

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

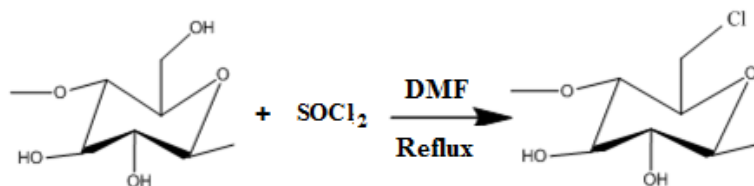
1. Introduction

The chemical structure of water makes it have special properties because of the way its atoms bond together to form a water molecule. This molecular structure gives the water molecule polarity, or a lopsided electrical charge that attracts other atoms. Due to that polarity water become a universal solvent for polar substances as they are easily dispersed uniformly within the water molecule. This dissolving power of water is very important for life as it enables it to harbour dissolved nutrients that support living things. This property of water's ability to split ionic compounds has contributed to 97% of the world's water being salty (Soteris, 2005). Most of those salt ions occur naturally in the soil, sedimentary and igneous rocks in many other 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 material 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 lead to accumulation capable of causing dental and skeletal fluorosis (Edmunds & Smedley, 1996). Consumption of fluoridated water has

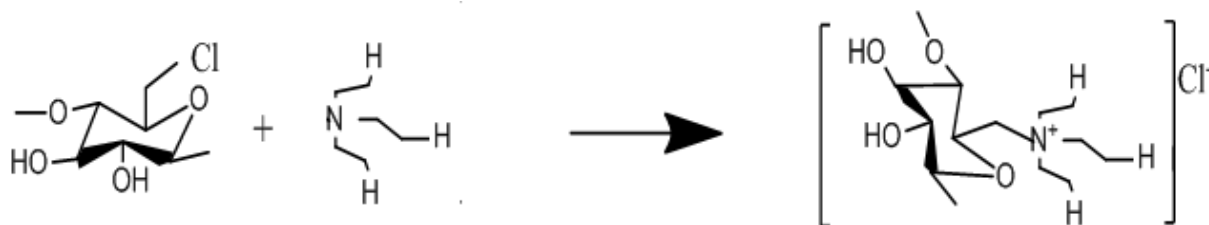
emotional problems as well. This is because persons with stained teeth are hesitant to provide a gleaming smile and in many occasions appear withdrawn. In Kenya for example, these problems are known to exist in areas along the eastern rift valley, western slopes of the Aberdare ranges and parts of the central province. These areas contain rocks with high fluoride content which pollute the adjacent water bodies (Williamson, 1953; Amini et al., 2008). Preliminary studies by Choi and co-workers (2012) have also shown a strong connection between exposure to fluoride in drinking water and decreased IQ scores in children.

To overcome the negative health effects of fluoride in water, it should therefore 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 precipitation (Cha et al., 1997). These conventional removal methods are not effective when the concentrations are in trace levels ranging from 1-20 $\mu\text{g/L}$ (Lodeiro et al., 2006). They are also expensive thus not affordable to the 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 et al., 2014). They have been found to be effective in removal of pollutants even at trace levels (Lodeiro et al., 2006). 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 & Dixon, 1992; Garg et al., 2008). These materials were used in their raw form and leached organic matter in the water which leads to change of colour and taste of the final treated water, a phenomenon termed as “secondary pollution” (Chen & Yang, 2005). The other challenge in the use of such materials is that they could not be regenerated posing a disposal problem. Bone char has also been widely used, but not welcome by many religious groupings (Feenstra et al., 2007). This study therefore aimed to overcome these limitations by developing an ion exchange biomaterial resin from maize tassels with a suitable functional group to complex fluoride ions and remove them from water. This was achieved by chemical modification of maize tassels with a tertiary amine. A resin material was obtained through chlorination of the carbon in position 6 of the cellulose molecule (of the maize tassels) to form an intermediate of chlorocellulose as an alkyl halide (Boehm, 1958; Bano, 2014). This was then followed by substitution of the chlorine atom in the chlorocellulose with the amine group. Below is a schematic presentation of the reaction.



Scheme 1. Chlorination of maize tassels using thionyl chloride

When the chlorinated maize tassels were treated with triethylamine, the chlorine atom was displaced by the nitrogen from the tertiary amine to form stable cationic quaternary amine cellulose which is permanently positively charged as shown in scheme 2:



Scheme 2. Synthesis of quaternary amine cellulose

The resulting solid material was capable of interacting with negatively charged species such as the fluoride ions in water and attracting it to its surface hence removing the fluoride from water. It was regeneratable and did not leach soluble organic compounds in the treated water.

2. Materials and Methods

2.1 Research Design

The focus of this study was to synthesis a sorbent through modification of maize tassels by anchoring functional groups capable of interacting with fluoride ions and removes them from the aqueous media. The protocol in preparation should use non toxic and environmentally friendly materials. This study was carried out in a several parts. This comprised of the synthesis, characterization of the modified material, optimization of removal parameters and then its subsequent application for the removal of fluorides from both synthetic and environmental waters samples.

2.2 Chemicals and Reagents

All the solutions were prepared in double distilled water and the reagents were of analytical grade. 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 g of sodium chloride and 4 g of 1,2-cyclohexanedinitrilo-tetraacetic acid (CDTA) in 1000 ml of distilled water. The above chemicals as well as triethylamine were all supplied by Kobian Kenya Ltd. which is Sigma Aldrich's outlet in Kenya.

