
0.7500	2	0.96±0.005	0.069324	13.85	52±0.3
0.7500	2.5	1.4±0.003	0.073324	19.09	44±0.1
0.7500	4	2.4±0.013	0.106652	22.50	40±0.3
0.7522	5	3.2±0.012	0.119649	26.75	36±0.2
0.7537	7.5	5.3±0.00	0.145947	36.31	29±0.0
0.7514	10	7.5±0.00	0.166356	45.00	25±0.0

According to table 4.6 above, there seems to be a decrease in the fluoride removal capacity as the initial concentration of fluoride ions in the aqueous solutions increases. The reason for the initial increase from 52% to 60% is that not all of the fluoride adsorption sites on the adsorbent had been saturated by the adsorbent, whose weight stays constant at 0.75 g per 50 mL of solution. At a fluoride concentration of 1.0 mgL^{-1} for 50 mL of the aqueous solution, saturation is achieved. Following that, a continuous decrease in the percentage of fluoride ions that are adsorbed in relation to the fixed amount of adsorbent in the water is caused by additional increases in fluoride concentration.

Table 4.7 below presents a comprehensive dataset detailing the adsorption characteristics of soapstone as an adsorbent. The table includes critical parameters such as the weight of the adsorbent, initial concentration of the adsorbate (Co), equilibrium concentration (Ce), amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (qe), and the percentage removal rate. These parameters are essential for understanding the adsorption capacity and efficiency of soapstone, facilitating the modeling of adsorption isotherms and the optimization of adsorption processes in various applications

Table 4. 7 Data for Soapstone Adsorption Isotherm

Wt in g of adsorbate	Co (mgL^{-1})	Average Ce (mg^{L-1}) n=3	qe mg/g	Ce/qe	Mean % Removal n=3
1.0007	0.5	0.347±0.003	0.008	45.39	31±1.4
1.0017	1	0.707±0.002	0.015	48.34	29±0.3
1.0025	2	1.5±0.00	0.025	60.15	25±0.0
1.0000	2.5	2±0.06	0.025	80.00	20±4.0
1.0021	4	3.2±0.06	0.040	80.16	20±2.5
1.0000	5	4.2±0.0	0.040	105.0	16±0.0
1.0040	7.5	6.5±0.10	0.050	130.5	13±1.3
1.0000	10	8.8±0.06	0.060	146.7	12±1.0

In the table 4.7 it indicates that the fluoride removal capacity appears to be declining steadily with an increase in the initial concentration of fluoride ions in the aqueous solutions, which is consistent with the observations made on table 4.6. As for the case above where soapstone is the adsorbent, a volume of 50 mL containing 0.5 mgL^{-1} of fluoride ions seems to have saturated the adsorption sites with 31% being adsorbed and removed. It can thus be concluded that relative to the weight of the adsorbent, further increase of fluoride ions leads to decline in % adsorption.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Based on the foregoing discussions, compositional analysis done using XRF reveals that soapstone and ca-bent adsorbents have abundance of silicates and substantial presence of aluminum-based oxides. These fit them well with the requisite compositional ratios of the minerals studied.

Results of FTIR further reveal the presence of hydroxyl groups which are found to be more abundant in ca-bent as compared to soapstone. The images of SEM surface analysis show that the two elements have different porosities with ca-bent having higher degrees of porosity allowing for internal penetration of the aqueous water leading to more adsorption of the targeted F^- ions.

Optimum contact time studies evaluated and determined the optimal contact time of ca-bent, optimum adsorbent dose, optimum pH for the adsorption of fluoride ions were determined. Heat treatment of the two minerals did not favour fluoride uptake and reduced their efficacy. Soapstone was found to be more heat stable.

Analysis of 8 samples from different water sources showed varying amounts of fluoride removed using the tow adsorbents. The results of isothermal studies show that ca-bent clay exhibits better adsorption capacity for fluorides in water as compared to soapstone.

In conclusion, this study has established that structure activity relationship may be feasible in adsorption application studies.

5.2 Recommendations

5.2.1 Recommendations from this Work

i. Based on the finding that the adsorbents can remove fluorides in water, there is need for the water sector regulators to encourage the use of these adsorbents for remediation of fluoride laden water.

ii. Packaging these materials for commercial application as defluoridants can be explored.

iii. Soapstone and waste from soapstone carvings should not be discarded but retained for use in defluoridation. This may also be an income generating activity as well as an environmental management strategy.

