DEFLUORIDATION OF WATER BY ADSORPTION WITH TRIETHYLAMINE MODIFIED MAIZE TASSELS

BY

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DECLARATION

This thesis is my original work and it has not been presented for a degree in any other university/institution.

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DEDICATION

This thesis is dedicated to my wife Leah Gathoni Kamathi, my sister Daisy Gathoni Mwangi and my parents Richard Mwangi Kahia and Nancy Nyambura Mwangi.

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TABLE OF CONTENTS

LIST OF FIGURES

ABBREVIATIONS, SYMBOLS AND ACRONYMS

CMT	Chlorinated Maize Tassels
FMT	Fluorinated Modified Maize Tassels
FTIR	Fourier Transform Infrared
ISE	Ion Selective Electrode
MMT	Modified Maize Tassels
NMR	Nuclear Magnetic Resonance
RMMT	Regenerated Modified Maize Tassels
TISAB	Total Ionic Adjustment Buffer
UMT	Unmodified Maize Tassels
WHO	World Health Organisation

ABSTRACT

Lack of access to safe drinking water is a major concern due to negative health effects experienced by people in many parts of the world. The quality of such waters is mainly affected by pollutants from natural and anthropogenic sources when they get incorporated in the water sources. These pollutants are either organic or inorganic species. Among the inorganic pollutants are fluorides. Continuous consumption of high concentrations of fluoride ions leads to their accumulation in the body tissues which causes dental fluorosis, skeletal fluorosis and other non-skeletal disorders. These health effects are irreversible and the only way to overcome them is by removing fluoride from water. Several methods for the removal of fluorides in water have been proposed, most of which rely on the use of biomaterials and bone char. In such processes, the adsorbents become loaded with the pre-concentrated pollutants leading to disposal problems. This study reports on the modification of the maize tassels with triethylamine followed by its subsequent application on the removal of fluoride ions from water. The maize tassels were collected, washed, dried, ground and then modified with triethylamine. Modification was carried out in two steps which included chlorination of maize tassels using thionyl chloride followed by amination using triethylamine. The modified and unmodified biomaterial were characterised using FTIR (Fourier transform infrared) spectrophotometer and then used in the removal experiments on both model solutions and water sample from Lake Baringo. The effects of pH, contact time, initial fluoride concentration and modified biomaterial resin dosage on removal of fluoride were investigated. The experimental data were analysed using Langmuir and Freundlich isotherms. FTIR spectrophotometer results confirmed the presence of the anchored functional group on the maize tassels. The removal of fluoride by the modified biomaterial increased with increase in concentration up to an optimum of 60 mg/L. The optimum pH and time were found to be 4.0 and 20 min, respectively. The biomaterial was very effective in fluoride removal as 86% was removed within the first 20 min in model solution containing 20 mg/L of fluoride. The amount adsorbed on the modified biomaterial increased with increase in the modified biomaterial dosage. The uptake of fluoride however, in real water sample from Lake Baringo was found to be slightly lower compared to the experimental water. The experimental data fitted best in the Langmuir isotherm with an adsorption capacity of 5.26 mg/g. This implied a monolayer chemisorption process. It was also found that when the adsorbent was packed in a SPE column, it could be regenerated by stripping the attached fluoride ions with dilute hydrochloric acid. The theory underlying the removal method was based on the interaction of the permanently charged quaternized material with the highly electronegative fluoride ion. This is a regeneratable, eco-friendly and sustainable water remediation method of this toxic water pollutant.

CHAPTER ONE

INTRODUCTION

1.1 Background of the study

The chemical structure of water makes it have special properties because of the way its atoms bond together to form the water molecule. This molecular structure gives the water molecule polarity, or a lopsided electrical charge that attracts other atoms. Due to that polarity, water becomes a universal solvent for polar substances as they are easily dispersed uniformly within the water molecules. This dissolving power of water is very important for life as it enables it to harbour dissolved nutrients that support living things. The ability of water to split ionic compounds has contributed to 97% of the world's water being salty (Soteris, 2005). Most of these salt ions occur naturally in the soil, sedimentary and igneous rocks in many places of the earth's crust. They are leached into water out of land by rainwater and accumulated into ground water sources and other water bodies (Renault *et al.,* 2009; Pique *et al.,* 2010). This renders this vital commodity polluted with dissolved materials of both organic and inorganic origin.

Among these pollutants, of serious concern is the fluoride ion (Suman and Anubha, 2014). The reported tolerance limit of fluoride concentration in drinking water is 1.5 mg/L (WHO, 1993). However, continuous consumption of high concentrations of fluorides in excess of 0.5-1.0 mg/L leads to accumulation in body tissues capable of causing dental and skeletal fluorosis (Edmunds and Smedley, 1996). Consumption of fluoridated water has emotional problems as well. This is because persons with stained teeth are hesitant to provide a gleaming smile and in many occasions appear withdrawn. Preliminary studies by Choi *et al.* (2012) have also shown a strong connection between exposure to fluoride in drinking water and decreased IQ scores in children. In Kenya for example, these problems are known to exist in areas along the eastern rift valley, western slopes of the Aberdare ranges and parts of the central province. These areas contain rocks with high fluoride content which pollute the adjacent water bodies (Amini *et al.,* 2008; Malago *et al.,* 2017).

To overcome the negative health effects of fluoride in water, it should be removed from water for the safety of consumers. This has previously been achieved by the use of methods such as ion exchange, reverse osmosis and chemical precipitation (Cha *et al.*, 1997). These conventional removal methods have not been effective when the concentrations are in low levels. They are also expensive thus not affordable to majority of the affected consumers. The use of phyto-biomass materials such as agricultural products and waste by-products in removal of pollutants has been reported (Waheed *et al.*, 2009; Grassi *et al.,* 2012; Randhir *et al.,* 2013; Koteswara and Mallikarjun, 2014). Phyto-biomass materials have been found to be effective in removal of pollutants even at trace levels (Bhatnagar and Minocha, 2006; Zhang *et al.*, 2012). These materials are available in large quantities and may have a potential to be applied as low-cost water remedial materials that are environmentally friendly (Deans and Dixon, 1992; Garg *et al.,* 2008).

Swathy *et al.* (2017) reported removal of fluoride ion from water using neem leaf as adsorbent. The material had removal efficiency of 86% in a solution containing fluoride of 10 mg/L. However, the material could not be regenerated. Similar cases were reported by Jadhav (2014) and Lavnya *et al.* (2017) while investigating the removal of fluoride using maize cobs and maize husk fly ash. The materials had removal capacity of 86 % and 59.6 %, respectively. A study conducted by Zvinowanda *et al.* (2008) noted that maize tassels have a mesoporous morphology. Their specific pore volume and surface area are significantly smaller than those of other adsorbents materials such as charcoal, zeolites and activated carbon. However, maize tassels in their raw form could not be regenerated and released organic material to the water. Therefore, considering both the need to develop both cheaper and regeneratable water defluoridation material, the finding here in reports on use of locally available maize tassels in developing a regeneratable modified biomaterial for defluoridation of fluoride laden water.

1.2 Problem statement

Consumption of water with high levels of fluoride causes dental and skeletal health problems. Studies have also shown that there is a strong connection between exposure to fluoride in drinking water and decreased IQ scores in children. This affects their cognitive ability hence making them dependent for life. Persons affected by fluorosis tend to have low self-esteem due to their stained teeth and are withdrawn. These health problems are known to exist in Kenya in areas along the Great Rift Valley and at the slopes of Mount Kenya. A study by Wambu and Muthakia (2011) along Gilgil-Elementaita area reported levels of fluoride of up to 200 mg/L in Lake water, 7.69 mg/L in piped water and 6.57 mg/L in borehole water. Bone char is commonly used in defluoridation of water along these regions. However, the material is disposed after use since it is not regeneratable. This transfers a problem from one location to another. The other commonly used method is chemical precipitation but it generates large amount of sludge that poses disposal problems. Other defluoridation methods such as ion exchange, reverse osmosis and electro-dialysis require high capital and operational costs. This makes them unaffordable to most local communities despite their high effectiveness in fluoride removal. It is therefore necessary to look for alternative remediation techniques for fluoride laden water which are effective and of low cost. The use of agricultural materials in defluoridation has been found to be economical due to their availability in large quantities. Among the agricultural materials maize tassels have been found to have high adsorption capacity than other adsorbents due to their mesoporous morphology (Zvinowanda *et al.,* 2008). This formed the basis of this study which focused on using locally available maize tassels to synthesize a regeneratable modified biomaterial for removing fluoride ions from water.

1.3 Justification of the study

The health effects of fluoride in drinking water are irreversible. The only remedy to these negative health problems can be achieved by removal of fluoride ions from water.

Some of the fluoride removal methods are expensive and not effective at low concentrations. Maize tassels after harvesting are discarded and many tones go to waste. This study provides a knowledge on the use of maize tassels to develop a modified biomaterial capable of removing fluoride ions from water.

1.4 Hypotheses

Modified maize tassels will have a high fluoride removal capacity from water and it’s a biomaterial that can be regenerated/recycled.

1.5 Objectives of the study

1.5.1 General objective

To remove fluoride ions from water by adsorption using modified maize tassels.

1.5.2 Specific objectives

The specific objectives of the study are as follows:

i. To characterize both modified and unmodified maize tassels using FTIR.
ii. To determine the effect of pH, contact time, initial fluoride concentration, and modified biomaterial resin dosage on removal of fluorides from water using modified maize tassels.
iii. To regenerate the modified biomaterial.

iv. To apply the modified biomaterial in removal of fluoride from Lake Baringo water sample.

1.6 Significance of the study

1.6.1 Community development

This study intended to develop a modified biomaterial resin for defluoridation of water. The use of maize tassels in developing the modified biomaterial resin is expected to improve accessibility to fluoride free water to most communities. This is because maize tassels are locally available in large quantities and have limited use. This will promote the health of both members of these communities and their animals. The effect of this is community development due to improved productivity.

1.7 Scope and limitations of the study

This study entailed preparation of water remediation biomaterial for fluoride removal. The biomaterial was characterized using FTIR spectrophotometer and then applied in fluoride removal of water samples. Water sample from Lake Baringo was investigated. The adsorption parameters including pH, contact time and concentration were investigated to establish their effect on fluoride removal. Seasonal variations, age of the maize plant and soil parameters were not considered. Only the male part of the maize plant was used in this study.