2.3 Instrumentation

The fluoride content in the solutions was determined by potentiometric method using fluoride Ion Selective electrode (JENWAY 3345 Ion Meter). The synthesised material was characterised using Fourier Transform Infrared (FT-IR) spectroscopy (Perkin Elmer 100 made in Waltham, MA, USA). The pH of the synthetic and real samples was monitored by a PHEP pH meter supplied by Hanna Instruments, Italy. Refluxing the reaction mixture was carried out using a WHM 120151 isomantle made in Korea.

2.4 Fluoride ion Selective Electrode (ISE)

In this study the determination of fluoride ions was carried out by use of fluoride ion selective electrode (ISE). This is a potentiometric method for determination of ions in solution where the output potential is proportional to the amount or concentration of the selected analyte (Sunitha & Reddy, 2014). The fluoride ion selective electrode utilizes a membrane that consists of a single crystal of Lanthanum fluoride doped with Europium (II) fluoride to improve its conductivity (Skoog et al., 2007). The method is simple to perform and has a good precision and sensitivity (Skoog et al., 2007). The concentration of the analyte is proportional to the electrode potential, E, as demonstrated in the Nernst Equation (1) below from which the concentration of the fluoride ions were evaluated.

$$E = E^0 \pm \frac{RT}{nF} \ln[C] \quad (1)$$

Where E is the potential difference, E^0 the standard cell potential, R the universal gas constant, T the absolute temperature, n the number of electrons, F the Faraday's constant and C the concentration of the relevant species.

The measurements were carried out at constant ionic strength. This was achieved by the use of a total ionic strength adjustment buffer (TISAB).

2.5 Modification of the Maize Tassels Biomaterial

The maize tassels samples were washed with distilled water and sun dried. They were ground, activated at 80 °C for 12 hr, cooled in a desiccator and later stored in clean plastic bottles. A sample of 10 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 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 (suction) through a sintered glass crucible no. 3 and dried in a vacuum at room temperature. A mass of 5.0 g chlorinated maize tassels was reacted with 25.0 ml triethylamine under reflux and mechanically stirred for 3 hr. The mixture was filtered through a sintered glass crucible and the solid dried in a vacuum at room temperature for 24 hr. The synthesized material was a solid derivative which was then used for sorption experiments.

2.6 Optimization Experiments

Optimization experiments were carried out in batch adsorption experiments on a mechanical thermostated reciprocating shaker (DKZ-1NO.1007827-USA).

2.6.1 Batch Experiments

The experiments were carried in a temperature controlled water bath shaker using 100 ml plastic bottles. The experiments were performed 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 for 60 min. 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).

2.6.2 Effects of pH

The effect of pH on removal of fluoride from model solutions was studied using 0.03 g of the modified biomaterial resin. 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 of 40 ml of 20 mg/L fluoride solution and 0.03 g of the modified biomaterial resin 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.

2.6.3 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. 0.03 g of the biomaterial resin 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.

2.6.4 Effect of Initial Concentration of Fluoride Ion

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 resin 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.

2.6.5 Effect of Biomaterial Resin Dosage

The effect of the modified biomaterial resin dose on uptake of fluoride was investigated by shaking 40 ml sample solutions of 20 mg/L at various doses ranging from 0.01 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.

2.7 Calculation of Fluoride Ion Uptake

The amount of fluoride ion uptake by modified maize tassels during the batch experiments was determined using the equation 2 as shown below.

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

Where,

q_e = Amount of F^- uptake per unit mass of biomaterial resin at equilibrium

C_0 = Initial concentration of F^- in mg/L

C_e = Concentration of F^- at equilibrium in mg/L

m = mass of biomaterial resin in g

V = volume of solution in L

3. Results and Discussion

3.1 FTIR characterisation of the biomaterial

Figure 1 represents the absorption spectra of parent maize tassel. The band at 3319 cm^{-1} may be as a result of presence of OH or NH groups while the peak at 2925.8 cm^{-1} may be attributed to stretching of C-H bonds (John, 2000).

