

**CLARIFICATION OF COLLOIDAL AND SUSPENDED MATERIAL
IN WATER USING TRIETHANOLAMINE MODIFIED MAIZE
TASSELS**

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DECLARATION

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


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DEDICATION

To my husband Alex Maina and my children Ngobe and Kinyua, I love you always.

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ABBREVIATIONS AND ACRONYMS

DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
EDX	Energy Dispersive X-Ray Analysis
ESCA	Electron Spectroscopy for Chemical Analysis
FT-IR	Fourier Transformed Infrared
NTU	Nepherometry Turbidity Unit
PolyDADMAC	Polydiallyldimethylammonium Chloride
QMT	Quaternized Maize Tassels
RPM	Revolution Per Minute
TGA	Thermogravimetric Analysis
TSS	Total Suspended Solids
WHO	World Health Organization

ABSTRACT

Suspended particles in water are a major concern in global pollution management. These particles are very small and are evenly distributed in the water. They originate from factors such as decomposing organic materials and algae. They are a significant factor in the water clarity, as they limit penetration of sunlight; provide a good environment for bacterial growth, contributing to fouling and unpleasant odours that compromise aesthetic appreciation of the water. They also complex with metals in the soil making them soluble and hence available for poisoning. Thus there is need for the removal of suspended matter in water. Removal of suspended solids is normally achieved through sedimentation or filtration. However, some suspended colloidal particles are very stable in water and cannot settle while others are able to pass through the filter because of their small sizes hence difficult to remove. In this regard, alternative methods for their removal need to be explored. This study investigated the use of a soluble polycation made from modifying maize tassels with triethanolamine to form a quaternary ammonium compound. The modified quaternary ammonium compound becomes permanently charged hence is suitable for flocculation of suspended particles in water. The modified maize tassels material was characterized using Fourier-transform infrared (FTIR). It was found that the triethanolamine was chemically anchored within the cellulose structure of the maize tassels. Clarification parameters such as settling time, reagent dosage and pH were investigated. This study reports that the best clarification was obtained at a pH of 6.0. The optimal flocculent dosage for modified flocculent that could clarify 250 ml of water having a turbidity of 12 NTU (Nephelometric Turbidity Units) was found to be 3.5 ml which clarified turbid water in less than 30 minutes. Therefore, this implies that the flocculent has a potential application for the remediation of turbid waters by aggregating suspended matter to clarify water.

CHAPTER ONE

INTRODUCTION

1.1 Background of the problem

The world is constantly in need of clean, safe and adequate drinking water for human consumption, medical, pharmacological, chemical and industrial applications. However, the quality of the available water has continually been compromised by anthropogenic activities such as industrial explosion and increased agricultural activities. This has a negative impact on the general health of the population and ecosystems. Consequently, this limits economic productivity hence development opportunities (Cohen *et al.*, 2010). Water, being a universal solvent, has a great influence on the solubility of nutrients and sedimentation resulting to pH effects and mobility of toxins such as heavy metals, non-metallic, persistent organics and pesticides hence altering the biological factors of a specific system (Allen *et al.*, 2008).

Migration of sediments and organic matter into water systems introduces a myriad of compounds from the soil. Such compounds may include nutrients which may result into algal bloom that eventually alters the chemistry of the water (Cohen *et al.*, 2010). Algal bloom has adverse effects on water bodies as an abode for fish, as it interferes with productivity and spawning of fish and as a habitat for bottom-dwelling invertebrates (Cohen *et al.*, 2010). It also interferes with light penetration in the water resulting into turbidity hence affecting photosynthesis of the aquatic plants. As such, algal bloom is a visual indicator of a contaminated water system whose quality for consumption cannot be guaranteed.

Water turbidity leads to a compromise in the transparency of water arising from colloidal material silt, finely divided organic and inorganic matter, plankton or other microscopic organisms. These cause aesthetic concern and the appreciation of that water. Sources of turbidity also host and encourage bacteria, viruses and parasites growth as it provides a good carbon source, rendering the water unsafe.

Suspended matter contaminants have the potential to enhance solubility of metals hence increase the mobilization of toxic trace metals from the soil and sediments. This makes them soluble and bioavailable to cause poisoning thus contributing to metal pollution (Henry and Cole, 1997; Losada *et al.*, 2001; Selivanovskaya and Latypova, 2003). Furthermore, the presence of suspended particles in water does not only cause undesirable turbidity but it also affects the colour, taste and odour in the water (Young *et al.*, 1996). Therefore, removal of suspended matter from water is necessary and needs to be investigated.

Conventional removal methods of suspended solids are through sedimentation or filtration in water treatment facilities to improve its drinking quality (Mark, 2004). Sand filtration is frequently used as a method to remove suspended solids from water. The filter medium consists of a multiple layer of sand of varying size and specific gravity. When the water flows through the filter, the some solid materials are trapped in the sand layers as residue and the water flows out of the filter. However some very small suspended solids have the ability to pass through such sand filters (Guo and Urbonas, 1996). This makes it very difficult to remove the

very fine colloidal particles from water and therefore alternative methods need to be explored.

The best option of settling such particles is by agglomeration of the very small colloidal particles in the water into flocs which will lead to a better clarification (Ebeling *et al.*, 2003). The flocculation mechanism involves the reduction of the charges on the suspended species by addition of suitable chemical compounds (Kawamura, 1996). This makes them accumulate into larger particles called flocs which can then settle by gravity and hence easy to remove. The resultant flocs can then be removed using solid-liquid separation processes such as settling, flotation and filtration.