CHAPTER TWO

LITERATURE REVIEW

2.1 Water and fluoride levels

Water is life and as such it is a very important natural resource. However, most of the available water is polluted as a result of anthropogenic and natural activities (Altaher, 2014). Such water when taken by human beings and animals has negative effects on their health. This has prompted various studies to be conducted in search for appropriate methods for the removal of pollutants from water. Such methods are expected to be efficient, environmental friendly and of low cost.

Water is a universal solvent and as it interacts with the environmental materials, it dissolves a hoist of minerals such as heavy metals, non-metals, persistent organic materials and pesticides (Allen *et al.*, 2008). Some of these elements are essential at trace levels but toxic at elevated concentrations while others are toxic at all levels. Water bodies will naturally have mineral elements that are found within a particular locality dissolved in different concentrations as a result of the geological composition of soils and bedrock (Malago *et al.,* 2017).

Among these mineral elements in water and of serious concern are the fluorides (Suman and Anubha, 2014). Fluorite, apatite, rock phosphate and topaz are the most common fluoride bearing minerals. High concentration of fluoride in water leads to decrease in dissolved calcium and magnesium ions in water. This is as a result of formation insoluble calcium fluoride and magnesium fluoride. These ions are important in the strengthening of the bone structure in both human beings and animals. It also leads to increased alkalinity in water (Roy and Dass, 2013).

Fluoridated water has been known to affect teeth surfaces and damage the skeleton frame and therefore unsafe when the concentration exceeds 1.0 mg/L (Lamberg *et al.*, 1997). High concentrations of fluorides have been observed to have severe skeletal manifestations (Eirik, 2013). It is therefore very important to remove fluoride ions from water for the safety of the consumers. According to Suman and Anubha (2014) defluoridation of drinking water is the best alternative to overcome the problem of excessive fluoride in water.

2.2 Health effects of fluoride

Continuous consumption of water with high fluoride levels leads to accumulation of fluorides in the hard tissues of the body. This causes mineralization of the teeth and bones leading to dental and skeletal fluorosis respectively (Blaszczyk *et al.*, 2012; Dhar and Bhatnagar, 2009). Dental fluorosis may be of varying degree depending on structural damage of the enamel layer. If the enamel is highly damaged, it may be more than a cosmetic damage (Maria *et al.*, 2011). In such a case it may result in pain. This adversely affects food choices, compromises the rate of chewing and may require complex dental treatment (Ramadan and Hilmi, 2014).

Skeletal fluorosis with adverse change in bone structure may be observed when water contains 3–6 mg/L while crippling fluorosis may be observed when water contains over 10 mg/L of fluoride (WHO, 1996). It is characterized by pain and stiffness of joints in the initial stages. This is later followed by hardening and calcification of the bones (osteosclerosis) and finally the spine, muscles and nervous system are damaged (Surendra and Gurcharan, 2013; Simon *et al.*, 2014). Fluorosis is an irreversible condition and the only remedy is prevention by keeping the fluoride levels in drinking water within the safe limits (Rajan and Alagumuthu, 2013; Surendra and Gurcharan, 2013).

East African Rift Valley is one of the regions in the world highly affected by fluorosis (Wambu and Muthakia, 2011; Hellen *et al.*, 2013). This is due to presence of fluorotic minerals from the volcanic rocks which often contaminate the ground water and later the adjacent water bodies with the fluoride ions (Sunitha and Sreenivasulu, 2015). In Kenya for example regions along the Great Rift Valley and at the slopes of Mount Kenya have been reported to have high fluoride levels. These regions have well documented cases of dental fluorosis and skeletal fluorosis (Gaciri and Davies, 1993; Ayenew, 2008). A study conducted by Malago *et al.* 2017 reports high fluoride levels as high as 1,640 mg/l and 2,800 mg/l in lakes Elementaita and Nakuru, respectively. Furthermore, they found that over 1,000 groundwater samples collected over the whole country, 61% exceeded 1 mg/L, about 20% exceeded 5 mg/L and 12% exceeded 8 mg/L.

2.3 Common fluoride removal methods

The main methods used in defluoridation of water include: electro dialysis, reverse osmosis, ion exchange, chemical precipitation and adsorption (Feenstra *et al.*, 2007). The method chosen in removal of fluoride depends on factors such as capital and operational cost, effect on the environment and effectiveness in fluoride removal of the method. For instance distillation has the capacity to remove ions from water but it is very expensive.

2.3.1 Electro dialysis

This method utilizes ion exchange membranes together with an electrical potential difference in removing ionic species from aqueous solutions (Oztekin and Altin, 2016). It consists of a series of cation and anion exchange membranes which are arranged between the cathode and the anode (Tongwen, 2005). The cations migrate to the cathode while anions to the anode. These ions permeate through the membrane and are retained by the oppositely charged electrodes (Zoulias *et al.*, 2004; Tongwen, 2005). The limitations of this method is that it is costly and has low efficiency for removal of trace concentration of pollutants from aqueous media (Bhatnagar and Minocha, 2006; Zhang *et al.,* 2012).

2.3.2 Ion exchange

Ion exchange is a process where the ion removed from aqueous solution is replaced by another ionic species. Ion exchange in water treatment involves passing of water through an ion exchange polymer which is a water insoluble substance capable of exchanging some of its ions with ions of similar charge in the aqueous media (Sanjeev and Sapna, 2013). The electrical charge of the contaminant and ions in the polymer must be of the same charge for the exchange to occur (Alguacil, 2003; Mbugua *et al.*, 2014).

According to Sanjeev and Sapna (2013) several natural organic materials possess ion exchange property or this property can be added to them through chemical modification. This property has been applied in preparation of ion exchangers from natural materials such as wood, fibres, peat, and coal through modification using nitric acid as an oxidant or concentrated sulphuric acid to introduce the sulphonic acid group. Water treatment using ion exchange method has been found to be environmentally friendly. However, it has limitations such as fouling by suspended solids in water and low efficiency for removal of trace concentration of pollutants (Bhatnagar and Minocha, 2006; Zhang *et al.,* 2012).

2.3.3 Chemical precipitation

This method involves the transformation of dissolved materials into insoluble solids followed by their removal through sedimentation or filtration (Harrison, 2005). In defluoridation process lime and alum are commonly used as precipitating agents (Meenakshi and Maheshwari, 2006). In this case fluoride is precipitated from the aqueous phase as insoluble calcium fluoride (Palishahjee *et al.,* 2013). Nalgonda technique has been commonly used and it is based on addition of lime and alum in a two-step process (Meenakshi and Maheshwari, 2006). This method has limitations in that it produces large amount of sludge which poses disposal problems and requires large amount of chemicals which must be added daily. It also alters the pH of water hence adjustment of pH is needed (Ayoob *et al.*, 2008).

2.3.4 Use of biomaterials as adsorbents

The use of biomaterials in removal of pollutants has gained a lot of attention today. This is because these materials are economically viable, produced in large quantities and come from renewable sources. Also these materials have been found to be effective in removing pollutants even at trace levels (Mohan *et al.*, 2007). Recent studies have demonstrated successful utilization of plant biomass such as spent tea, rice husks, papaya seeds, orange peels and jack fruit peel in fluoride removal (Waheed *et al.,* 2009; Grassi *et al.,* 2012; Randhir, 2013). Adsorption using these materials may be due to formation of Van der Waals forces, ion exchange, hydrogen bonding, ligand exchange or chemical modification on the surface of adsorbent (Mohammad and Ansari, 2009; Sanjeev and Sapna, 2013). The main challenge facing these methods is the introduction of secondary pollution to water due to organic leaching and lack of regeneration capacity (De Souza *et al.,* 2012).

Various studies have shown that the use of untreated natural materials such as fruits and vegetable wastes tends to generate several problems such as low pollutant removal and high chemical oxygen demand due to release of soluble organic compounds from the plant materials (Patel, 2012; Mwangi *et al.,* 2012; De Souza *et al.*, 2012). Therefore plant wastes need to be modified prior to their use. In a study conducted by De Souza *et al.* (2012) the modification of orange peels, bagasse and peels mixed with bagasse with citric acid to introduce carboxylate group resulted in improvement of biomaterial property and high removal capacity of lead.

2.3.5 Reverse osmosis

This method works by using high pressure to force water molecules through a semi-permeable membrane (Amir *et al.*, 2010). This pressure must be enough to overcome the osmotic pressure. The amount of pressure required depends on the concentration of the contaminant in the feed water (Bina *et al.*, 2014). The water molecules pass through the membrane but salts and other contaminants do not go through the membrane and are discharged through the concentrate stream. The reverse osmosis membrane rejects contaminants based on their size and charge (Yeomin and Lueptow, 2005). The permeate water obtained has about 95% to 99% of the contaminants removed from it. These contaminants may be ions, particles, colloids or bacteria from the feed water (Sunil, 2013). This method is highly efficient, has no waste production, and does not require pH balancing and regeneration (Amir *et al.,* 2010). However, it requires high capital and operational cost, creates disposal problem for the waste water concentrated with fluoride ions and 20-40% of the water is lost through this treatment (Feenstra *et al.*, 2007).

2.3.6 Use of bone char

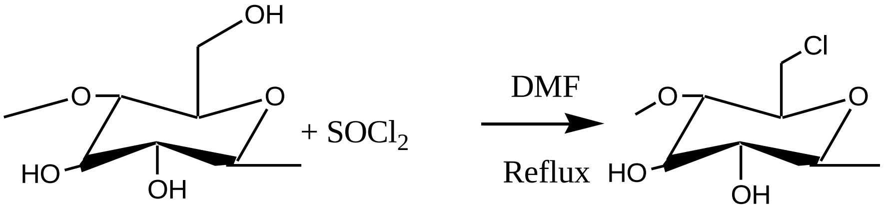
Bone char technology has been successively used in removal of fluoride from water since 1940s (Fawell *et al.,* 2006). To produce bone char, animal bones have to be collected first from various sources such as butcheries and restaurants (Naohito *et al.*, 2009). Dry animal bones are then charred at temperatures between 350-400 °C which makes them brittle and easy to crush. This is followed by thorough washing using sodium hydroxide to reduce residual organic matter (CDN *et al.,* 2007; Korir *et al.*, 2009). In the defluoridation process using this method bone char powder is added to water followed by calcium-phosphate pellets which enable formation of robust calcium carbonate (Korir *et al.,* 2009).

Bones are affected by fluoride ions since calcium in the bones interacts with fluoride ions to form a salt with high lattice energy that contributes to fluorosis (Amir *et al.*, 2010). However, its defluoridation capacity is low and limited as compared to some specific organic materials (Bregnhoj, 1995).