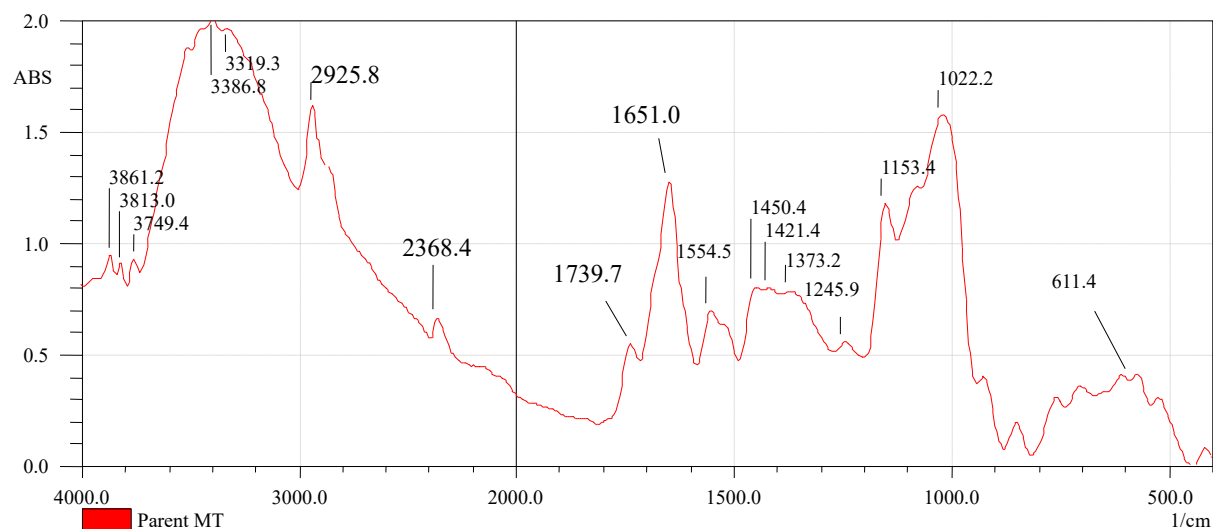


Figure 1. FTIR spectrum for parent maize tassels

Figure 2 below represents the chlorinated maize tassels spectrum. There is appearance of a new peak at 744.5 cm^{-1} . This corresponds to the absorption peak of C-Cl. The C-Cl stretch ranges from $550\text{--}850\text{ cm}^{-1}$ (John, 2000).

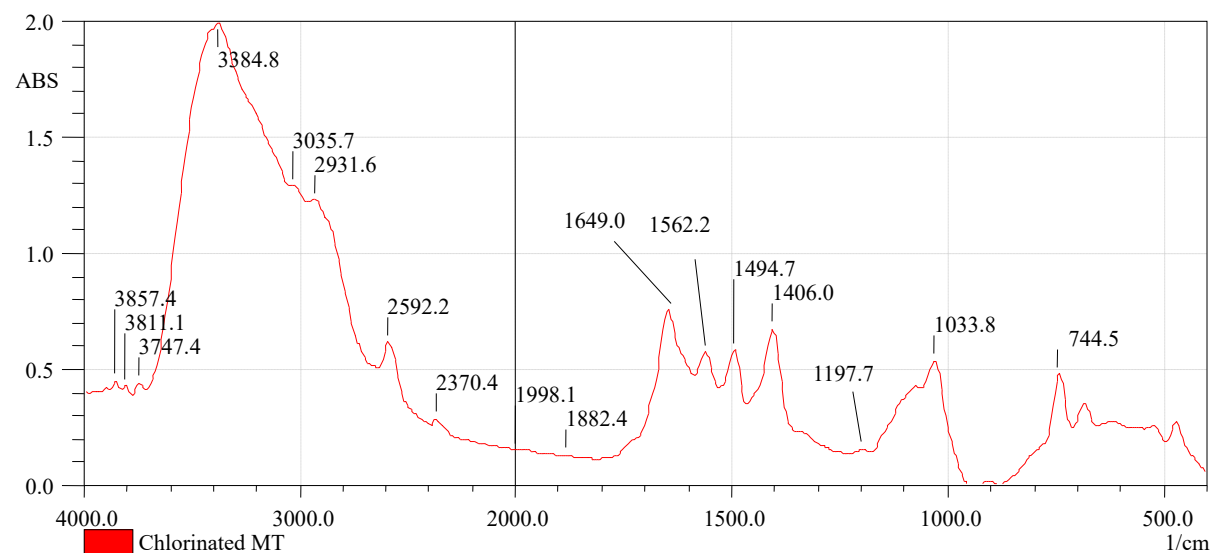


Figure 2. FTIR Spectrum for chlorinated maize tassels

The band 744.5 cm^{-1} in the chlorinated maize tassels (Figure 2) disappeared in the spectrum of modified maize tassels (Figure 3). This illustrates the substitution of the chloro group by the triethylamine.