According to Gudrun and Simona (2013), flocculants are high molecular weight materials such as starch or polyelectrolytes which are commercially for water treatment. There exists both inorganic and organic flocculants in the market. Inorganic flocculants include salts of multivalent metals like aluminum and iron (Sharma *et al.*, 2006). These have been reported to having introduced a lot of soluble mineral ions in the water which have negative health implications (Jackson, 1981).

Organic flocculants, which are mainly synthetic or natural water-soluble polymeric materials, are preferred to inorganic materials (Jackson, 1981). Examples of synthetic polymers include polyacrylamide, polyacrylic acid, polystyrenic sulphonic acid and polydiallyl dimethyl ammonium chloride (DADMAC). Natural polymers include guar gum, starch, cellulose and alginic acid among others. The synthetic flocculants are available in cationic, anionic and non-ionic forms. Organic based

flocculants (polymers) are easy to use and require minute quantities to clarify turbid waters. They have good settling ability in comparison to the simple coagulating electrolytes of their inorganic counterparts (Kleimann *et al.*, 2005). The flocculating efficiency of polymers increases with increasing molecular weight (Kleimann *et al.*, 2005). This study therefore intended to improve the flocculation property of naturally available bio-material from maize tassels by modifying it with triethanolamine which not only increases its molecular mass but also makes it permanently charged.

1.2 Problem statement

The presence of suspended matter in water affects its aesthetic appearance and appreciation as it is a sign of contamination. It also inhibits photosynthesis and contributes to oxygen deficiency in such waters. Suspended material from organic sources contains functional groups capable of forming complex compounds with metals in the sediments, thus making them bioavailable. Such waters are a good habitat for bacterial growth that thrives under oxygen-depleted environments. The bacterial growth leads to fouling which, in turn, gives rise to unpleasant taste and odour of the water. Hence the need to remove the suspended matter. The best option to remove the suspended matter in water is to settle them through agglomeration into flocs which will lead to a better clarification (Ebeling *et al.*, 2003).

Conventional methods for the removal of suspended solids in water treatment facilities are through sedimentation or filtration. However, these processes have a challenge. (Aguilar *et al.*, 2005). Inorganic flocculants like aluminum and iron salts

have been reported to introduce a lot of soluble mineral ions in the water which have negative health implications (Jackson, 1981). Organic flocculants, which are mainly synthetic or natural water-soluble polymeric materials, are easy to use and require minute quantities for achievement of expected results. (Kleimann *et al.*, 2005). Commonly used synthetic polymers for clarification of water are costly and non-biodegradable (Lu *et al.*, 2009). There is need therefore for synthesis of flocculants from easily available sources using environmental friendly and sustainable methods for water treatment. Natural polymers, which are mainly polysaccharides, can offer a solution as they have functional groups, which can be modified (derivatized) to produce better flocculants. Such natural products are biodegradable, easily available from renewable resources and safe for human health.

Maize tassels, being a plant material, contain cellulosic surface hydroxyl groups that can be chemically modified by introducing positive sites through quaternization process (Qiu and Hu, 2013). These sites are capable of interacting with negatively charged colloidal particles causing them to agglomerate into flocs. The use of maize tassels in absorbents and adsorption of heavy metals has been reported (Zvinowanda *et al.*, 2009; Mwangi *et al.*, 2012; Dehvari *et al.*, 2013). However, there are no previous studies which have reported on the use of triethanolamine modified maize tassels as a flocculant. The utilization of tassels as a flocculating agent will attach some economic value to this waste material that currently has little or no economic value. This will contribute towards good water quality and waste management in the country. This study therefore involved modifying maize tassels with triethanolamine which was used to remove colloidal and suspended material in water.

1.3 Rationale of the study

There is a need for treatment of water to enhance its safety and aesthetics. This study modified maize tassels with triethanolamine for purposes of water clarification. The overall aim was to enhance water treatment process and hence improve its quality for use by consumers.

1.4 Hypothesis

Maize tassels modified with triethanolamine can clarify 95% of turbid waters.

1.5 Objectives of the study

1.5.1 General objective

The general objective was to clarify colloidal and suspended material in water using triethanolamine modified maize tassels.

1.5.2 Specific objectives

The specific objectives were to:

- i. To modify maize tassels with triethanolamine and to characterize both the unmodified and the modified maize tassels using FTIR.
- ii. To optimize the various clarification parameters including 30 minutes settling time, pH of 6 and an optimal dosage.
- iii. To use the modified maize tassels on lowering the turbidity of environmental/raw water samples.

1.6 Significance of the study

The flocculant was modified from cheap material of natural origin, locally available that has no other known economic value. It was then used in the clarification of swampy water. With further treatment, the clarified water can then be used for both industrial and domestic consumption.

1.7 Scope and Limitations

The study developed a method for removal of colloidal and suspended material in water using triethanolamine modified maize tassels. The modified maize tassels were applied on stagnant swampy water samples. Other suspended particles and compounds present in water were the limitations to this study. Seasonal variations of colloidal and suspended material in water were not considered.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Water used for domestic consumption and for recreation purposes needs to be free from biological, chemical, and physical contaminants. One of the sources of such pollutants is the suspended material. Increased sedimentation and other colloidal particles in water reduce the amount of light that is able to penetrate into a water body. With less light available, photosynthetic production and primary productivity of an ecosystem will decrease, affecting aquatic life. Fine sediments do attract nutrients such as phosphorus and toxic contaminants from pesticides and enhance the growth of algae due to eutrophication which leads to high water turbidity (Allen *et al.*, 2008).