5.2.2 Recommendations for Further Research

i. Actual mechanisms of adsorption of fluorides in aqueous solutions using ca-bent and soapstone should be established to validate this concept.

ii. It would be prudent to determine how the efficiency of defluoridation would be affected by mixing different ratios of the two adsorbents.

iii. There is a need to determine methods of domestic regeneration of these materials for their sustainability and to mitigate disposal challenges.

iv. Designing appropriate defluoridation apparatus to be used with these adsorbents should be explored

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APPENDICES

Appendix 1: The Abstract of our Study Publication

IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 16, Issue 2 Ser. I (February 2023), PP 18-27
www.iosrjournals.org

Remediation of Fluoride Laden Water by Sorption using Kenyan Kisii Soapstone and Calcium Bentonite

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Abstract

Background: *The aim of this study was to evaluate the adsorption potential of natural and locally available soapstone and Calcium bentonite clay for fluoride removal from aqueous solution and to determine the optimum conditions for use. Adsorption potential was anchored on the availability of hydroxyl and aluminum ions inherent in both minerals which have been established to have ability for fluoride adsorption in aqueous solutions. Adsorption potential was investigated using batch equilibrium experiments.*

Materials and Methods; *Mineralogical characterizations were done using X-ray fluorescence spectroscopy. Fluoride ion selective electrode was used in determination of fluoride content in aqueous solution. Optimization studies on initial pH of the solution, contact time, initial fluoride concentration, adsorbent dose, and heat pretreatment of the adsorbent were done in batch adsorption experiments at room temperature.*

Results: *It was observed that calcium bentonite exhibited better adsorption capacity of 0.21mg/g while soapstone had 0.08mg/g at a contact time of 45 min and 5 min respectively. The optimum pH for both adsorbents was established at 3.6. The experimental data for bentonite fitted well with Langmuir isotherm indicating a monolayer adsorption while for soapstone fitted better into Freundlich adsorption, indicating multilayer adsorption with heterogeneous energetic distribution of active sites.*

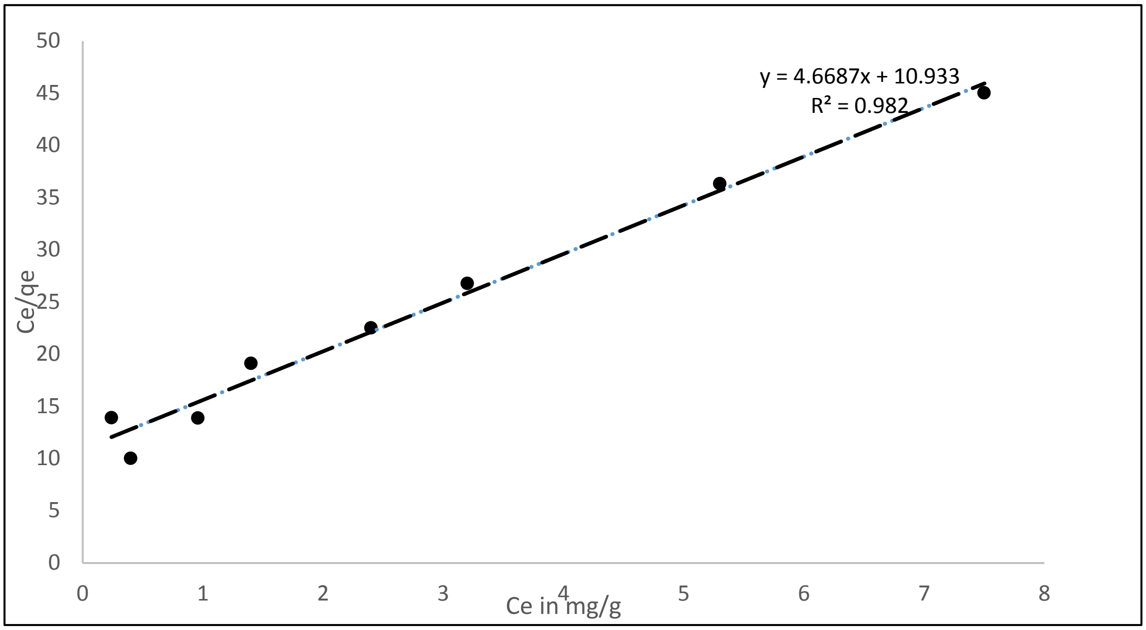
Conclusion: *Based on these findings, the two adsorbents can be fitted into household defluoridation apparatus for domestic remediation of fluoride contaminated water.*