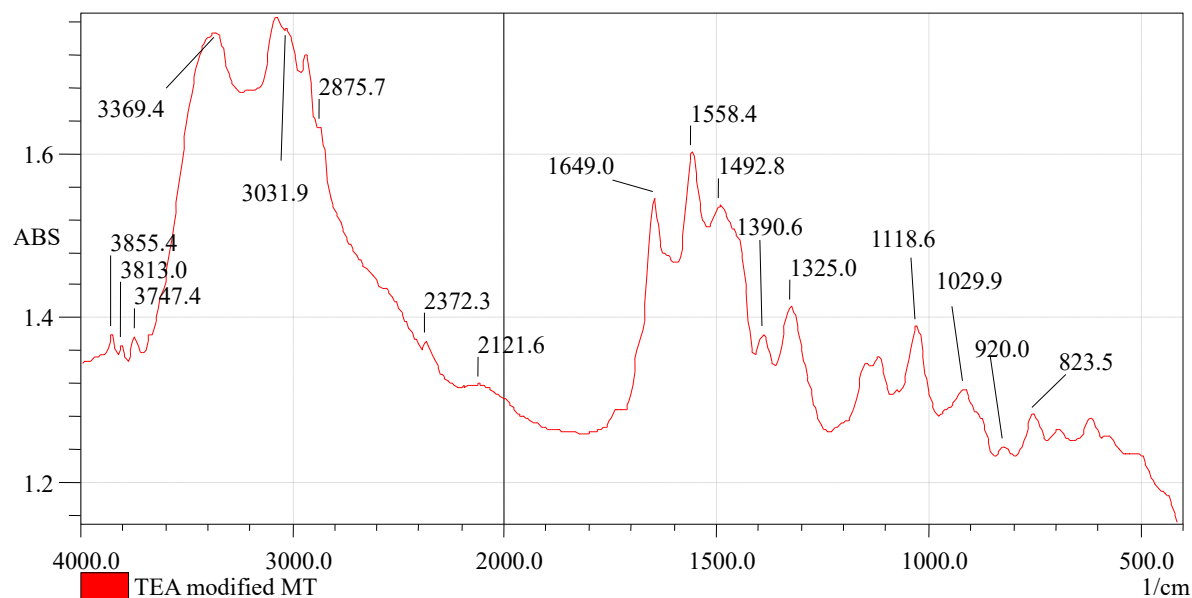


Figure 3. FTIR spectrum for triethylamine modified tassels

The peak obtained for modified material at 1492 cm^{-1} corresponded to the methyl of the ethyl groups in the tertiary amine (Loubakiet al., 1991). The band at 1325.0 cm^{-1} was referenced as the C-N stretching vibration (Kacurakova et al., 1994; Pal et al., 2005). Therefore, it can be concluded that the maize tassels were successfully quaternized (Song et al., 2008).

The modified material was interacted with fluoride ions in water. The results obtained were as presented in Figure 4.

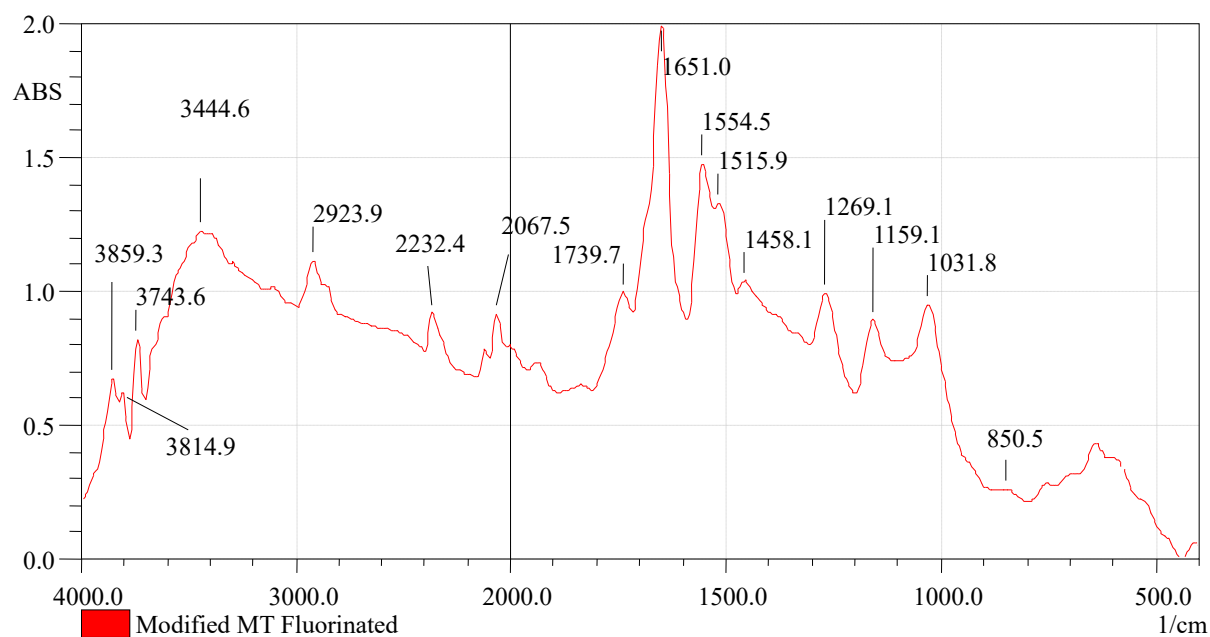


Figure 4. FTIR spectrum for fluorinated modified maize tassels

It was observed that the band at 3369.4 cm^{-1} shifted to 3444.6 cm^{-1} after fluorination. The shift is because of the interaction of the highly electronegative fluoride ion with the positively charged nitrogen atom. The electron density is 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 (Blanksby and Ellison, 2003). This implies that the fluoride ion interacts with the positively charged nitrogen atom and thus, it can be applied for the removal of the fluoride ion from water. The parameters that affect the complexation of the modified material and fluoride ions were investigated.

3.2 Optimization of Complexation Parameters.

3.2.1 Effect of pH on Removal of Fluoride Ions by Modified Maize Tassels

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). The pH has effect on interaction of the fluoride ions with nitrogen containing moieties as well. This is because pH influences the charge of the nitrogen atom of the sorbent and the chemistry of the ion (Unlu and Ersoz, 2006). 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.

In this study the effects of pH on removal of fluoride from models solutions using modified maize tassels were investigated using 0.03 g of the modified maize tassels at a stirring rate of 120 r/min. The solutions had a fluoride concentration of 20 mg/L and the temperature set at $25\text{ }^{\circ}\text{C}$. The model solutions were buffered at various pH values ranging from 2.0-14.0. The results obtained were presented in Figure 5.