Turbidity is not necessarily due to nutrient polluted water. It could even be caused by suspended solid sediments. One of the most efficient ways of removing turbidity is by adding a flocculant to enhance settling of such suspended particles by agglomeration of the very small colloidal particles into flocs. Salts, such as ferrous (III) or aluminum salts, which were used as flocculants in the past, have many drawbacks (Jackson, 1981; Sharma *et al.*, 2006). One of them is the introduction of high concentration of metal ions in drinking water which is unhealthy. Another drawback is the formation of a large volume of sludge with heavy metals which is toxic to micro organisms (Jackson, 1981; Sharma *et al.*, 2006). Therefore, this prompted their replacement with water-soluble polymers of organic origin. A little concentration of these organic flocculants can produce large aggregates that can be

separated easily. Their flocculation mechanisms as well as the results of the separation process are influenced by the properties, such as the charge and molecular weight, of both the polymer and the dispersed material (Schwarz, 2014).

Small, neutral or negatively charged colloidal suspended particles which cannot be effectively separated by filtration, flotation or sedimentation have a high affinity to water soluble polycationic molecules (Morgane and Ulf, 2010). After being attracted to the polycations, they agglomerate into flocs, and can then be easily separated from the water.

2.2 Particles in Water

According to Kohli (2009), particles found in water can be classified into three categories. These are;

- Chemicals in solution.
- The colloidal solids.
- The suspended solids.

Chemicals in solution are usually stable in water due to their electrical charge which interacts with the water. Therefore they never settle out of water. They are also invisible due to their small size (less than 1 μ m).

The colloidal solids are also called nonsettleable solids. Although they are electrically charged, they do not dissolve in water. They have a small particle size of between 1 and 500 μ m. These particles will not settle out of water even after several years, and cannot be removed by the filtration process alone (WHO, 2004).

The suspended particles are also known as settleable solids. They usually settle out of water over a period of time. They have a large particle size, above 1,000 μ m and can be seen with the naked eye (Kohli, 2009).

2.3 Total Suspended Solids

According to Ebeling (2003), Total Suspended Solids (TSS) can be defined as particles that are larger than 2 microns found in the water column. They are mostly made up of inorganic materials or inorganic matter. This may be anything drifting or floating in the water, from sediment, silt and sand to plankton and algae. Organic particles from decomposing materials also contribute to the TSS concentration (Fernanda and Lúcia, 2012). When algae, plants and animals undergo decomposition, small organic particles break away and enter the water column as suspended solids. Chemical precipitates from pesticides and fertilizers are also considered as suspended solids (Deborah, 1998).

The most significant effect of the total suspended solids in water is their influence on the water clarity (Rossi *et al.*, 2006). If there are more solids suspended in water, the water is less clear. Although some solids can settle as sediments at the bottom of a water body over a period of time, others remain unsettled and are called colloidal or non-settleable solids. Such colloidal solids are usually too small or too light to settle.

2.3.1 Factors Affecting Total Suspended Solids

2.3.1.1 High Flow Rates

The concentration of the total suspended solids in a water body is highly influenced by the flow rate of the water (Wilson, 2010). If the water has a fast flow rate, it carries with it more particles and large sized sediments of organic nature, sand, clay and silt. Also, when the direction of water current changes, the particulate matter settled at the bottom is usually resuspended (Puig *et al.*, 2000).

2.3.1.2 Soil Erosion

Human activities such as mining, building roads, logging and forest fires lead to disturbance of the land surface. This results in soil erosion when the eroded soil particles are carried by storm water into the surface of the water bodies (Puig *et al.*, 2000). This in turn increases the TSS of the water body.

2.3.1.3 Urban Runoff

During storm episodes, soil particles and debris from streets, industrial and residential areas are easily washed into streams (Edwards *et al.*, 2015). This is because of the numerous pavements that decrease infiltration, increase water velocity and minimize the natural settling sites. Consequently, sediments are carried through storm drains directly to creeks and rivers.

2.4 Water turbidity and its causes

According to Allen and co-workers (2008), turbidity is a measure of the relative clarity of water. It is caused by suspended and colloidal matter such as clay, silts, finely divided organic and inorganic matter, plankton and other microscopic organisms (Shilpa, 2012). Some of the factors that increase turbidity in water include increase in stream flow due to heavy rains, increased soil erosion due to decreased vegetation along the banks, different types of runoffs from agricultural, industrial activities and sewage treatment. Aquatic organisms which dwell at the bottom of the water bodies such as cat fish also stir up sediments which have built up at the bottom of the water bodies and this increases the turbidity of the water. Other sources of sediments include organic matter like planktons and decaying plant and animal matter that are suspended in the water.

Turbid water usually appears cloudy, murky or colored, that consequently affects its physical appearance. The turbidity in water is determined by the amount of light scattered by particles in the water sample. If the concentration of the particles present is high, the amount of light that will be scattered is high (Chris, 2010). Turbidity is used to indicate changes in the total suspended solids concentration in water and is therefore a relative measure of the water clarity.