2.4 Maize tassels and the adsorption mechanism

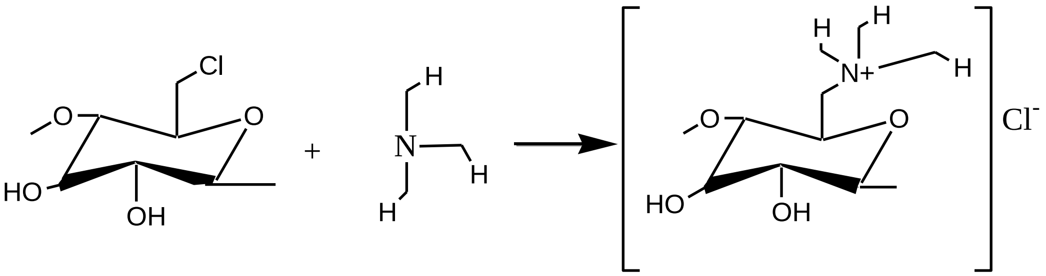
Maize tassel is the male part of the maize plant which is usually discarded after harvesting. It is a lignocellulosic material and possess desirable characteristics for an adsorbent; a low cost material and mesoporous with the high adsorption capacity as compared to other materials such as activated carbon, zeolites and charcoal (Zvinowanda *et al.*, 2008). A study conducted by Nana *et al.* (2016) in removal of phosphorous using both modified and unmodified maize tassels noted that when the maize tassels were chemically modified their removal capacity largely improved. When used in their raw form the maize tassels leached organic material into the water due to presence of high amount of soluble organic substances. A similar case is reported by Mwangi *et al.* (2012) while removing heavy metals from water using both modified and unmodified maize tassels. They noted that modification of the maize tassels improved their adsorption capacity, stability in water and reduced leaching of organic matter. Also, the material was easily regenerated as compared to the unmodified form which could not be regenerated. Jadhav (2014) carried out fluoride removal from water using maize fly ash as an adsorbent and recorded 86% percent removal after equilibration of 120 min at pH of 2.0 and adsorbent dose of 2 mg/50 ml of the solution. Lavnya *et al.* (2017) used maize cobs to remove fluoride and reports a 56.6 % removal.

Attachment of the amine functional group on the maize tassels can be done by first chlorinating the carbon in position 6 of the cellulose molecule in maize tassels to form an intermediate of chlorocellulose as an alkyl halide as presented in scheme 1 (Eyley and Thielemans, 2014).



Scheme 1: Chlorination of maize tassels using thionyl chloride

When the chlorinated maize tassels are treated with triethylamine, the chlorine atom is displaced by the nitrogen from the tertiary amine to form stable quaternary amine cellulose as shown in Scheme 2:



Scheme 2: Quaternary amine cellulose

According to Neelo *et al.* (2013) amine functional groups react with the fluoride according to the following reaction:

$\text{Matrix-NR}_3^+ \text{Cl}^- + \text{F}^- \rightarrow \text{Matrix-NR}_3^+ \text{F}^- + \text{Cl}^-$.

After all the sites in the biomaterial have been occupied it is backwashed with hydrochloric acid to regenerate the resin. This recharges the resin again with new chloride ions. Fluoride is capable of replacing other anions due to the fact that it is strongly electronegative.

2.5 Factors affecting the rate of fluoride removal

2.5.1 Effect of contact time

Contact time between the adsorbing material and the aqueous solution is a major factor in fluoride removal. Studies have shown that the rate of removal of pollutants from water using biomaterials is higher at the beginning of the remediation process (Waheed *et al.,* 2009). This is because as the interaction process progresses the sites for the reaction becomes exhausted resulting in lower uptake rate of the pollutant (Waheed *et al.,* 2009; Mbugua *et al.,* 2014).

2.5.2 Effect of pH

The effect of pH is a vital parameter in removal of fluoride from aqueous phase. The pH effect is due to the fact that fluoride reacts with the protons at low pH to form hydrogen fluoride. Also, at high pH there is abundance of hydroxide ions which hinder the diffusion of fluoride ions (Anusha and Raja, 2014). Thus pH of the solution has a significant effect on the removal of fluoride ions from water since it determines the surface charge of the adsorbent.

2.5.3 Effect of dosage

Increased dosage of the biomaterial results in increased removal of the pollutants from aqueous phase. This has been attributed to higher availability of surface and pore volume at higher doses (Patil *et al.*, 2012). However, adsorption density decreases due to unsaturated adsorption sites and particle interaction caused by high adsorbent dose (Mbugua *et al.*, 2014).

2.5.4 Effect of initial concentration

The capacity of the biomaterial gets sharply exhausted with increase in the initial concentration of the fluoride in aqueous phase. This is due to the fact that the adsorption sites for a fixed amount of biomaterial are limited and become saturated at high concentration (Palanisamy *et al.*, 2012).

2.5.5 Effect of interfering ions

Aqueous solutions may contain different anions such as carbonate, chloride, nitrate, phosphate and bicarbonate in addition to fluoride. Concentration of these ions may vary depending on geographical regions. The order of interference for fluoride removal is as follows HCO_3^- > SO_4^{2-} > Cl^- for various biomaterials (Ramchander *et al.,* 2013; Sudhanshu *et al.,* 2015). In most of the studies chloride, sulphate and nitrate ions do not show a decrease in fluoride uptake, but the bicarbonate highly decreased the uptake of fluoride ions. This was attributed to the ability of bicarbonate to compete for active site with the fluoride ions (Ramchander *et al.,* 2013; Sudhanshu *et al.,* 2015; Sanjay *et al.,* 2007).

2.6 Methods of analysis

There are various methods that have been employed in determination of fluoride levels. The methods may be classified into spectrophotometric, chromatographic and potentiometric methods. The principle of functioning of spectrophotometric methods is based on metal ion displacement from a coloured complex by fluoride or formation of a mixed ligand complex (Barghouthi and Sameer, 2012; Kalanithi *et al.,* 2015). This results into bleaching of the metal complexes**.** The magnitude of bleaching is proportional to fluoride ion concentration in the sample solution and is determined using a spectrophotometer (Barghouthi and Sameer, 2012). The process of colour development is progressive and accurate timing is required so as to obtain consistent results. The waiting period therefore becomes a source of annoyance. Distillation step is also necessary so as to avoid interferences (Quentin, 2009).

Chromatographic methods are based on the partitioning behaviour of solutes between the mobile phase and stationary phase. Ion chromatography has been used in fluoride determination where fluoride is separated from other components on an ion exchange. According to Tokalioglu *et al.* (2004) chromatographic methods are expensive and time consuming.

Specific details of the functional groups on the adsorbent material may be achieved by getting vital information on their physical, chemical and surface properties. Nuclear magnetic resonance spectroscopy (NMR) and Fourier transform infrared (FTIR) have been the commonly used methods in determination of functional groups in a given material. NMR is based on the absorption of the electromagnetic radiation by the nuclei in the radiofrequency region (Skoog *et al.,* 2007).

2.6.1 Fluoride ion selective electrode (ISE)

An ion selective electrode (ISE) is an electrode that produces a potential when placed in a solution containing a given ion. There are variety of ion selective electrodes (ISE) that respond to various cations and anions. All ion selective electrodes (ISE) have a common feature in their design in that the ion sensing part consist of a membrane (Aleksandar *et al.,* 2013). The membrane may be plastic, glass or ionic crystal. One side of the membrane contains the test solution while the other contains the standard solution (Pungor, 2001).

Fluoride ion selective electrode (ISE) method is an electrochemical method of analysis where the output potential is proportional to the amount or concentration of the selected ion in solution (Sunitha and Reddy, 2014). The electrode utilizes a membrane consisting of a single crystal of lanthanum fluoride doped with europium (II) fluoride to improve its conductivity (Skoog *et al.,* 2007). Transformations at the boundary between the electrode/analyte boundary can be evaluated using the Nernst equation as shown in equation 1;

$$E_{cell} = E^{\circ} - \frac{RT}{ZF} \ln \frac{[reduced]}{[oxidised]} \qquad (1)$$

Where

E = potential difference
E° = standard cell potential
R = universal gas constant
T =absolute temperature
Z= the charge of the ion
F =Faraday constant

The equation shows that there is a linear relationship between the logarithm of concentration of the reduced with the potential difference.

This method is simple to perform, has good precision and sensitivity. In the analysis, the measurements are carried out at constant ionic strength. This is achieved by the use of a total adjustment buffer (TISAB) which adjusts the pH of the solutions in the range of 5.0–5.5. This prevents formation of complexes with hydrogen at pH below 5.0 and interferences by hydroxide ions at pH above 7.0 (Tokalioglu *et al.,* 2004)**.**

2.6.2 Fourier transform infrared (FTIR)

Infrared spectroscopy is an analytical technique that deals with analysis in the infrared region of the electromagnetic spectrum (Park *et al.,* 2007). The radiation has a longer wavelength and lower frequency than visible light thus it is of low energy. The analysis is based on interaction of the radiation and atoms within functional groups that are sensitive to the incident radiation at certain specific frequencies. Atoms in the functional groups vibrate at different frequencies and undergo transitions that correspond to their characteristic bond's natural frequencies (Braun and Smirnov, 1993). As each functional group has unique arrangement of atoms and molecules, it is highly unlikely for any two compounds to be excited by the same frequency. This makes infrared spectroscopy a tool for qualitative analysis.

The Fourier transform facility of the Infrared spectroscopy is a powerful technique based on Michelson interferometry. It enables the instrument to analyse a wide range of radiation wavelengths simultaneously. The signal produced by Michelson interferometer (interferogram) is processed by a mathematical process known as the Fourier transform, to produce IR spectrum (Sperling and Parak, 2010). The different functional groups can thus be selectively analysed (Braun and Smirnov, 1993).

The characterization of the modified biomaterial was thus carried out using Fourier Transform Infrared (FTIR) spectrophotometer. This method is used for both qualitative and quantitative analysis of molecular species of all types. The group frequency region which encompasses radiation from 4000 cm^{-1} to approximately 1250 cm^{-1} is used in identification of functional groups (Skoog *et al.,* 2007). The identification process involves passing an IR radiation on a sample to obtain a spectrum which is then compared with a spectrum of a pure compound.

Absorption in the IR region results in changes in both rotational and vibrational status of the molecule. Absorption frequency is dependent on the vibrational frequency of the molecule while absorption intensity is dependent on how energy is transferred to the molecule which in turn depends on the change in dipole moment. As a result a molecule absorbs IR radiation if the radiation causes a change in dipole moment (Skoog *et al.*, 2007).