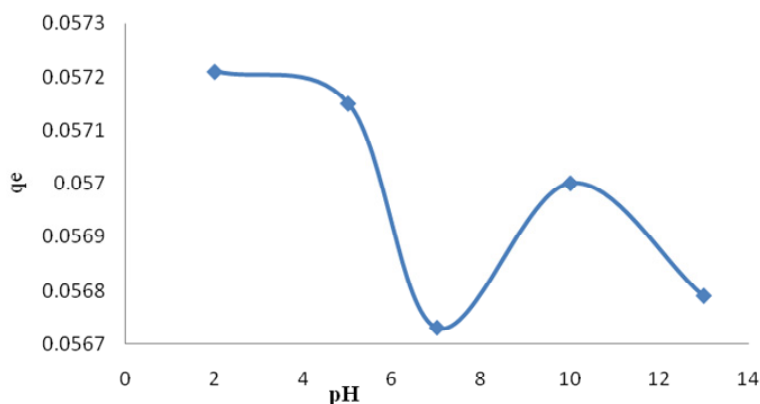


Figure 5. Effects of pH on complexation of fluoride ions

It was observed that at higher pH values, the removal of fluoride ions from water was low. Decrease in fluoride removal at higher pH may be due to gradual increase in number of hydroxide ions on the biomaterial surface causing repulsion of fluoride ions (Tembhurkar and Shilphadonge, 2006). At lower pH values (2.0-4.0), removal of fluoride increased significantly but decreased at the physiological pH of water. This is in agreement with other researchers who reported a maximum fluoride uptake at pH 4.0 as they investigated removal of fluoride from water using bio-adsorbents (Anusha and Raja, 2014; Ramchander et al., 2013). This could be due to increasing of the positive charge on the surface of the adsorbent leading to greater complexation of fluoride (Chowdhury et al., 2011; Patil et al., 2012). A similar case was observed by Sahira et al., (2012) while they removed fluoride from water using Zirconyl- Impregnated activated carbon prepared from lapsi seed stone. At high pH (>8) there is high concentration of hydroxide ions which hinders fluoride ions diffusion leading to low uptake of fluoride (Tembhurkar and Shilphadonge, 2006). The hindrance comes as a result of development of repulsive forces between the negatively charged fluoride and the negatively charged hydroxide ions

3.2.2 Effect of Chloride Ions

The effect of chloride ions on removal of fluoride ions by modified maize tassels was investigated by varying the pH of the solution using 0.1 mol/L hydrochloric acid while keeping all the other variables constant. This was meant to investigate the effect of chloride ions on the fluoride complexation. The results obtained were presented in Figure 6.

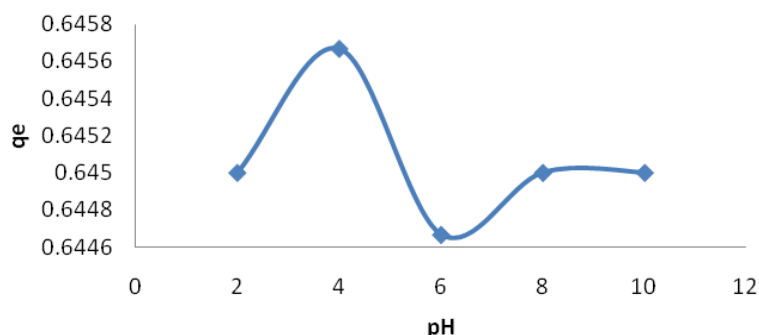


Figure 6. Effects of chloride ions on complexation of fluoride ions

It was observed that at pH values lower than 4.0, chloride ions hindered the complexation of fluoride ions on the modified biomaterial. This could be due to competition between the fluoride and chloride ions for interaction sites. 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 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 zeolitic tuff. Therefore, our study exploited the use of hydrochloric acid to regenerate the synthesized material. From this study the optimum pH for the removal of fluoride ions was found to be pH 4.0.

3.2.3 Effect of Contact Time

The effect of contact time was investigated by varying contact time from 5 min to 60 min at pH 4.0, stirring rate of 120 r/min and temperature of 25 °C. The initial fluoride concentration was 20 mg/L and 0.03 g of modified biomaterial was used for each sample solution. The results obtained were presented in Figure 7.

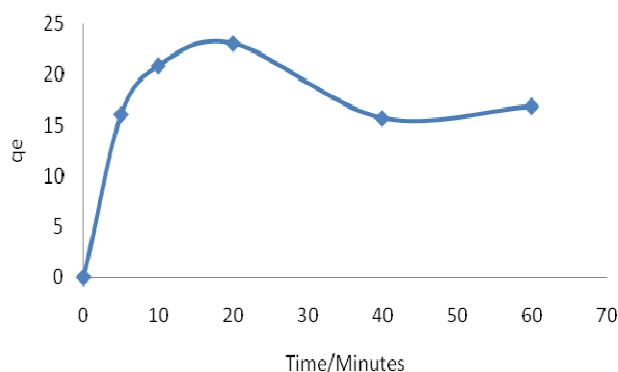


Figure 7. Effect of contact time on fluoride removal

The results show that the uptake of fluoride increases with time up to 20 min where maximum removal occurs. Beyond, 20 min the uptake of fluoride decreases gradually. The high uptake rate at the beginning may be 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.