2.4.1 Turbidity levels

Turbidity is measured in nephelometric turbidity units (NTU). According to World Health Organization (WHO), turbidity of less than 5 NTU is officially considered safe for most consumers. However, WHO unofficially considers turbidity of 0.1 NTU to be the maximum limit for disinfection of water (Pichler *et al.*, 2012). This is

because suspended particles promote the growth of micro-organisms in water and therefore decrease the effectiveness of the disinfection procedure (Pichler *et al.*, 2012).

2.4.2 Effects of water turbidity

High turbidity leads to a lower rate of photosynthesis, hence decreasing the primary production in an ecosystem. Consequently, this affects the aquatic life. Reduced clarity also makes water less aesthetically pleasing and although this may not be necessarily harmful, it makes water undesirable for a number of uses. Further, suspended particles in cloudy waters absorb sunlight, warming the surrounding water, and the increase in temperature increase the competition for dissolved oxygen hence threatening aquatic life.

According to Christopher and Amy (1988), water clarity is defined by how clear or transparent water is. It is determined by the depth that sunlight can penetrate in water. The deeper the sunlight can reach, the higher the water clarity and the clearer the water, the greater the potential for photosynthetic ability (Metrovic *et al.*, 2001).

2.4.2.1 Effects of increased nutrients in water

Nutrients are chemical elements that plants and animals need to grow (Thorgeirsdóttir *et al.*, 2005). Nitrogen is used by plants and animals to synthesize protein. One form in which nitrogen enter the ecosystem is in form of its chemical compounds. Nitrate is a compound containing nitrogen and exists in the atmosphere or as a dissolved gas in water. Some main sources of nitrates are runoff of fertilizers,

animal manure, sewage treatment plant discharges, storm water runoff, car emissions and failing septic tanks.

Phosphorus is a vital nutrient for converting sunlight into usable energy, and essential to cellular growth and reproduction. Under natural conditions phosphorus is scarce in water (Morgane *et al.*, 2010). However, it occurs in dissolved organic and inorganic compounds from fertilizers, industrial and domestic chemicals such as detergents, or it is attached to sediment particles. When it remains in the sediments it is generally not available for use by algae but when bottom-feeding rough fish stir up bottom sediments, phosphorus is released back into the water.

Excessive nutrients lead to an overgrowth of algae known as algae bloom. These algae emit toxins which, when in contact with humans, cause stomach aches and rashes. Excess nitrogen in drinking water can pose particular risk to infants younger than six months old (Fawell and Nieuwenhuijsen, 2003). To add insult to injury, chemicals, such as chlorine (used to treat nutrient-polluted drinking water) react with the algae in the water to form disinfection by-products that have been associated with reproductive and developmental health problems (Fawell and Nieuwenhuijsen, 2003).

Algal blooms in water bodies consume large amounts of oxygen that aquatic organisms need to survive. They also make water cloudy, reduce the ability of aquatic life to find food, and clog fish gills. Toxins in some algal blooms can sicken or kill some aquatic organisms.

2.5 Water treatment techniques for domestic and industrial consumption

Natural waters contain a host of compounds which are regarded as pollutants. These include suspended solids, colloidal matter, dissolved matter and micro-organisms. The pollutants have to be removed or brought to safe levels to make the water safe for consumption. Suspended material are treated according to their sizes, either by filtration, sedimentation, clarification, or refined by making them soluble if they are safe to consumers (Awaleh and Soubaneh, 2014). Clarification is the initial stage in water treatment process and it involves coagulation, flocculation, decantation or flotation and filtration of the suspended solids and colloids present in the raw water (Majam *et. al.*, 2004). This is achieved through a chemical process of addition of appropriate coagulant/flocculant that enable all suspended material to aggregate into flocs that finally settle at the bottom and clear water is obtained (Katja and Mika, 2007).

2.5.1 Coagulation and Flocculation

This initial coagulation step is aimed to eliminate colloidal particles. Such particles have a negative surface charge and are light in weight which makes their electrostatic forces outweigh their force of gravity (Christian *et al.*, 2014). This makes them naturally settle very slowly and therefore need a coagulant to enhance their settling rate. According to (Ukiwe *et al.*, 2014) a coagulant is a metallic salt such as aluminium sulphate, aluminium polychloride, aluminium chlorosulphate, ferric chloride, ferric sulphate, ferric chlorosulphate, which when added, neutralizes the surface charge of the particles, such that the positive ions present in the raw water attract the negatively charged ions and enable contact between the particles

leading to their agglomeration. The particles are therefore destabilized from their ligands which bind them together, and form hydroxide precipitate that collect as aggregate called flocs (Mosquera, 2014).

Flocculation stage involves the addition of reactant (flocculant) that enhances the agglomeration and settlement of the various flocs. Speed of agitation is an important parameter because if the speed is too high, flocs are destroyed and if too slow, the contact between two particles is lessened. According to Pascal and David (2007), too fine or too light a floc leads to poor settling. This produces loaded decanted water that rapidly fouls filters so that they require frequent washing.

According to The Oxford Dictionary, a flocculant is a substance which promotes the clumping of particles, especially used in waste water treatment. Flocculation of solid particles suspended in waste water during water treatment is brought about by the action of high molecular weight materials such as starch or polyelectrolytes. These materials physically form a bridge between two or more particles, uniting the solid particles into a random, three-dimensional structure, which is loose, and porous (Demz and Delice, 2005).