2.6.3 pH meter

A pH meter is voltage dependent meter which measures the concentration of hydrogen ions in aqueous media. It measures the difference in electrical potential between pH responsive electrode (indicator electrode) and reference electrode (Hammond *et al*., 2005). The pH responsive electrode is a glass electrode that consists of a high resistance glass tube with a thin low resistance glass bulb at the bottom. The reference electrode is a mercury mercurous chloride (calomel) electrode, although a silver-silver chloride electrode is sometimes used. When the two electrodes are immersed in a solution the glass electrode develops a potential directly proportional to concentration of hydrogen ions in the solution. The potential between the two electrodes is measured in terms of pH using a suitable voltmeter. Calibration of the pH meter is performed with at least two buffer solutions. One of the buffers is at pH 7 and the other depends on whether the measurements will be made in aqueous or basic media (Kulasekaran *et al.,* 2015).

2.6.4 Langmuir and Freundlich isotherms

Langmuir and Freundlich isotherms provides information on the nature and physico-chemical interactions involved in the adsorption (Fan *et al.,* 2003). From the isotherms, the maximum adsorption capacity of fluoride ions on the modified maize tassels can be evaluated. Langmuir isotherm is based on the assumption that active sites are homogeneously distributed on the surface of the adsorbing material (Vijayakumar *et al.*, 2012). The active sites have the same affinity for adsorption of a mono molecular layer and there is no interaction between the adsorbed particles on the surface (Senthil and Kirthika, 2009). The results for the Langmuir model are analysed using the linearized Langmuir equation as shown in equation 3;

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L C_e}{K_L} \qquad (3)$$

Where C_e is the equilibrium concentration in mg/L, which is the fluoride ion concentration remaining in the solution at equilibrium, K_L is the equilibrium constant, q_e is the ion concentration taken up by the sorbent per unit mass of the sorbent at equilibrium in mg/g, and a_L is a constant in the Langmuir model.

Equation 4 represents the linearized Freundlich equation used to establish a heterogeneous surface (Dada *et al.*, 2012);

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (4)$$

Where K_f is an indicator of adsorption capacity, 1/n a measure of adsorption intensity, C_e is the equilibrium concentration in mg/L and q_e is the adsorbed amount in mg/g.

CHAPTER THREE

RESEARCH METHODOLOGY

3.1 Research design

The study focused on the modification of maize tassels using triethylamine, characterization of the modified material and subsequent application of the material in removal of fluoride from model solutions and water samples from Lake Baringo.

3.2 Chemicals and reagents

All the solutions were prepared in double distilled water and the reagents were of analytical grade supplied by Kobian Kenya Limited which is a Sigma Aldrich's outlet in Kenya. Fluoride standard stock solution of 1000 mg/L was prepared by dissolving 2.21 g of sodium fluoride in 1000 ml of water. It was from this solution that subsequent working solutions were prepared from. A solution of 0.1 mol/L nitric (V) acid and 0.1 mol/L sodium hydroxide solutions were also used to adjust the pH of the working solutions to the required value. The total ionic strength adjustment buffer (TISAB) was prepared by mixing 57 ml of acetic acid, 58.00 g of sodium chloride and 4.00 g of 1,2-cyclohexanedinitrilo-tetraacetic acid (CDTA) in 1000 ml of distilled water.

3.3 Instrumentation

The fluoride content in the solutions was determined by potentiometric method using fluoride ion selective electrode (JENWAY 3345 Ion Meter). This was done by mixing 25 ml of the test solution with 25 ml of total ionic strength buffer (TISAB) which maintained constant ionic strength. The calibration of the ISE was done using standard solutions with concentration of 2, 3, 5, 6 and 10 mg/L.

The modified maize tassels were characterised using Fourier Transform Infrared (FTIR) spectroscopy. An FTIR spectrophotometer (Perkin Elmer 100 made in Waltham, MA, USA) in the range 4000 cm^{-1}-400 cm^{-1} was used in order to give accurate information on the functional groups present in unmodified maize tassels, chlorinated maize tassels, aminated maize tassels, fluorinated modified maize tassels and the regenerated modified maize tassels. The pH of the synthetic and environmental water samples was monitored using pH meter (PHEP pH meter supplied by Hanna Instruments, Italy). Refluxing the reaction mixture was carried out using a WHM 120151 isomantle made in Korea.

3.4 Modification of the maize tassels biomaterial

3.4.1 Chlorination of maize tassels

The maize tassels were sourced from various farms in Nyeri county, Kirimukuyu location, Kenya. They were washed with distilled water and sun dried. Then activated at 80 ˚C for 12 hr (Mwangi *et al.*, 2012; Kinyua *et al.*, 2015), cooled in a desiccator and later stored in clean plastic bottles. A sample of 10.00 g activated maize tassels was suspended in 200 ml dimethylformamide (DMF) in a three neck flask. This was followed by slow addition of 35 ml thionylchloride ($SOCl_2$) from a dropping funnel under mechanical stirring at a temperature of 80 °C for 4 hr. The chlorinated maize tassels (CMT) obtained were washed thrice with 25 ml aliquots of 2 mol/L ammonium hydroxide to adjust pH to neutrality which was confirmed with an indicator paper. The solid was separated by filtration (sunction) through a sintered glass crucible no. 3 and dried at room temperature.

3.4.2 Amination of the chlorinated maize tassels

A mass of 5.00 g chlorinated maize tassels was reacted with 25 ml triethylamine under reflux and mechanical stirring for 3 hr. The mixture was filtered through a sintered glass crucible and the solid dried at room temperature for 24 hr. The synthesized material was a solid derivative which was then used for adsorption experiments.

3.4.3 Characterisation of unmodified and modified biomaterial

The FTIR analysis of the unmodified maize tassels, chlorinated maize tassels, aminated maize tassels, aminated maize tassels after defluoridation and the regenerated material was done. This was aimed at identifying the functional groups present in each stage and the changes that occurred on the surface of the biomaterial after each treatment. In this process 1.00 mg of dried sample of each of unmodified maize tassels, chlorinated maize tassels, aminated maize tassels, fluorinated modified maize tassels and the regenerated modified maize tassels was mixed with 50.00 mg of KBr (1:50) and ground into a fine powder and pressed in a vacuum into a pellet. The pellet was analysed by an FTIR spectrophotometer (Perkin Elmer 100 made in Waltham, MA, USA) in the range 4000 cm^{-1}–400 cm^{-1}.

3.5 Adsorption experiments

Batch adsorption experiments were carried out on a mechanical thermo stated reciprocating shaker (DKZ-1NO.1007827-USA).

3.5.1 Batch experiments

The experiments were carried in a temperature controlled water bath shaker using 100 ml plastic bottles at the same shaking speed. The pH of the sample solutions was adjusted to desired values using 0.1 mol/L nitric (V) acid and 0.1 mol/L sodium hydroxide drop wise. A known weight of modified biomaterial was added to each of the solution and allowed to equilibrate. The resulting mixture was filtered using Whatman No. 1 filter paper and the fluoride ions in the filtrate determined using fluoride Ion Selective Electrode (ISE).

3.5.2 Effects of pH

The effect of pH on removal of fluoride from model solutions was studied using 0.03 g of the modified biomaterial. The pH of the solutions was varied from pH 2.0 to pH 13.0 using 0.1 mol/L nitric (V) acid and 0.1 mol/L sodium hydroxide drop wise. At each pH a mixture containing 40 ml of 20 mg/L fluoride solution and 0.03 g of the modified biomaterial were equilibrated for 1 hr at a shaking speed of 120 r/min. At the end of contact time, the mixtures were filtered and the final concentration of the fluoride in the filtrate determined. The procedure was repeated using 0.1 mol/L hydrochloric acid in place of 0.1 mol/L nitric acid in varying of the pH.

3.5.3 Effects of contact time

The effect of contact time on fluoride removal was investigated at various contact time of 5, 10, 15, 20, 40 and 60 min using 40 ml of sample solution in 100 ml screw cap bottles. A mass of 0.03 g of the modified biomaterial was added in each sample solution. The pH of the sample solutions was adjusted to pH 4.0 using 0.1 mol/L nitric (V) acid and 0.1 mol/L sodium hydroxide drop wise. The mixtures were shaken at a speed of 120 r/min, then filtered and the concentration of fluoride ions in the filtrate determined.

3.5.4 Effect of initial concentration of fluoride ions

The effect of initial concentration on uptake of fluoride was determined by agitating 40 ml samples of fluoride solutions of 10, 20, 40, 60 and 100 mg/L in 100 ml screw cap plastic bottles with 0.03 g of the modified biomaterial in a water bath shaker at 25 °C. The pH of the solutions was adjusted to pH 4.0 using 0.1 mol/L nitric (V) acid and 0.1 mol/L sodium hydroxide drop wise. The mixtures were shaken at a speed of 120 r/min for 20 min after which they were withdrawn and filtered. The concentration of the fluoride ions in the filtrate was determined.

3.5.5 Effect of modified biomaterial resin dosage

The effect of the modified biomaterial dose on uptake of fluoride was investigated by shaking 40 ml sample solutions of 20 mg/L at various doses ranging from 0.03 to 0.1 g. The pH of the solutions was adjusted to pH 4.0 using 0.1 mol/L nitric (V) acid and 0.1 mol/L sodium hydroxide drop wise. The mixtures were shaken at a speed of 120 r/min for 20 min after which they were withdrawn and filtered. The concentration of the fluoride ions in the filtrate was determined.

3.5.6 Regeneration of the modified biomaterial and application studies

Varying masses (0.01–0.30 g) of the modified material were packed in separate columns. Each column was then loaded with 100 ml of model solution with fluoride concentration of 0.1 mg/L at a pH value of 4.0 and the solution allowed to run slowly out of the column. After all the solution run through the column the adsorbent loaded with fluoride was washed off with 5 ml of 3.0 M hydrochloric acid and the eluent solution analysed for the fluoride content. The materials after defluoridation and regeneration were also analysed using FTIR spectrophotometer.

3.5.7 Analysis of real water samples

Real water sample was obtained from Lake Baringo from one location and put in a plastic bottle. The pH of the water was determined using pH meter. A mass of 0.03 g of the modified biomaterial was added to 50 ml of the real water sample and shaken for 20 min. The mixture was filtered and concentration of fluoride determined. The procedure was repeated with 50 ml of real water samples spiked with known mass of fluoride ranging from 0.1-2 mg in a litre of the real water sample.