3.2.4 Effect of Biomaterial Resin Dosage

The effect of modified maize tassels material dosage was investigated using masses of 0.03, 0.04, 0.05, 0.06, 0.08, 0.09 and 0.1 g in 40 ml of the model solution at an optimum pH of 4.0. The concentration of the model

solution was kept at 20 mg/L with an equilibration time maintained at 20 min. The results obtained were presented as shown in Figure 8 below.

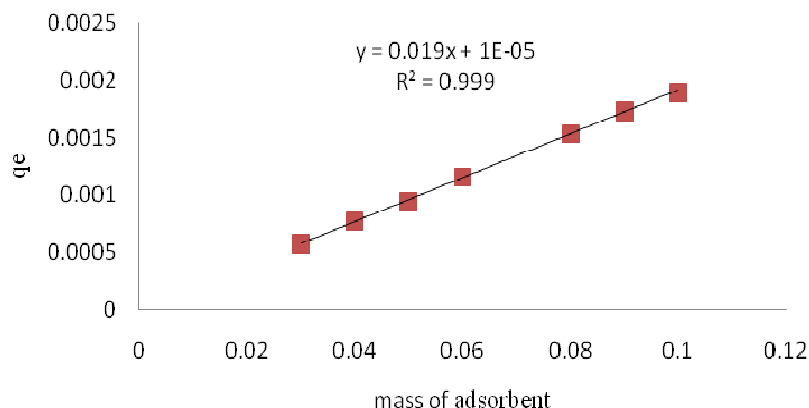


Figure 8. Effect of biomaterial resin dose

The result showed an increase in fluoride removal with increase in the biomaterial resin 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 (Patil et al., 2012; Mulu, 2013). 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 complexation increased with increase in biomaterial resin dose.

3.2.5 Effect of Initial Concentration

In this study, the initial concentration of the model solutions was varied from 10 to 100 mg/L while maintaining the biomaterial dosage of 0.03 g and optimal pH value of 4.0 and contact time of 20 min. The results obtained were as presented in Figure 9.

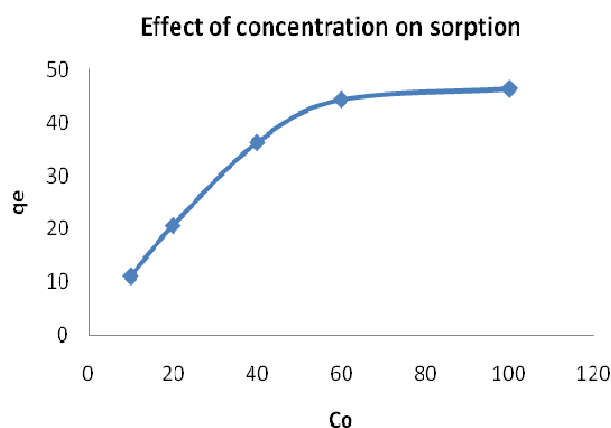


Figure 9. Effect of initial concentration on fluoride removal

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 9. The active sites for complexation 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 all the active sites are exhausted at high concentration due to their saturation 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 and adsorption sites for a fixed amount of biomaterial are limited and become saturated at high concentration.

3.3 Analysis of Real Water Samples

The removal efficiency from model water samples and real water samples was investigated. The real water samples were obtained from Lake Baringo whose pH value was found to be 10.0. The fluoride concentration in that water was 41.24 mg/L. The test solutions comprised of 50 ml of synthetic water of varying concentrations ranging from 10 to 100 mg/L. To the real water samples, known fluoride ion concentration (0.1-2 mg/L) were spiked into each and 0.03 g of the biomaterial added. The resulting mixtures were equilibrated for 20 min and then filtered. The concentration of the fluoride ion in each of the filtrate was determined. The results obtained were as presented in Figure 10 below.

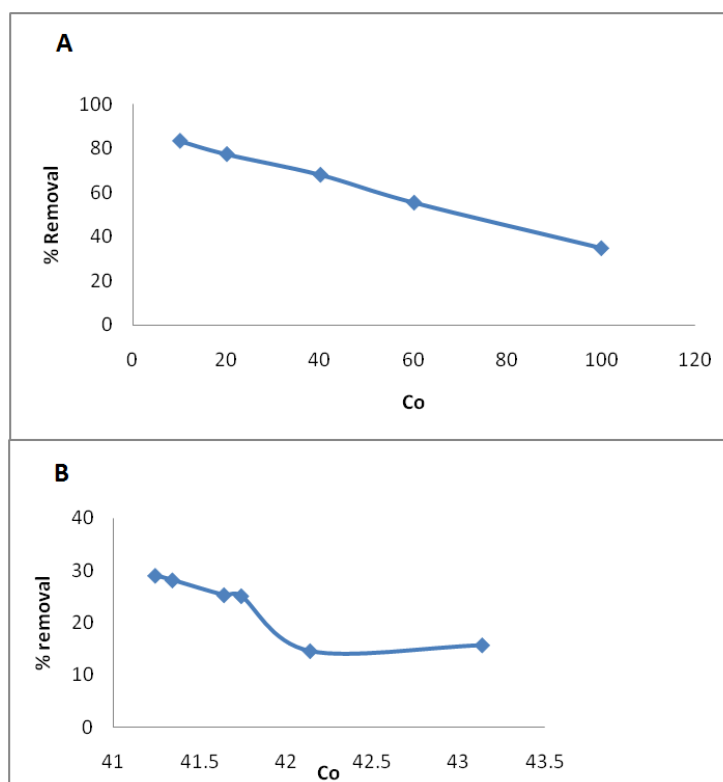


Figure10. Analysis of model (A) and real water samples (B)

The profile observed was 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 increases. A similar trend was observed in the analysis of real water samples. However the percentage removal was slightly lower as compared to that of model solutions. This may 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).