2.5.1.1 The chemistry of coagulation and flocculation

The chemistry behind flocculation process is based on the electrical attraction and repulsion of negatively and positively charged particles in water. Many of the particles that are suspended in water have a negative surface charge (Christian *et al.*, 2014). They therefore tend to repel each other, and this makes them to stay

dispersed, whether in colloidal or dissolved form. When polycation coagulants/flocculants are added into water, the positive charges of the coagulant are electrically attracted to the negatively charged particles in water. The combination of positive and negative charges results in a neutral charge. As a result, the repulsive forces of the particles are destabilized. The next force which affects the particles is known as van der Waal's forces.

Van der Waal's forces refer to the tendency of particles in nature to attract each other weakly if they have no charge (Beereddy, 2013). The van der Waal's forces makes the neutral particles to be attracted to each other and this makes them join together into a group. When the group is large enough, the particles become flocs which settle out of water.

2.5.2 Significance of flocculation process

Waste water treatment starts by removal of solids suspended in water. Successful waste water treatment depends on the efficiency of this step. Most naturally occurring organic matter have a negative surface charge. This charge results into repulsion forces between the particles thus reducing the tendency for the particles to agglomerate and settle. Other factors such as particle size, particle density, and liquid density also exert considerable influence on the tendency of fine particles to settle (Pillai, 1997). Flocculants work by increasing particle sizes resulting in faster settling rates of the particles. Because particles are negatively charged, a positively charged flocculant is added to neutralize the negative surface charge by the positive charge. The particles then aggregate to larger particle sizes and settle down. There

are several factors which can affect flocculation. These include: polymer type, water pH, slurry solids, flocculant dilution, shear and molecular weight.

2.5.2.1 Polymer type

The main functional groups in polymer flocculants determine the functionality of the flocculant (Tripathy and De, 2006,). The amide group in copolymers is used for adsorption by hydrogen bonding while the carboxylate group extends the polymer chain in solution by electrostatic repulsion, enabling bridging to take place. The activity of a polymer flocculant is related to uncoiling or extension of the polymers. Any ideal flocculant for an application should balance the adsorbing groups (amide group) with the groups that extend the molecule (carboxylate group).

2.5.2.2 pH of the water

According to Pillai (1997), the pH of the raw water is an important factor when feeding a coagulant into the water. This is because the coagulation process requires an adequate amount of trivalent or even high ionic species in order to effectively reduce the electrical charge of the colloidal particles (Kamal, 2011). For instance, when using alum sulfate as a coagulant, there is an interrelation between pH and the type of aluminum hydroxide formed (Kamal, 2011). This in turn determines the charge on the hydrous oxide complex by influencing solubility of the inorganic coagulant (Ravina, 1993). The other way pH affects the coagulation process is that it has influence on the charge of the suspended material by interfering with functional groups available in such material (Ünlü and Ersoz, 2006).

For flocculants, low pH of 4 and below affects performance of the nonionic polymers better than the anionic polymers. This is because at this pH range, there is high number of hydrogen bonds in nonionic polymers than in anionic polymers (Thomas *et al.*, 2015). When the pH increases, the anionic flocculant becomes ionized and the polymer becomes active.

At high pH levels above 9, highly anionic flocculants perform the best, because the polymer flocculant is fully uncoiled and at the peak of activity. On the other hand, the nonionic flocculant decreases its activity. This is because the molecules hydrolyze, resulting in a drop in activity. Since the raw water pH is an important factor for adjusting the physicochemical environment and colloids removal, it is necessary to consider any additive effect that can alter this value either positively or negatively. This will lead to obtaining optimum turbidity removal and/or the economic coagulant dose.

2.5.2.3 Slurry solids

The concentration of solids in the slurry and the size of the particles influence the distribution of flocculant in the slurry (Pillai, 1997). This in turn affects the dispersion of the flocculant throughout the slurry. The higher the concentration of solids, the more difficult it is to distribute the flocculant uniformly through the slurry. Small particle sizes have large surface area therefore, when the particle size decreases and the solids concentration increases, the demand of the flocculant increases.

2.5.2.4 Flocculant dilution and shear

When a flocculant is diluted, its distribution in the slurry improves, therefore improving its performance. On the contrary, excessive mechanical action can tear apart a floc, therefore when distributing the flocculant in the slurry it is important to balance between distribution and floc shear.

2.5.2.5 Molecular weight

The molecular weight of the polymer affects the inter-particle bridging, a mechanism by which the flocculant functions (Su, 2013). High molecular weight flocculants are viscous and they do not easily distributed through the slurry. This interferes with the adsorption process which is very rapid and irreversible, hence a loss in activity of the flocculant results. Also, increasing molecular weight of a polymer decreases the number of polymer chains per unit of weight (Su, 2013) .This reduces the number of polymer molecules used to flocculate the solids especially in high solids slurries.

2.5.2.6 Dosages for chemical reagents

A designed dosage for chemicals is based on experience with similar types of waters or with bench-scale and pilot tests. The most effective coagulant and flocculant dosage is monitored by parameters such as turbidity, zeta potential, streaming current, and particle counts.

2.5.3 Decantation or flotation

In this step, the flocs settle under the force of gravity (decantation) and accumulate at the bottom of the decanter as sludge. Alternatively, the flocs can be made to float on the surface of water by blowing air bubbles (flotation) so that the flocs may then be removed with a skimmer.