Keyword: *Adsorption, adsorbent, defluoridation, fluorides, soapstone, bentonite, clay*

Date of Submission: 04-02-2023 Date of Acceptance: 13-02-2023

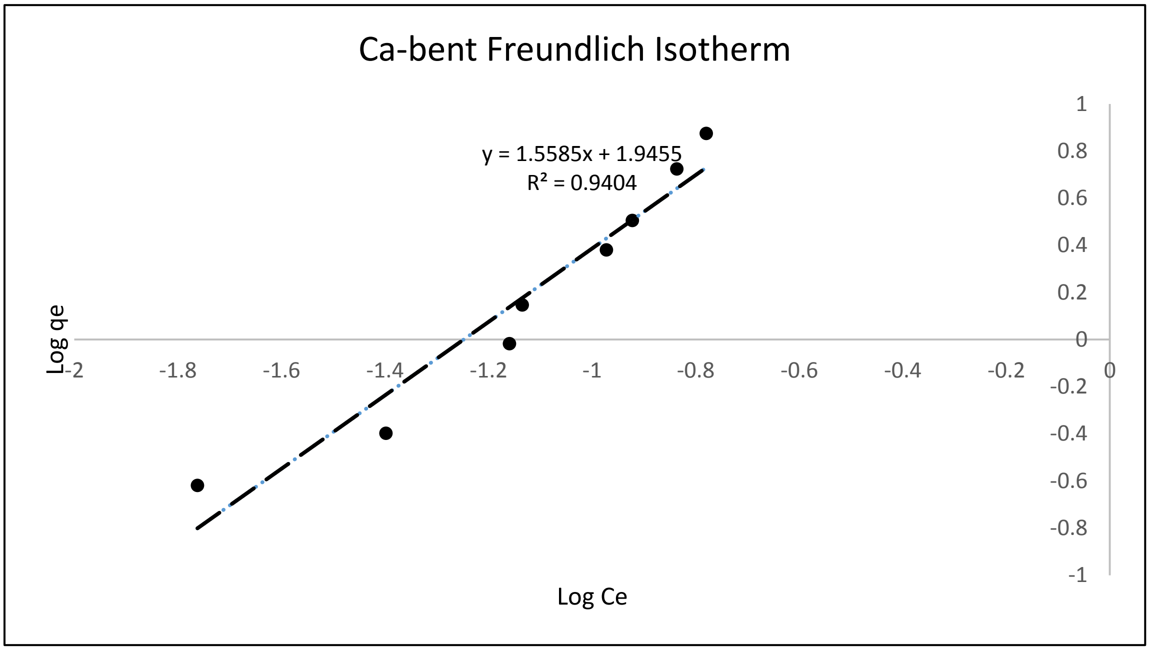
Appendix 2: The Adsorption Isotherms

Appendix 2.1: Langmuir Isotherm for Ca-bent

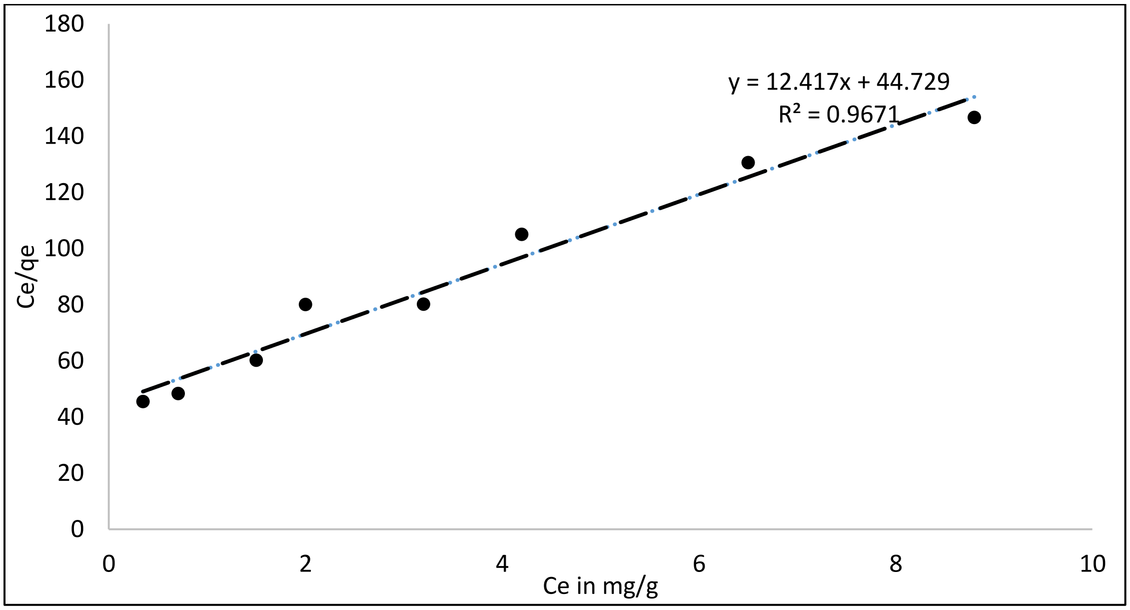


The Langmuir constant KL, for this isothermal process was found to be -0.1355 and