3.3.1 Application Studies

Varying masses (0.01–0.30 g) of the modified material were packed in separate columns. Model solutions, 100 ml, having a concentration of 0.1 mg /l had their pH adjusted to the optimum value and loaded onto the column. The adsorbed fluoride ions were stripped from the column using 5 ml of 3.0 M hydrochloric acid and analysed for the fluoride content. 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 and could be regenerated by stripping the attached fluoride ions with the dilute acid. This implies that the modified bio-material could be packed in a cartilage in a domestic plumbing system and be used to remove fluorides in water for human consumption.

3.4 Data Analysis

To determine the complexation capacity and mechanism of the fluoride ions on the modified bio-material, the experimental data was treated with the Langmuir and Freundlich adsorption isotherms. This was to provide the nature and physico-chemical interactions involved in the complexation (Fan et al., 2003). From that treatment,

the maximum complexation capacity of fluoride ions on the modified maize tassels could also be evaluated. Langmuir isotherm is based on the assumption that active sites are homogeneously distributed on the surface of the complexing material (Vijayakumar et al 2012). The active sites have the same affinity for complexation of a mono molecular layer and there is no interaction between the complexed particles on the surface (Senthil and Kirthika, 2009). The results for the Langmuir model were analysed using the linearised Langmuir equation as shown in equation 3.

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

Where C_e is the equilibrium concentration in mg/L, which is the analyte ion concentration remaining in the solution at equilibrium, K_L is the equilibrium constant, q_e is the analyte 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.

The experimental data was also treated with the linearised Freundlich equation 4 to establish the heterogeneous surface (Dada et al., 2012).

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

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 complexed amount in mg/g. The results obtained were recorded in Figure 11.

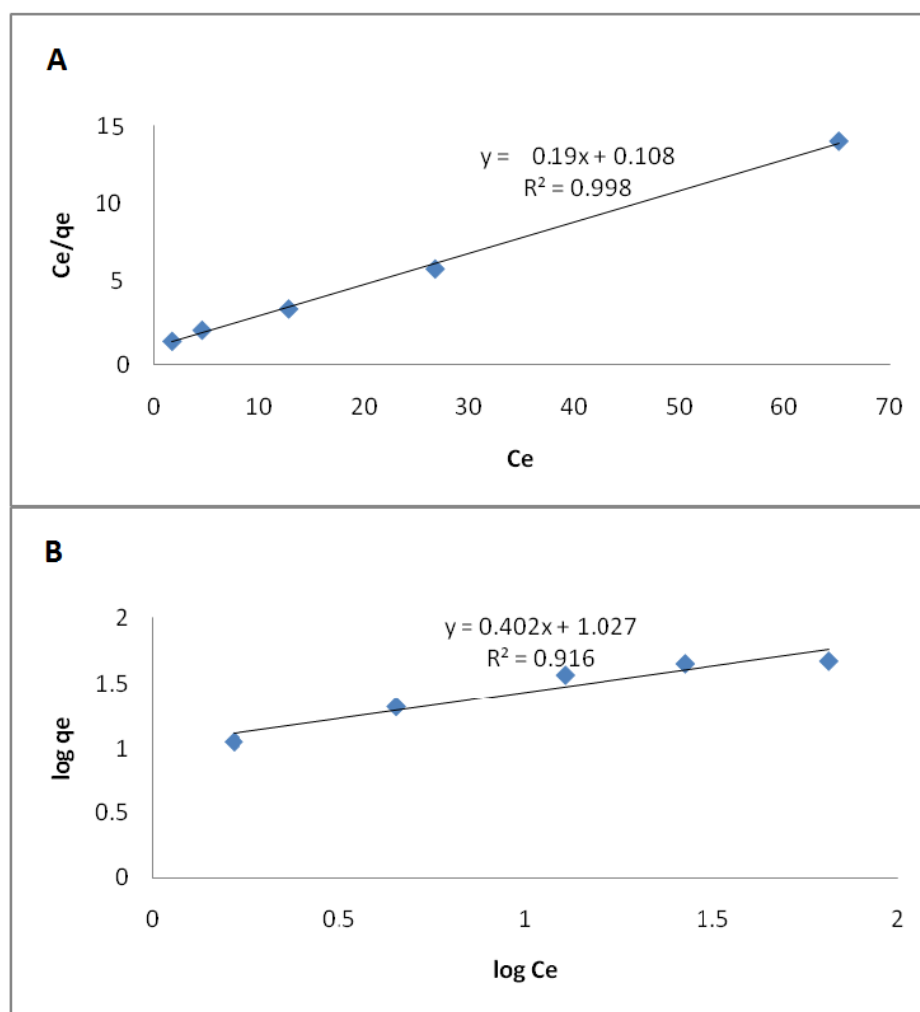


Figure 11. Langmuir (A) and Freundlich (B) plots for the sorption of fluoride ions

The plots gave straight line whose linear regression was 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 indicating that the sorption prescribes the Langmuir

model, thus a chemisorptions process. The slope $\frac{a_L}{K_L}$ is the theoretical saturation capacity which was 0.19 mg/g.