2.5.4 Filtration

The main purpose of the filtration stage is to clarify a liquid that contains few suspended solids by running it through a granular or porous medium like sand or granulated activated carbon so as to eliminate residual particles. The water runs through a filtering bed made up of granular matter, and the suspended solids are retained in the inter-granular spaces. Clarification may be optimized by optimizing parameters such as coagulant or flocculant dosage, pH of water to be treated, decantation speed, filtration speed and filter granulometry.

2.6 Natural flocculants

Natural flocculants are water soluble anionic, cationic or nonionic polymers. Some of the most common natural flocculants include the starch derivatives which are pregelatinized to make them water-soluble. They include corn and potato-starches, the polysaccharides especially guar gums, and the alginates, mostly used in portable water treatment.

2.6.1 Maize tassels

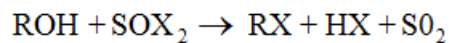
Tassel is the 'male' flower of the maize plant that forms at the top of the stem. Once the useful nutrient rich portions of maize plants have been harvested, the remaining portion of the plant is usually either ploughed back into the land or is discarded as agricultural waste. Maize tassels contain amino acids, polypeptides chains and some simple sugars (Zvinowanda *et al.*, 2009). Being a plant material, tassels contain cellulosic surface hydroxyl groups that can be chemically modified by introducing positive sites through quaternization process (Qiu and Hu, 2013). These sites are capable of interacting with negatively charged colloidal particles causing them to agglomerate into flocs.

The utilization of tassels as a flocculating agent will attach some economic value to this waste material that currently has little or no economic value. This will contribute towards good water quality and waste management in the country. The use of maize tassels in absorbents and adsorption of heavy metals has been reported (Zvinowanda *et al.*, 2009; Mwangi *et al.*, 2012; Dehviri *et al.*, 2013). However, there are no previous studies which have reported on the use of triethanolamine modified maize tassels as a flocculant.

2.6.2 Chemical modification of maize tassels

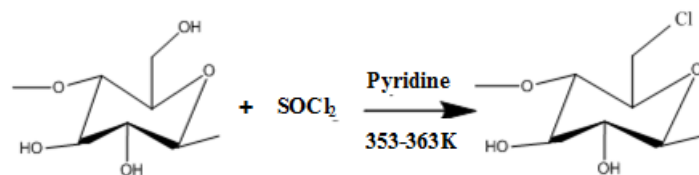
The chemical modification of maize tassel is carried out in two steps. The first step involves chlorination of the carbon in position 6 of the cellulose molecule to form an intermediate of chlorocellulose as an alkyl halide. The second step involves substitution of the chlorine atom in the chlorocellulose with an amine group. Alkyl

halides are prepared by the reaction of alcohols with mineral acids (HCl and HBr) or with reagents such as thionyl chloride, thionyl bromide, PX_3 and PX_5 (Bano, 2007). According to Boehm (1953), thionyl halides are commonly used in the preparation of halogen compounds from alcohols and their halogenation reaction proceeds as follows:



The halogenation reaction mostly occurs between hydroxyl compounds and thionyl halides. Presence of a tertiary base and an excess of thionyl halide facilitates the formation of the halides.

Maize tassels are made up of cellulose molecules which contain hydroxyl groups on the surface. When cellulose molecules are activated, the hydroxyl groups are enhanced and made accessible for reaction with chemicals (solvents and reagents) (Cumpstey, 2013). When a cellulose molecule reacts with thionyl chloride in presence of pyridine, a chlorine atom is included onto the polymeric structure at carbon 6, as shown in Scheme 1:

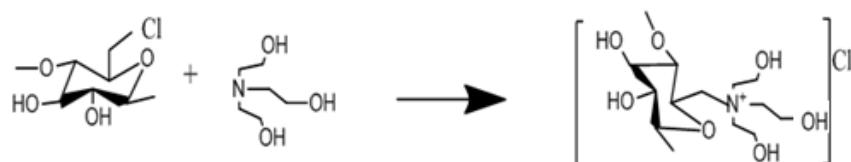


Scheme 1: Chlorination of cellulose using thionyl chloride

The next step of the chemical modification involves nucleophilic attack, which is provided by organic molecules embracing basic centers to act as chelating agents in the corresponding structure, such as nitrogen, sulfur, oxygen and/or phosphorous

atoms (Edson *et al.*, 2013). A nucleophile attacks the sp^3 carbon of the halide, the C-X bond breaks forming a stable ionic product.

In the C-X bond of alkyl halides, the carbon has a positive dipole. Halides are good leaving groups therefore nucleophiles attack primary and secondary alkyl halides, displacing the leaving group. When the chlorinated maize tassel molecule is attacked by triethanolamine molecule, 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

2.7 Analytical methods

2.7.1 Fourier Transform infrared spectroscopy in characterization

Infrared radiation method of analysis is based on the interaction of infrared radiation within the region ($4000\text{--}400\text{ cm}^{-1}$) of wave numbers with molecular dynamics. This interaction results in the absorption of radiation, which in turn causes the symmetric stretching vibrations, asymmetric stretching vibrations and deformation vibrations (Reichenbacher *et al.*, 2012). Modern FT instruments are capable of analysing liquids and solids, with minimal sample preparation. The data obtained is mainly qualitative and it gives information on functional groups present in the solid or liquid material under analysis.