3.6 Calculation of fluoride ion uptake

The amount of fluoride ion uptake by modified maize tassels during the batch experiments was determined using equation 2;

$$q_e = \frac{(C_0 - Ce)V}{W} \tag{2}$$

Where,

qe = Amount of F^- uptake per unit mass of modified biomaterial resin at equilibrium
Co = Initial concentration of F^- in mg/L
Ce = Concentration of F^- at equilibrium in mg/L
w = mass of the modified biomaterial in g
V = volume of solution in litres

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

The chapter reports on the results obtained from this study which involved modification of maize tassels using triethylamine, characterization of both modified and unmodified maize tassels using FTIR spectrophotometer, optimization of fluoride removal parameters from water using the modified material and the regeneration of the fluorinated modified maize tassels.

4.2 FTIR characterisation of the biomaterial

4.2.1 Spectrum of the unmodified maize tassels

Figure 4.1 represents the absorption spectra of unmodified maize tassels (UMT).

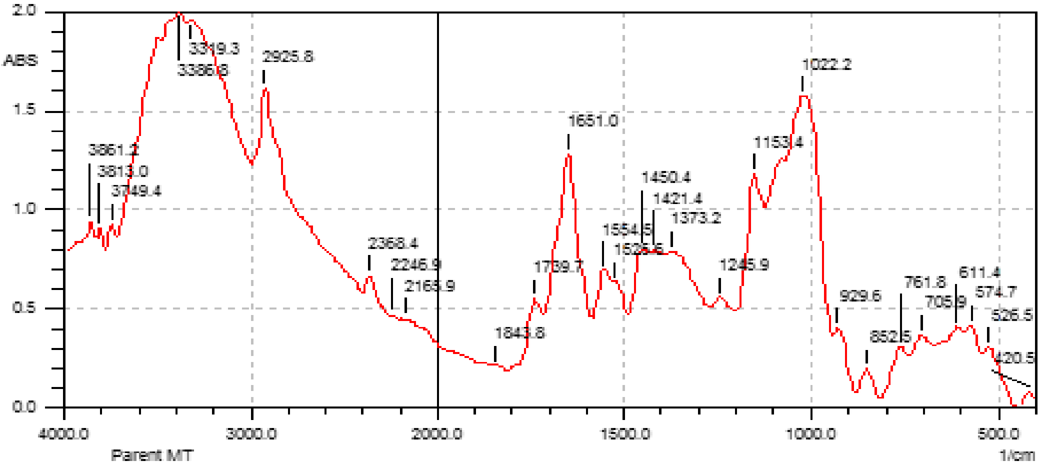


Figure 4.1: FTIR spectrum for unmodified maize tassels (UMT)

From figure 4.1, the spectrum shows strong bands at 3319 cm^{-1} and 3386.8 assigned to –OH in alcohols or –NH in amines which absorb in the region 3200-3640 cm^{-1} and 3250-3400 cm^{-1}, respectively. The peak at 2925.8 cm^{-1} was attributed to stretching of C-H bonds while the one at 1651.0 cm^{-1} to carbonyl group (John, 2000). A band observed at 1022.2 cm^{-1} was assigned to C-O stretching vibration in alcohols which ranges from 1000-1320 cm^{-1} (Nurul *et al.*, 2013).

4.2.2 Spectrum of the chlorinated maize tassels

Figure 4.2 represents the chlorinated maize tassels (CMT) spectrum.

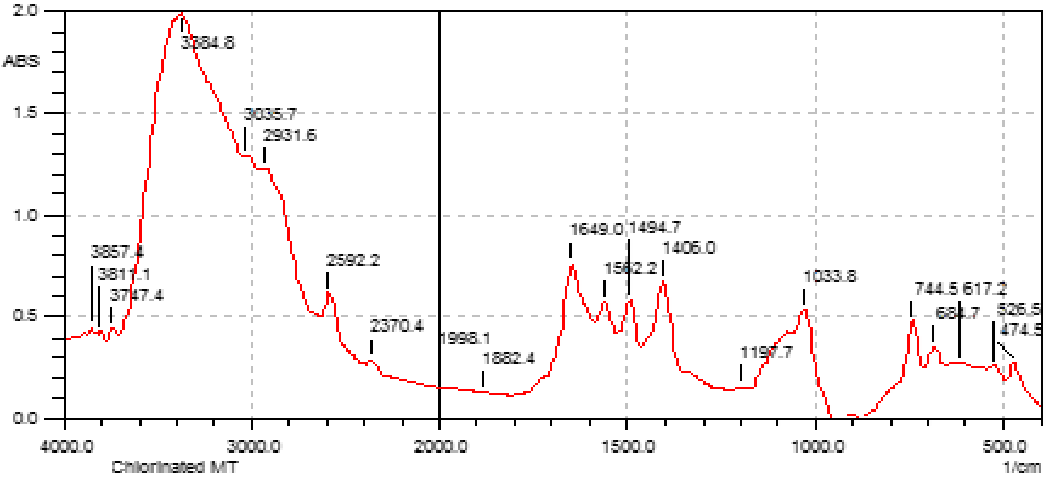


Figure 4.2: FTIR spectrum for chlorinated maize tassels (CMT)

The spectrum of chlorinated maize tassels shows the appearance of a new peak at 744.5 cm^{-1}. This corresponds to the absorption peak of C-Cl which ranges from 550-850 cm^{-1}. The peak at 1022.0 cm^{-1} which was attributed to the –OH group in alcohols in the unmodified maize tassels disappeared after chlorination which confirmed the replacement of the –OH group by the chlorine atom. Also, the peak at 3319.3 cm^{-1} shifted to 3384.8 cm^{-1} which suggested that the initial peak at 3319.3 cm^{-1} was due to the –OH group in alcohols and changed upon chlorination. The bands at 3035.7 cm^{-1} and 2931.6 cm^{-1} were assigned to the C-H stretching vibration (John, 2000).

4.2.3 Spectrum of the aminated maize tassels

Figure 4.3, gives the FTIR spectrum of the aminated maize tassels.

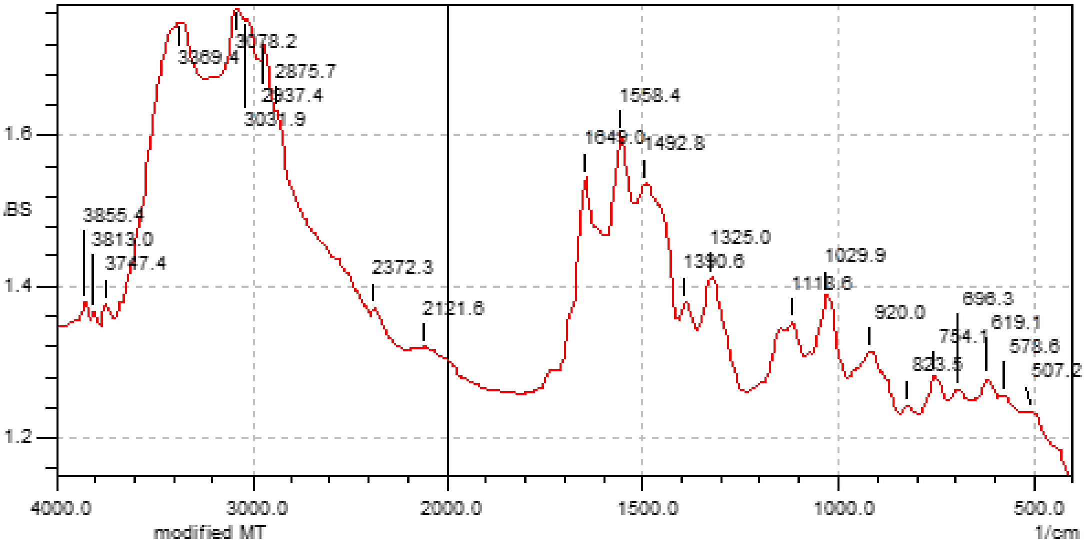


Figure 4.3: FTIR spectrum for triethylamine modified maize tassels (MMT)

The band at 744.5 cm^{-1} in the chlorinated maize tassel in figure. 4.2 disappeared in the spectrum in figure 4.3 which illustrated the substitution of the chlorine atom by triethylamine. Also, a new peak was obtained at 1492 cm^{-1} which corresponded to the methyl of the ethyl groups in the tertiary amine (Loubaki *et al.*, 1991). The band at 1029.9 cm^{-1} was referenced as the C-N stretching vibration while that at 3369.4 cm^{-1} was assigned to the amine functional group (Kacurakova *et al.*, 1994; Pal *et al.*, 2005; Song *et al.*, 2008). This confirmed that the triethylamine was successfully anchored on the maize tassels.

4.3 Adsorption parameters

4.3.1 Effect of pH on removal of fluoride ions by modified maize tassels

The results for the effects of pH on removal of fluoride from water were as presented in figure 4.4.

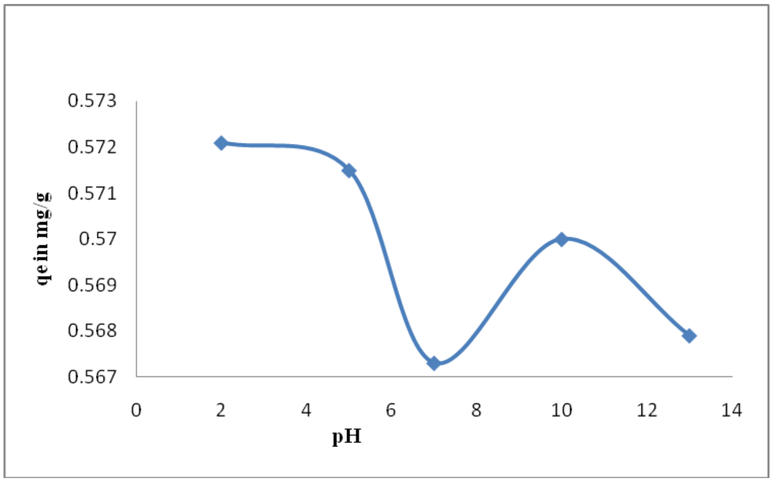


Figure 4.4: Effects of pH on adsorption of fluoride ions

(Temp of 25° C, Initial fluoride concentration of 20 mg/L and 0.03 g of adsorbent)

It was observed that at high pH values the removal of fluoride ions from water was low and high at low pH values. The high uptake at low pH (2.0-4.0) was attributed to the high concentration of hydrogen ions at low pH which increases the positive charge on the surface of the adsorbent leading to greater removal of fluoride (Chowdhury *et al.*, 2011; Patil *et al.*, 2012). Similar cases were observed by Sahira *et al.* (2012) while they removed fluoride from water using Zirconyl-Impregnated activated carbon prepared from lapsi seed stone. They noted that pH had significant effect on interaction of the fluoride ions with the adsorbent since it alters the surface charge of the material. The pH has effect on interaction of the fluoride ions with nitrogen containing moieties as well This is because it influences the charge of the nitrogen atom of the adsorbent and the chemistry of the ion (Unlu and Ersoz, 2006).