the qa as 0.21mgg-1 at pH of 7 and temperature of 24±1°C for bentonite adsorbent.

Appendix 2.2: Freundlich Isotherm for Ca-bent

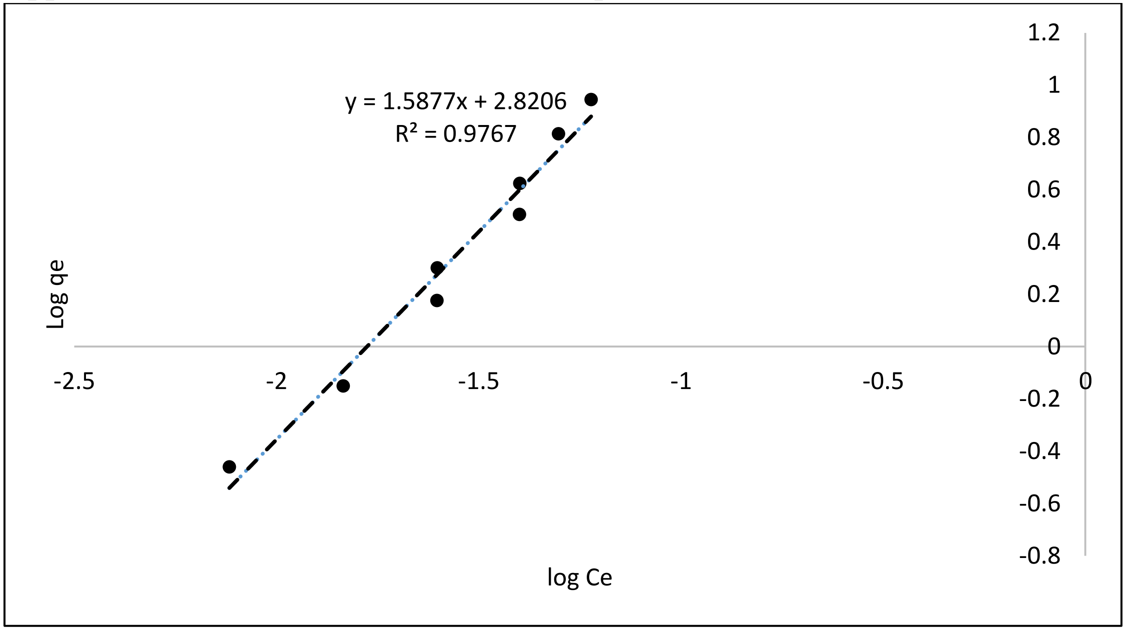


Appendix 2.3: Langmuir Isotherm for Soapstone



The Langmuir constant, KL for this isotherm was found to be -0.654 and the adsorption capacity qa as 0.08mgg-1 at pH of 7 and temperature of 24±1^{o}C for soapstone adsorbent.