FTIR equipment is associated with weak signals and attenuated reflectance (ATR) or diffuse reflectance (DR) techniques. These techniques which are based on the principle of light diffusion in the sample and the resulting light which emerges from the sample are then used for analysis. ATR is commonly used for elastic and viscous substances that are insoluble, infusible and difficult to grind up in order to get information of the sample surface. On the other hand, diffuse reflectance technique is mainly used for substances in powder form or those that can be turned into powder and those with rough surfaces. Tassel powders which were used in this study were characterized by FTIR before and after modification, and after application in the water treatment.

2.7.2 Turbidity measurements

A turbidity measurement involves measuring the amount of light scattered at right angles to an incident light beam by particles present in a liquid sample. When light passes through 'absolutely pure' water, light beam travel along straight undisturbed paths. However, when water contains suspended particles, the paths of light are distorted (Michael, 1998). This is because as light passes through, the particles absorb the light energy and re-radiate it in all directions.

Particles much smaller than the wavelength of the incident light scatter light of equal intensity in all directions. In contrast, particles larger than the wavelength of the incident light scatter light in the forward direction, away from the incident light (Sadar, 1996). A turbid meter measures the scatter of light at a 90 degree angle to

the incident beam and it relates this reading to the turbidity of the liquid. This angle is considered to be very sensitive to light scatter by particles in a sample.

2.7.3 pH measurements

2.7.3.1 Definition of pH

pH is a measure of the level of acidity or basicity of a given solution (McMillan, 1994). pH measurement is carried out by determining the concentration of hydrogen ions $[H^+]$ in a particular solution, which gives its pH value. These values range from 0 to 14. When the values are below 7, the solution has acidic properties. Above 7, the solution shows basic properties. At pH 7 the solution is neutral and neither shows acidic nor basic properties. Mathematically, pH is expressed as the negative logarithm of the hydrogen ion concentration as shown below:

$$\text{pH} = -\log[H^+]$$

Where $[H^+]$ is hydrogen ion concentration in mol/L.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Research design

This study was carried out in several stages. This comprised of the synthesis of a flocculant by modification of maize tassels, characterization of the modified material, optimization of the clarification parameters and finally application for clarification of raw/environmental water samples.

3.2 Materials and reagents

All the solutions were prepared in double distilled water and the reagents were of analytical grade. Triethanolamine, thionyl chloride, pyridine, hydrochloric acid, ammonia and ethanol were supplied by Sigma Aldrich (Kobian, Nairobi Kenya).

3.3 Instrumentation

Fourier transform infrared (FTIR) spectrophotometer with attenuated total reflectance (ATR) mode (Perkin Elmer 100 with sampling accessory-Waltham, MA, USA) was used to characterize the parent and the modified maize tassels (Mukamel, 2000). The content of suspended matter in both the synthetic water sample and the environmental water samples were determined with the help of a Turbidity meter model LP 2000 from Hanna Instruments to determine the extent of turbidity (Wijnen *et al.* 2014).

3.4 Experimental procedures

3.4.1 Sample preparation

Maize tassels were obtained from a farm in Gachie Sub-county in Kiambu County, Kenya. They were cleaned with water and then with 1M hydrochloric acid. The cleaned materials were air dried for three days and then dried in an oven for 24 hours at a temperature of 60 °C. This is to minimize the hydroxyl groups from water so as to ensure maximum chlorination of the hydroxyl groups in the maize tassels. The dried material were then ground into powder and then stored in a clean, dry plastic container.

3.4.2 Quaternization (modification) of maize tassels

A 10 g sample of the biomaterial previously activated at 80 °C for 12 hours was suspended in 200 ml pyridine (in a 500 ml three-necked flask), followed by a drop-wise addition of 35 ml of thionyl chloride (SOCl_2) at 80 °C, under mechanical stirring. After the addition was complete, stirring was continued at the same temperature for another 5 hours. The resulting solid was separated by filtration through a Buchner funnel, washed with distilled water and dried in an oven at 70 °C for 12 hours (Tashiro and Shimura, 1982). A sample (5 g) of the chlorinated material was placed in a three-necked flask containing 200 ml of ethanol. To this, 100 ml of triethanolamine were added while stirring. The mixture was further mechanically stirred for 7 days and then refluxed at 80 °C for 12 hours to obtain the modified liquid material.

3.5 Preparation of the synthetic samples

The synthetic samples were prepared using a known mass of maize flour suspended in water. Preparation entailed mixing 1.0 g of maize flour with 90 ml of distilled water and then boiling the mixture to obtain a uniform suspension. From this suspension, subsequent dilutions were made to obtain the various samples for analysis. A fresh sample was prepared for each analysis.

3.6 Settling time

To establish the settling rates, replicate samples (three) were placed in 100 ml measuring cylinders. Their pH values were adjusted to pH 6. Different dosages (3, 3.5 and 4 ml) of the flocculant were added to the cylinders, and they were agitated to enable thorough mixing of the flocculant reagent with the water sample. The mixture was allowed to settle and the settling rate monitored. This was done by recording the displacement of the settling material from the meniscus of the water at an interval of 10 minutes for 60 minutes, until there was no further change in the displacement.