At high pH (>8) there was high concentration of hydroxide ions which hindered fluoride ions diffusion leading to the low uptake of fluoride. The hindrance comes as a result of development of repulsive forces between the negatively charged fluoride and the negatively charged hydroxide ions (Tembhurkar and Shilphadonge, 2006).

When the pH was varied using dilute hydrochloric acid in place of nitric acid. The results obtained were as presented in figure 4.5.

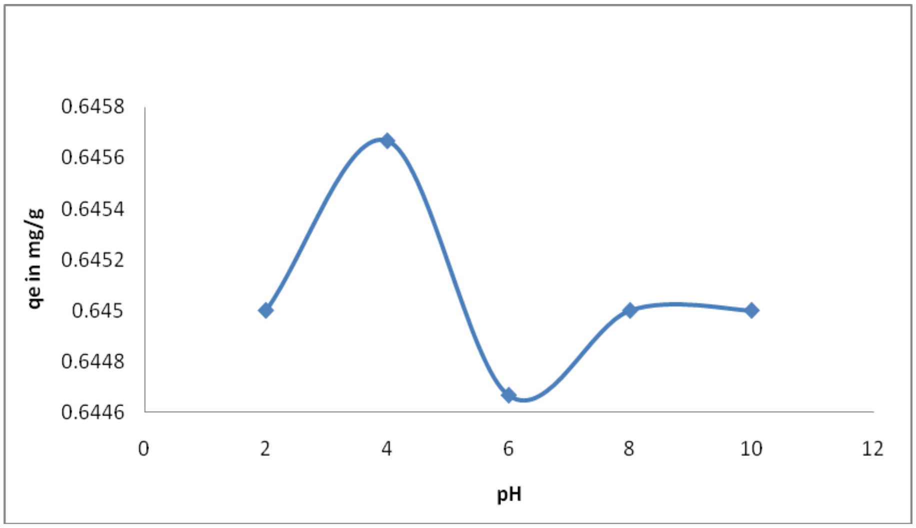


Figure 4.5: Effects of chloride ions on adsorption of fluoride ions

(Temp of 25° C, Initial fluoride concentration of 20 mg/L and 0.03 g of adsorbent)

It was observed that at pH values lower than 4.0, the uptake of fluoride was low. This was explained by the fact that chloride ions competed with the fluoride ions for the active sites. At low pH the concentration of chloride ions and hydrogen ions was high when hydrochloric acid was used. A similar observation was reported by Meenakshi and Maheshwari (2006) as they investigated quaternary ammonium functional groups containing fluoride ions whose sorption capacity was affected negatively by chloride ions. When the concentration of the chloride is elevated, concentration becomes the driving force for the sites in the solid material (Ilhan *et al.,* 2004). From that observation, it was realized that more chloride ions in solution replaced the fluoride ions leading to recharge of the modified biomaterial resin and starting the process again. Other ions such as NO^{3-} and SO_4^{2-} had no effect on the interaction of fluoride and the study material. Such observation was also reported by Velazquez *et al.* (2015) in the study on the removal of fluoride ions by modified zeoiltic tuff.

4.3.2 Effect of contact time

The effect of contact time was investigated by varying contact time from 5 min to 60 min. The results obtained were as presented in figure 4.6.

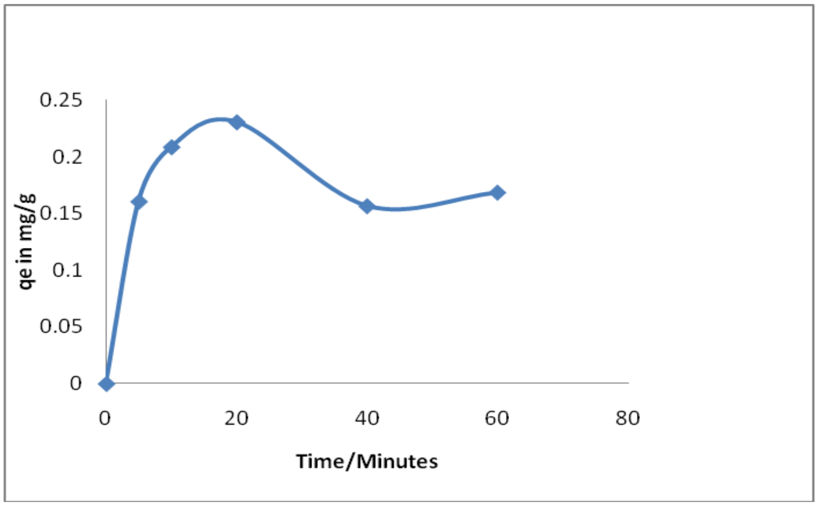


Figure 4.6: Effect of contact time on fluoride removal

(pH of 4.0, Temp of 25° C, Initial fluoride concentration of 20 mg/L and 0.03 g of adsorbent)

The results in figure 4.6 showed that the uptake of fluoride increased with time up to 20 min where maximum removal occurred. Beyond 20 min the uptake of fluoride decreased gradually. The high uptake rate at the beginning was attributed to high availability of binding sites at the initial stage (Murugan and Subremanian, 2006;

Bhaumik *et al.*, 2011). As the interaction process progresses the sites for the reaction becomes exhausted resulting to lower uptake rate of the fluoride (Waheed *et al.*, 2009; Mbugua *et al.*, 2014). After the sites have been saturated, an equilibrium is established, hence the observed phenomenon (Murugan and Subremanian, 2006; Bhaumik *et al.*, 2011). The optimum time for equilibration was 20 min and was used in the subsequent studies.

4.3.3 Effect of initial concentration of fluoride ions

In investigating the effect of the initial concentration on fluoride removal the concentration was varied from 10 to 100 mg/L. The results obtained were as presented in figure 4.7.

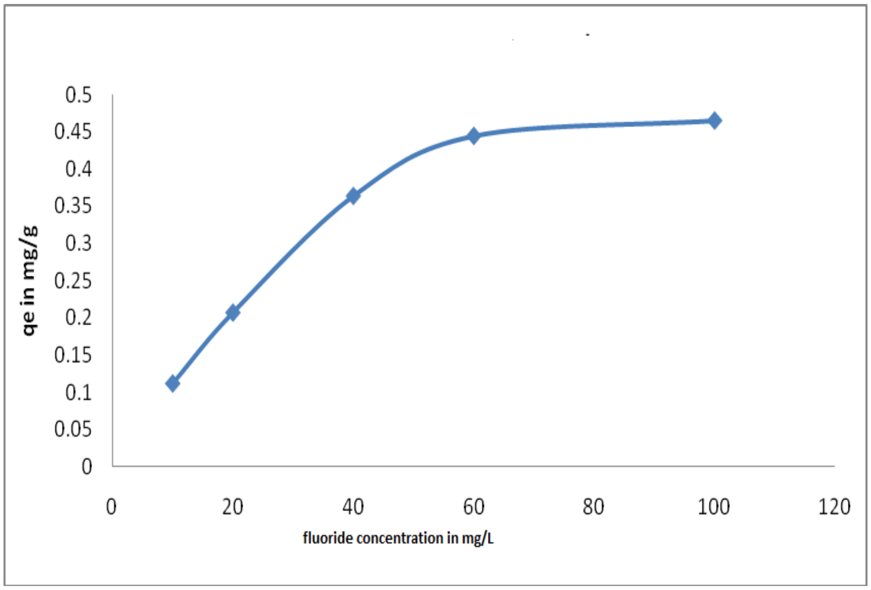


Figure 4.7: Effect of initial concentration on fluoride removal

(pH of 4.0, Temp of 25° C, contact time of 120 min and 0.03 g of adsorbent)

The profile of fluoride removal was observed to increase with increase in initial fluoride concentration up to 60 mg/L where a plateau is formed as illustrated in figure 4.7. The active sites for adsorption are fixed and as the concentration increases more of these sites are occupied resulting in the observed increase in fluoride uptake. But, it gets to a point where nearly all the active sites are filled up at high concentration which accounts for the formation of plateau at high concentrations. According to Palanisamy *et al.* (2012) the capacity of the biomaterial gets sharply exhausted with increase in the initial concentration of the fluoride in aqueous phase. The adsorption sites for a fixed amount of biomaterial are limited and become saturated at high concentration (Bhaumik *et al.*, 2011).

4.3.4 Effect of modified biomaterial resin dosage

Figure 4.8 represents the results obtained when various masses of the biomaterial were used in the equilibration process.

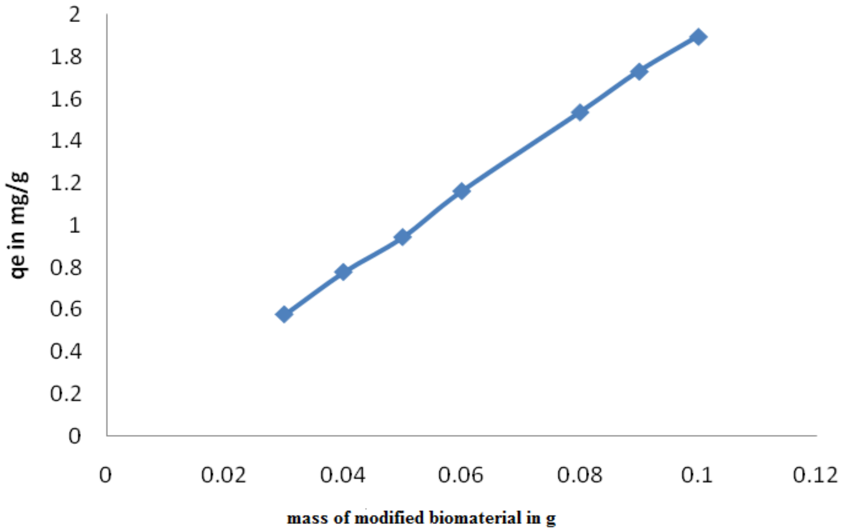


Figure 4.8: Effect of modified biomaterial resin dose

(pH of 4.0, Temp of 25° C, Initial fluoride concentration of 20 mg/L and contact time of 20 min)

From figure 4.8, the results show an increase in fluoride removal with increase in the modified biomaterial dose. This can be explained by the fact that at high doses there is high availability of surface and pore volume which increases the amount of fluoride removed from the aqueous phase. The number of binding sites resulting from increased adsorbent dosage and availability of more effective sites for interaction contributed to the observed phenomenon (Patil *et al.*, 2012; Mulu, 2013). This implied that the number of active sites for adsorption increased with increase in modified biomaterial dose.