3.5 Regeneration of Fluorinated Modified Maize Tassels

The fluorinated modified maize tassels were regenerated by backwashing with hydrochloric acid. This recharged the resin again to sorb fresh fluoride ions. The spectrum for the regenerated modified maize tassels is as presented in Figure 12 below.

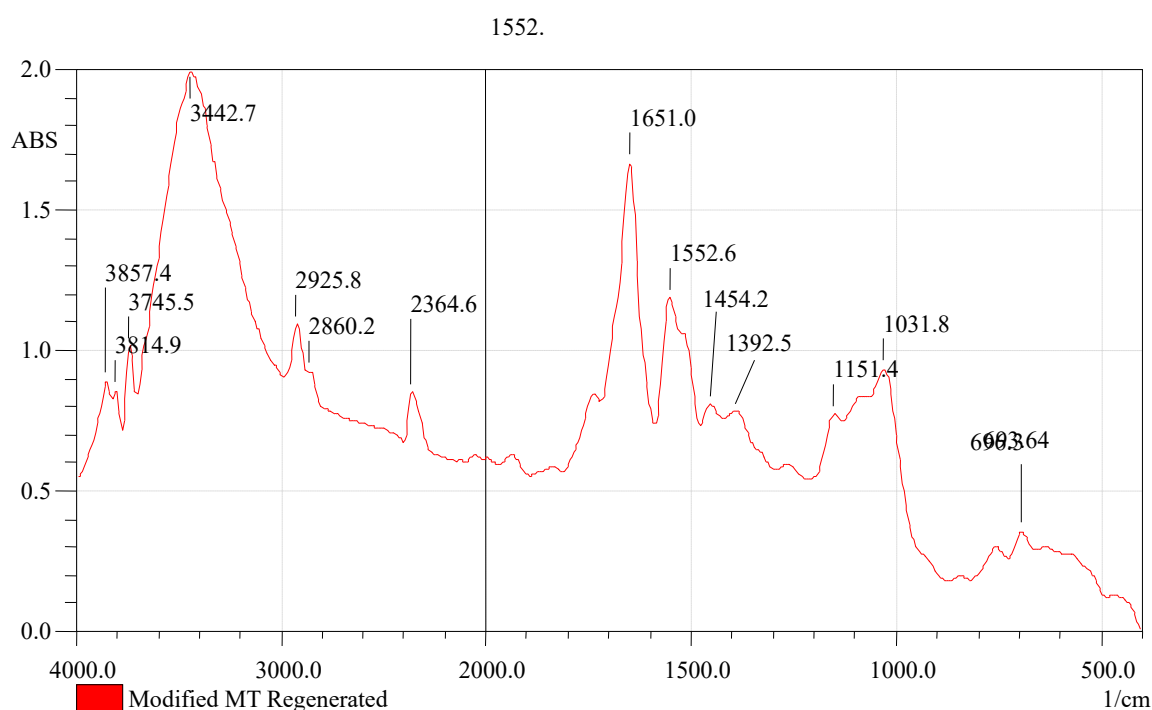


Figure 12. Regenerated modified maize tassels

From the spectrum it was observed that the band at 3444.6 cm^{-1} in the fluorinated modified maize tassels in Figure 4 shifts to 3442.7 cm^{-1} in the regenerated modified maize tassels. The spectrum is closely similar to that of modified maize tassels in Figure 3 apart from the band at 696.3 cm^{-1} which was attributed to the chlorine atom (Stanculescu et al., 2010). This confirms that the fluoride ions in the resin were replaced with the chloride ions, hence the biomaterial was recharged successfully and thus available for reuse. The driving force in the regeneration process is due to the availability of a high concentration of the chloride ions (Ilhan et al., 2004).

4. Conclusion

The study confirms that the biomaterial resin was successfully synthesized and this was confirmed by FTIR analysis which indicated the presence of the anchored functional group. The biomaterial resin was found to be very effective in fluoride removal with up to 86% removal within the first 20 min. However, the uptake in real water samples was slightly lower compared to that of the synthetic water due to other species in solution. The effects of the pH, contact time, adsorbent dosage and initial concentration were investigated. The optimum pH and contact time were found to be 4.0 and 20 min respectively. The fluoride uptake per unit mass of biomaterial

increased with increase in concentration up to 60 mg/L where a plateau was formed due to saturation of active sites. It was also noted that increase in biomaterial dosage resulted in increased fluoride uptake. This was attributed to increased adsorption sites with increase in dosage. The data fitted best in Langmuir isotherm which had the highest linear regression R^2 value of 0.998 and maximum adsorption capacity of 0.19 mg/g. It was also observed that the sorbent in the SPE column could be regenerated by stripping the attached fluoride ions with a 3.0 M hydrochloric acid. It was observed that the adsorbent in the SPE column achieved a pre-concentration factor of 20 and could be regenerated by stripping the attached fluoride ions with dilute hydrochloric acid. This work confirmed that quaternized maize tassels had potential application in the removal of fluorides in water for domestic consumption.

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