Appendix 2.4: Freundlich Isotherm for Soapstone

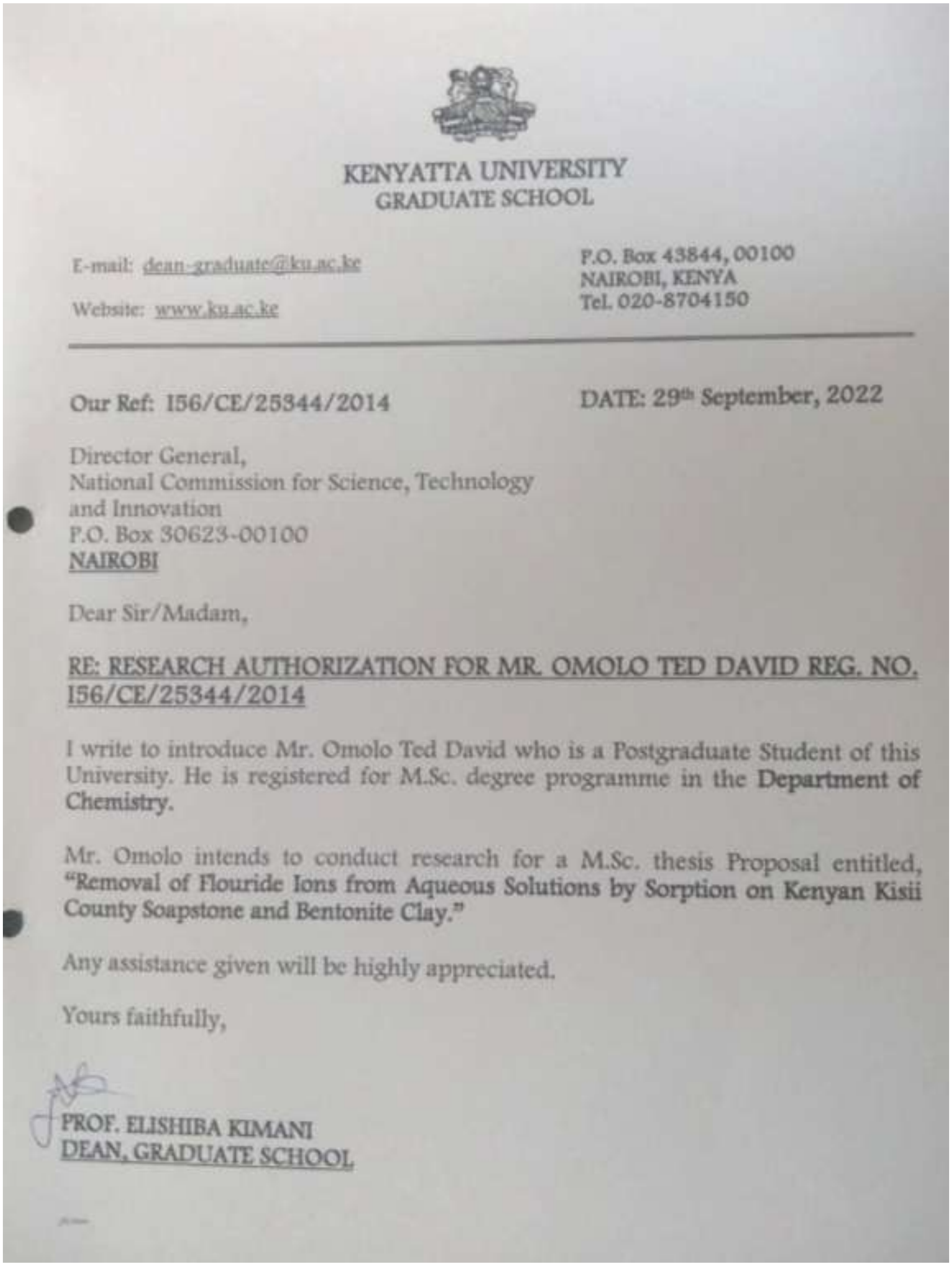


Appendix 3: Map of Nakuru Suburb Where 7 Water Samples were Drawn

Key

🟨 Sample generation site

Appendix 4: Research Authorization



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Our Ref: I56/CE/25344/2014

DATE: 29th September, 2022

Director General,
National Commission for Science, Technology
and Innovation
P.O. Box 30623-00100
NAIROBI

Dear Sir/Madam,

RE: RESEARCH AUTHORIZATION FOR MR. OMOLO TED DAVID REG. NO. I56/CE/25344/2014

I write to introduce Mr. Omolo Ted David who is a Postgraduate Student of this University. He is registered for M.Sc. degree programme in the **Department of Chemistry.**