4.4 Analysis of environmental water samples

The environmental water from Lake Baringo had a pH value of be 10.0 and fluoride concentration of 41.24 mg/L. Known fluoride ion concentration (0.1-2 mg) had been spiked into the environmental water to obtain new concentrations. The results in figure 4.9.represents the percentage removal of fluoride in both model solutions and environmental water from Lake Baringo.

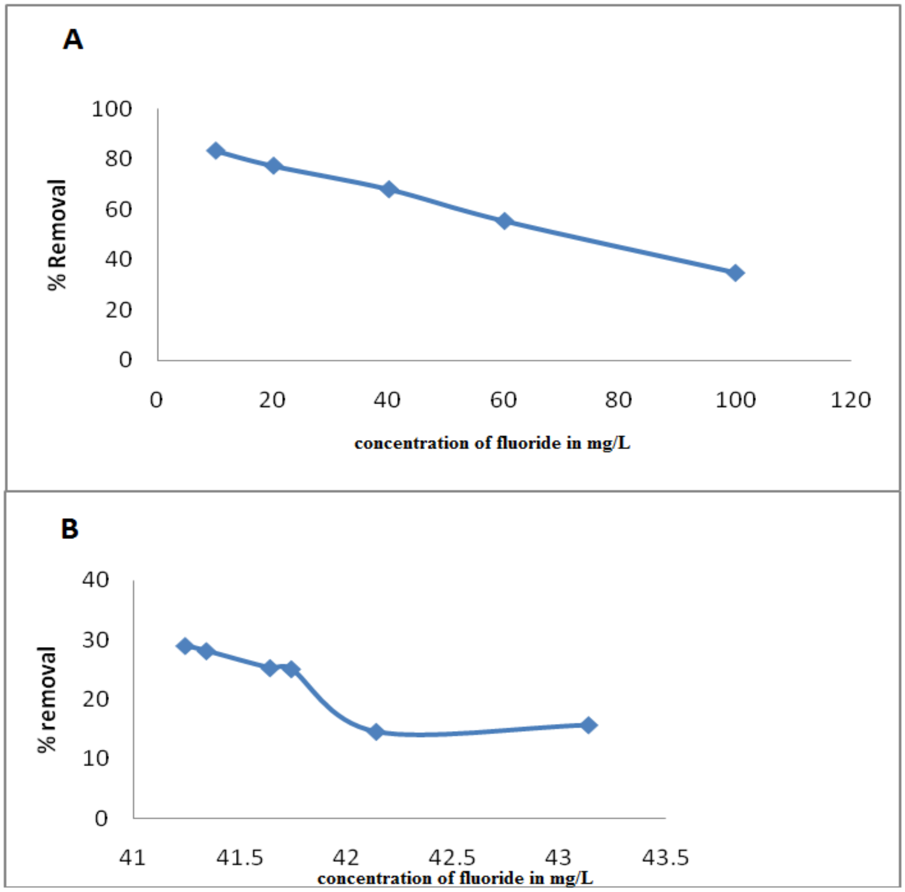


Figure 4.9: Analysis of model (A) and environmental water samples (B)

The profile observed in figure (4.9A) shows that the removal efficiency from model solutions decreased from 84-42% with increase in the concentration of the sample. This was due to decrease in the availability of the binding sites as the concentration increased. A similar trend was observed in the analysis of environmental water samples from Lake Baringo. However, the percentage removal was slightly lower as compared to that of model solutions. This can be attributed to the environmental factors such as presence of other ions which may compete with the uptake of fluoride ions in the environmental water (Topperwien *et al.,* 2007).

4.5. Application studies and regeneration

After stripping off the adsorbed fluoride ions in the various columns using 5 ml of 3.0 M hydrochloric and analysing the fluoride content in the eluent solution it was observed that all the masses of more than 0.22 g of the adsorbent in the SPE column achieved a pre-concentration factor of 20. Figure 4.10 represents the spectrum of the material obtained after defluoridation.

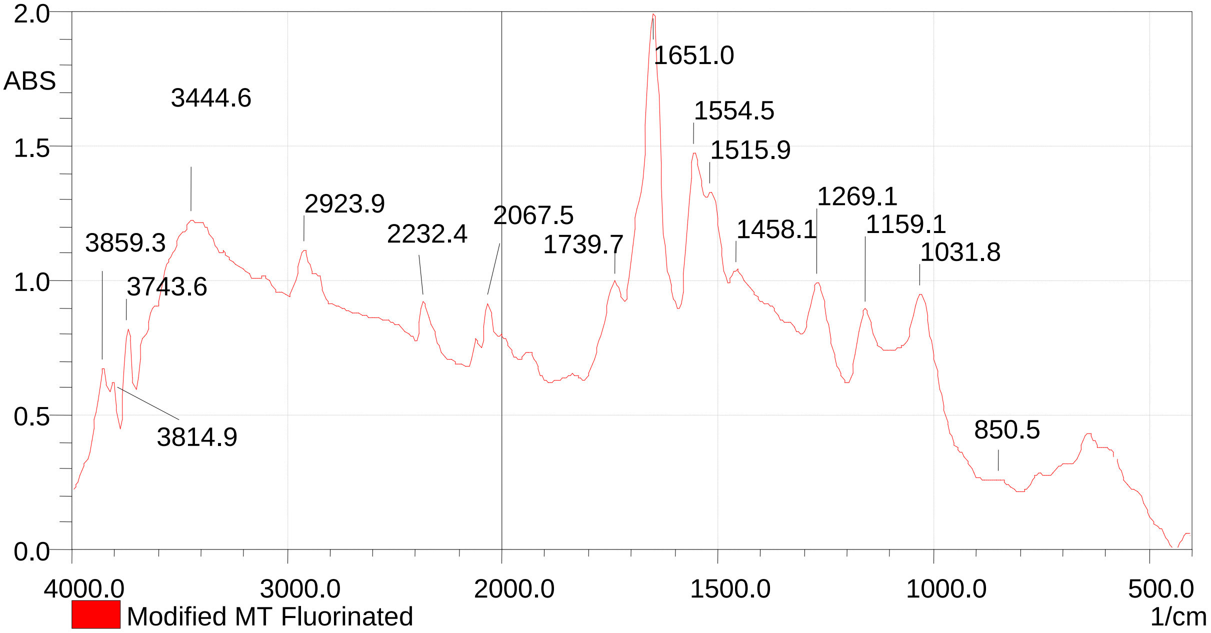


Figure 4.10: FTIR spectrum for fluorinated modified maize tassels (FMT)

From figure 4.10 it was observed that the band at 3369.4 cm^{-1} assigned to amine functional group in the spectrum of modified maize tassel in figure 4.3 shifted to 3444.6 cm^{-1} and the one at 1029.9 cm^{-1} assigned to C-N bond shifted to 1031.8 cm^{-1}. This was due to the interaction of the highly electronegative fluoride ion with the positively charged nitrogen atom. The electron density was concentrated around the fluorine, leaving the nitrogen relatively electron poor making it more positive (Blanksby and Ellison, 2003). This contributed to the shift in the wavelength of absorption. This implied that the fluoride ion interacted with the positively charged nitrogen atom.

The modified maize tassel after defluoridation was regenerated by backwashing with hydrochloric acid. This recharged the modified biomaterial resin again. The spectrum for the regenerated modified maize tassel (RMMT) is as presented in figure 4.11.

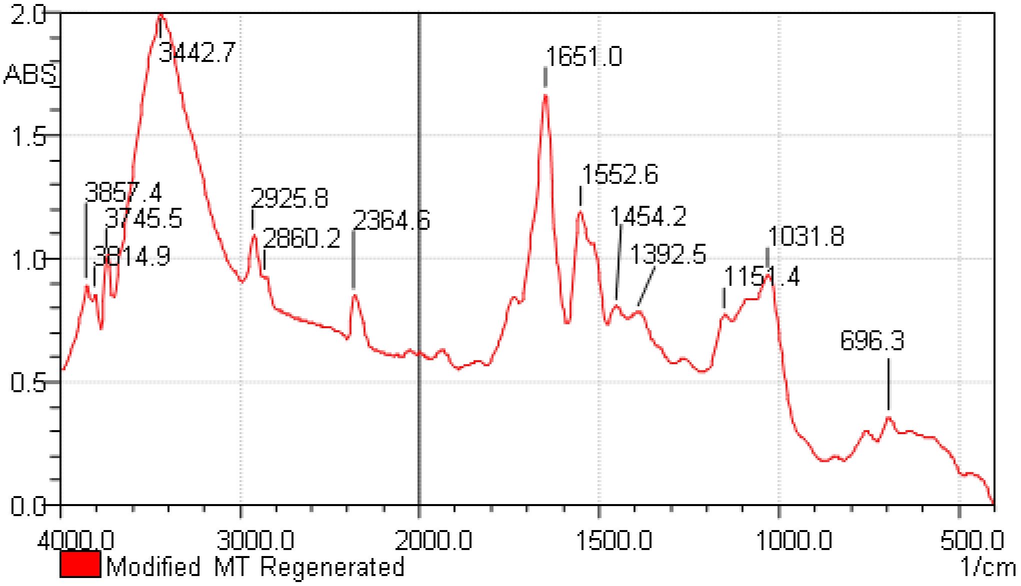


Figure 4.11: Regenerated modified maize tassel (RMMT)

Upon regeneration the chloride atom replaces the fluorine atom in the fluorinated modified maize tassels. From the spectrum it was observed that the band at 3444.6 cm^{-1} in the fluorinated modified maize tassels in figure. 4.10 shifted to 3442.7 cm^{-1} in the regenerated modified maize tassels (RMMT). This shift may due to the replacement of highly electronegative fluorine atom by the chlorine atom which is less electronegative. The spectrum is closely similar to that of modified maize tassels in figure 4.3 apart from the band at 696.3 cm^{-1} which was attributed to the chlorine atom (Stanculescu *et al.*, 2010). This confirmed that the fluorine atom in the fluorinated modified maize tassel was successfully replaced by the chlorine atom. The driving force behind the regeneration process was the high concentration of the chloride ions (Ilhan *et al.*, 2004).

4.6 Capacity and mechanism of the fluoride ions on the modified bio-material

To determine the adsorption capacity and mechanism of the fluoride ions on the modified bio-material, the experimental data were treated with the Langmuir and Freundlich adsorption isotherms. The results obtained were recorded in figure 4.12.