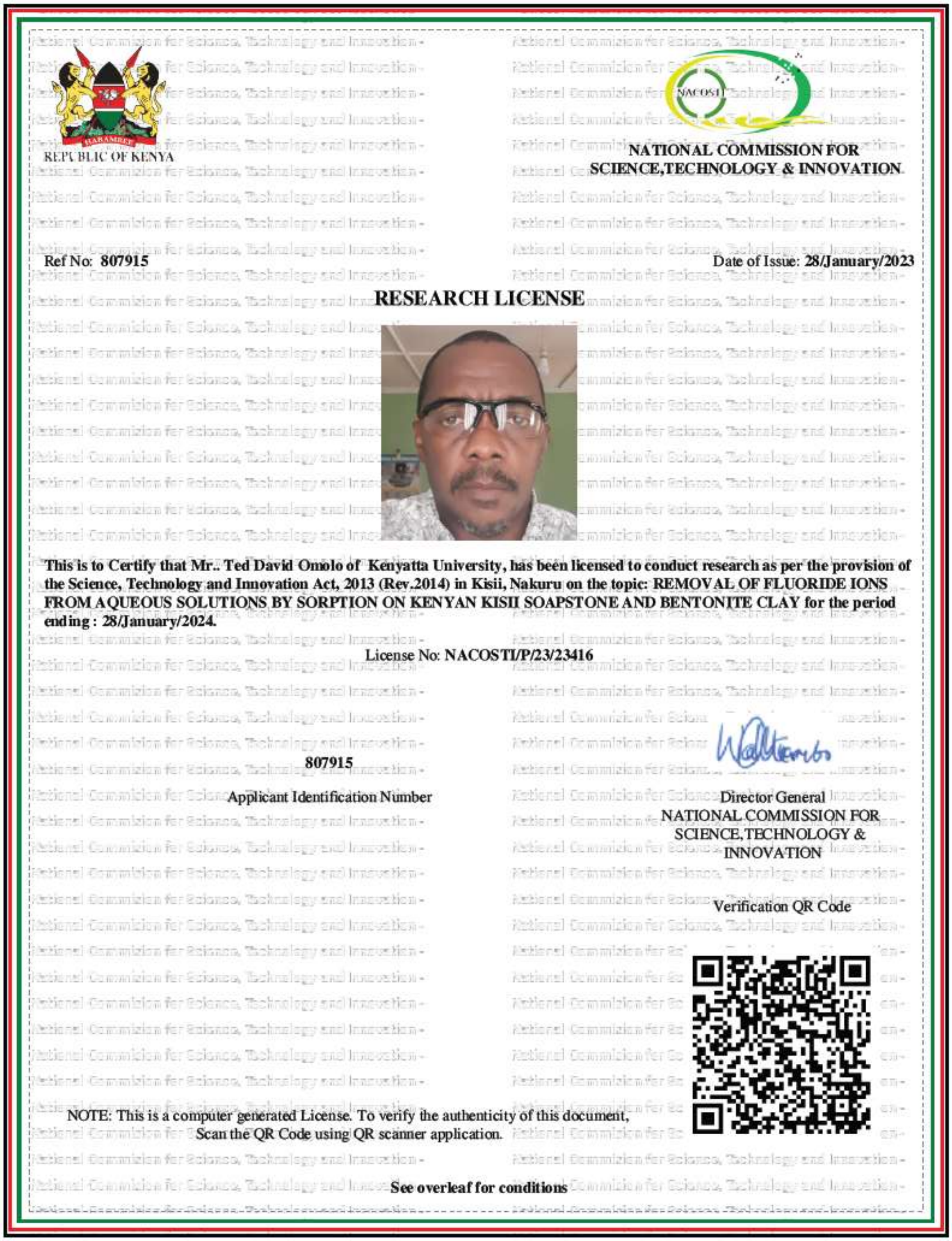
Mr. Omolo intends to conduct research for a M.Sc. thesis Proposal entitled, **"Removal of Flouride Ions from Aqueous Solutions by Sorption on Kenyan Kisii County Soapstone and Bentonite Clay."**

Any assistance given will be highly appreciated.

Yours faithfully,

PROF. ELISHIBA KIMANI
DEAN, GRADUATE SCHOOL

Appendix 5: Research Permit from NACOSTI



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RESEARCH LICENSE

This is to Certify that Mr.. Ted David Omolo of Kenyatta University, has been licensed to conduct research as per the provision of the Science, Technology and Innovation Act, 2013 (Rev.2014) in Kisii, Nakuru on the topic: REMOVAL OF FLUORIDE IONS FROM AQUEOUS SOLUTIONS BY SORPTION ON KENYAN KISII SOAPSTONE AND BENTONITE CLAY for the period ending : 28/January/2024.

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