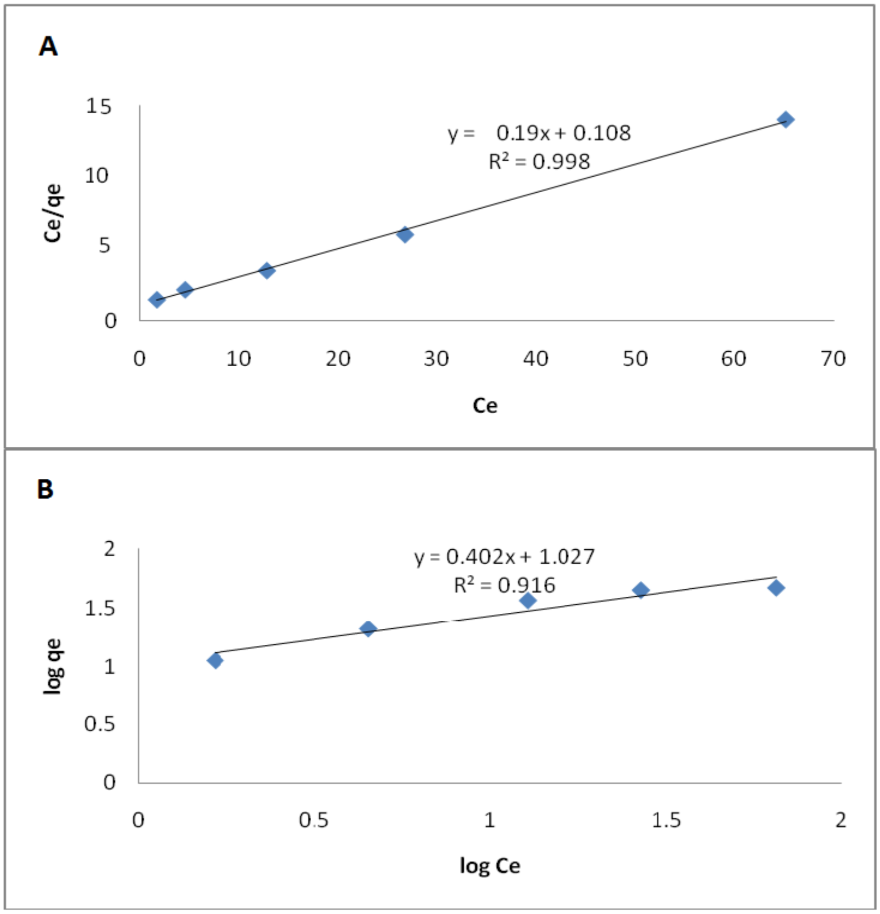


Figure 4.12: Langmuir (A) and Freundlich (B) plots for the sorption of fluoride ions.

The plots gave straight lines whose linear regressions were 0.998 and 0.916 for the Langmuir and Freundlich, respectively.

From the data, a plot of $\frac{C_e}{q_e}$ versus C_e gave a linear plot with a higher linear regression of 0.998 indicating that the sorption prescribed the Langmuir model, thus a chemisorption process. The adsorption capacity in Langmuir isotherm was 5.26 mg/g.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The modified biomaterial was successfully synthesized and this was confirmed by FTIR analysis which indicated the presence of the anchored functional group. It was found to be very effective in fluoride removal with up to 86% removal within the first 20 min. However, the uptake in environmental water samples was slightly lower compared to that of the synthetic water due to other species in solution. The optimum pH and contact time were found to be 4.0 and 20 min, respectively and the fluoride uptake per unit mass of biomaterial increased with increase in concentration up to 60 mg/L where a plateau was formed. It was also noted that increase in biomaterial dosage resulted in increased fluoride uptake.

The data fitted best in Langmuir isotherm which had the highest linear regression R^2 value of 0.998 and maximum adsorption capacity of 5.26 mg/g. It was also observed that the adsorbent in the SPE column could be regenerated by stripping the attached fluoride ions with a 3.0 M hydrochloric acid. The adsorbent in the SPE column achieved a pre-concentration factor of 20. This work confirmed that quaternized maize tassels had potential application in the removal of fluorides in water for domestic consumption.

5.2 Recommendations

5.2.1 Recommendations from this work

i. The government under the ministry of water and natural resources should sensitize the public on the use of maize tassels in defluoridation of water, which is less expensive and locally available.

5.2.2 Recommendations for further work

There is need to:

i. Assess other locally available biomaterials for application in defluoridation of water.

ii. Use other modification methods in the preparation of the target material.

iii. Educate the public on the use of locally available agricultural waste materials in water treatment.

iv. Have the modified maize tassels packed for commercial purposes in defluoridation of water.

v. Use of other methods in determination of functional groups present in the modified biomaterial.

vi. Explore toxicity and shelf life studies on the modified material.

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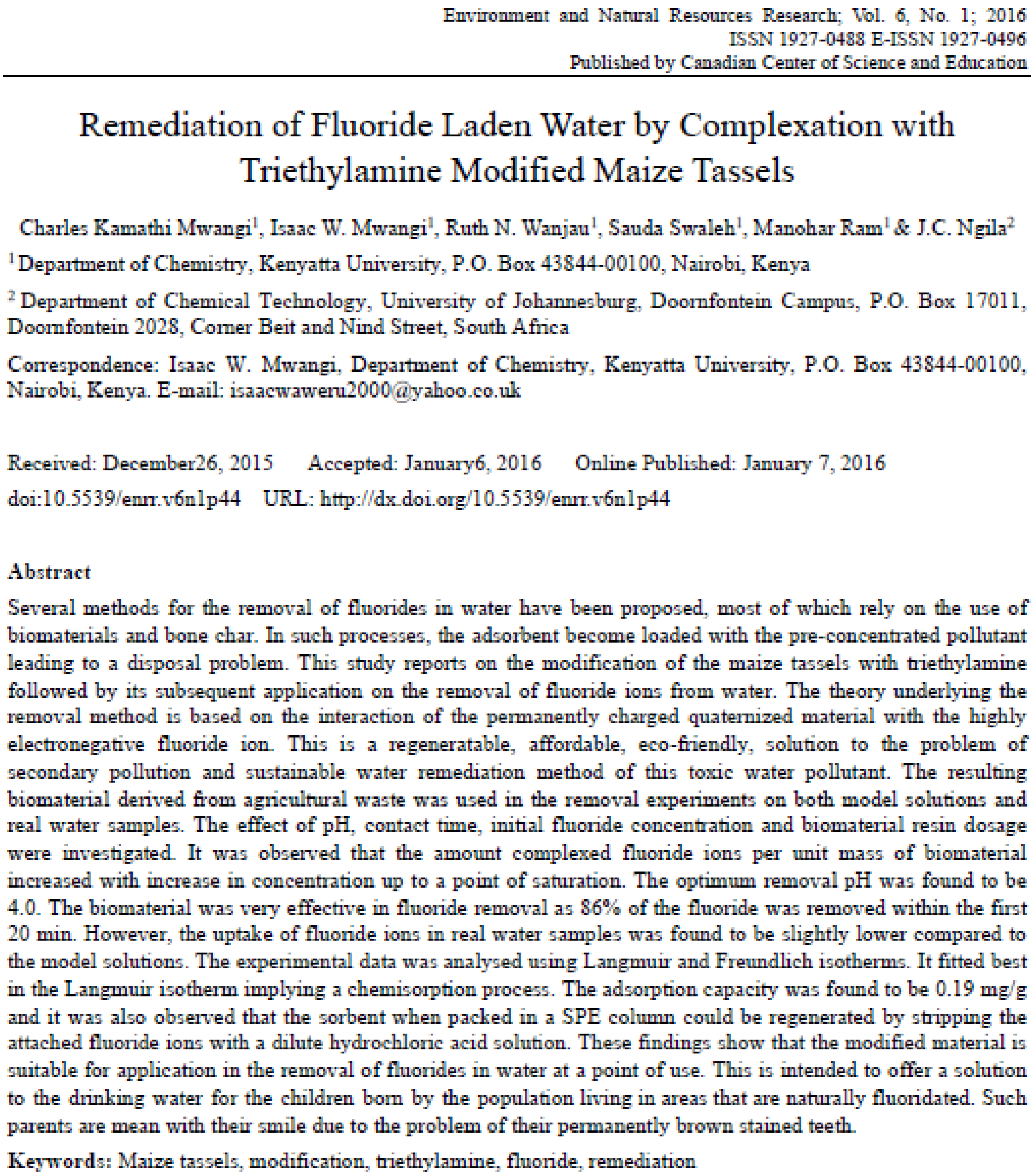
APPENDICES

APPENDIX 1

The abstract of our publication



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Remediation of Fluoride Laden Water by Complexation with Triethylamine Modified Maize Tassels

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Abstract

Several methods for the removal of fluorides in water have been proposed, most of which rely on the use of biomaterials and bone char. In such processes, the adsorbent become loaded with the pre-concentrated pollutant leading to a disposal problem. This study reports on the modification of the maize tassels with triethylamine followed by its subsequent application on the removal of fluoride ions from water. The theory underlying the removal method is based on the interaction of the permanently charged quaternized material with the highly electronegative fluoride ion. This is a regeneratable, affordable, eco-friendly, solution to the problem of secondary pollution and sustainable water remediation method of this toxic water pollutant. The resulting biomaterial derived from agricultural waste was used in the removal experiments on both model solutions and real water samples. The effect of pH, contact time, initial fluoride concentration and biomaterial resin dosage were investigated. It was observed that the amount complexed fluoride ions per unit mass of biomaterial increased with increase in concentration up to a point of saturation. The optimum removal pH was found to be 4.0. The biomaterial was very effective in fluoride removal as 86% of the fluoride was removed within the first 20 min. However, the uptake of fluoride ions in real water samples was found to be slightly lower compared to the model solutions. The experimental data was analysed using Langmuir and Freundlich isotherms. It fitted best in the Langmuir isotherm implying a chemisorption process. The adsorption capacity was found to be 0.19 mg/g and it was also observed that the sorbent when packed in a SPE column could be regenerated by stripping the attached fluoride ions with a dilute hydrochloric acid solution. These findings show that the modified material is suitable for application in the removal of fluorides in water at a point of use. This is intended to offer a solution to the drinking water for the children born by the population living in areas that are naturally fluoridated. Such parents are mean with their smile due to the problem of their permanently brown stained teeth.

Keywords: Maize tassels, modification, triethylamine, fluoride, remediation