3.7 Turbidity measurements

The sample cell was filled with the samples collected and then capped. The surface of the cell was then wiped using a soft, lint-free cloth to remove water spots and fingerprints. A thin film of silicone oil was then applied on the surface of the cell and then wiped with a soft cloth to obtain an even film over the entire surface. The instrument was turned on while placed on a flat, sturdy surface. The cell was then placed into the cell compartment and the orientation mark aligned with the raised

orientation mark in front of the cell compartment. The turbidity of the sample was then read out and recorded in NTU.

3.8 The experimental Jar Test Procedure

The jar test procedure was adopted. This was as used by Hudson and Singley (1974) as they determined the effect of pH, dosage on clarification and the settling rate of both synthetic and raw/environmental samples. Water samples were placed into six beakers and their respective pH adjusted to the desired value using both 0.01 M sodium hydroxide and 0.01 M hydrochloric acid. Different dosages of the flocculant were added to each beaker. The mixtures were stirred at a constant speed of 100 revolutions per minute (rpm) for 2 minutes, followed by a slow stirring at 20 rpm for 30 min. The sample was then left to settle for 30 minutes. Aliquots (10 ml) of the supernatant were drawn (5 cm below the meniscus), and their respective turbidity was measured using a calibrated Turbidimeter.

3.9 pH measurements

3.9.1 How to Measure pH

pH in an aqueous solution is measured by use of a pH-sensitive glass electrode, a reference electrode and a pH meter (Beckman, 1983). Other methods for determining the pH of a solution include:

Indicators- Indicators are papers which are designed to change color when exposed to different pH environments. The color of a wetted sample paper is compared to a color chart to determine the pH value (Beckman, 1983). These papers are mainly used for small volume and for preliminary measurements. Although a pH paper is

relatively cheap, it cannot be used for continuous monitoring of a process, and it can easily be attacked by a solution which interferes with the color change (Beckman, 1983).

Colorimeter- A colorimeter is a device that uses a vial filled with a sample to which a reagent is added. As the reagent is added, a color change takes place. The color of the solution is then compared to the spectral standard to infer the pH value of the sample under measurement. A colorimeter is mainly used for grab sample measurements, but not for continuous on-line measuring (McMillan, 1994). In this study, a pH meter was used for precise and continuous measurements.

3.9.2 Obtaining the optimum pH value

The pH of six synthetic water samples at 25 °C contained in measuring cylinders was set at 4, 6, 6.5, 7, and 8 by dropwise addition of 0.01 M sodium hydroxide and 0.01 M hydrochloric acid drop wise. 3.0 ml of the flocculant was added to each cylinder and the mixtures thoroughly mixed and then left to settle. A stop watch was then started and the displacement of the settling material from the top of the cylinder was recorded at a time interval of 10 minutes for one hour. The pH that recorded the fastest rate of settling was taken to be the optimum pH.

3.9.3 Effect of pH on clarity

The jar test procedure was carried out to determine the effect of pH on water clarity. Water samples were placed into three beakers and their respective pH adjusted to 4, 6 and 8 respectively using both 0.01 M sodium hydroxide and 0.01 M hydrochloric acid. Different dosages (1, 1.5, 2, 2.5, 3 and 3.5ml) of the flocculant were added to

each beaker. The mixtures were stirred at a constant speed of 100 revolutions per minute (rpm) for 2 minutes, followed by a slow stirring at 20 rpm for 30 min. The sample was then left to settle for 30 minutes. Aliquots (10 ml) of the supernatant were drawn (5 cm below the meniscus), and their respective turbidity was measured using a calibrated Turbidimeter.

3.10 Flocculants Dosage optimization

The jar test procedure was carried out to determine the optimum dosage of the flocculant in water clarity. Water samples were placed into six beakers and their pH adjusted to pH value of 6. Different dosages (2, 2.5, 3, 3.5, 4 and 4.5 ml) of the flocculant were added to each beaker. The mixtures were stirred at a constant speed of 100 revolutions per minute (rpm) for 2 minutes, followed by a slow stirring at 20 rpm for 30 min. The samples were then left to settle for 30 minutes. Aliquots (10 ml) of the supernatant were drawn (5 cm below the meniscus), and their turbidity was measured using a calibrated Turbidimeter. The dosage that gave the lowest turbidity was taken to be the optimum dose of the flocculant.

3.11 Application on raw water samples

Water samples were collected from a swampy field in Wangige, Kiambu County in Kenya. The analysis of the water characteristics was done in the laboratory. The water sample had an initial turbidity of 25.14 NTU at a temperature of 24.0°C and a pH of 7. Using the jar test procedure, the samples were treated with 3.0, 3.5 and 4.0 ml of the QMT dosage, and the turbidity of their supernatant samples was drawn and measured at intervals of 10 minutes during settling time.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Modification of maize tassels using triethanolamine

Maize tassels were modified by quaternization process with triethanolamine to form a polycation which is Quaternized Maize Tassels (QMT). The modified product was then used for clarification of water. The product obtained was a water-soluble derivative of cellulose. It was a liquid at room temperature and at pH above 4. Below this pH (4), the product crystallized out. The relative density of this liquid was 0.85. This liquid was then applied as a flocculent on various experiments. The effect of pH and dosage on coagulation flocculation, sedimentation and turbidity were monitored using the standard jar test procedure as used by Hudson and Singley (1974).

4.2 FTIR Characterization

4.2.1. Characterization of unmodified maize tassels

The unmodified maize tassels were characterized using the FTIR. The results obtained were as presented in figure 4.1.

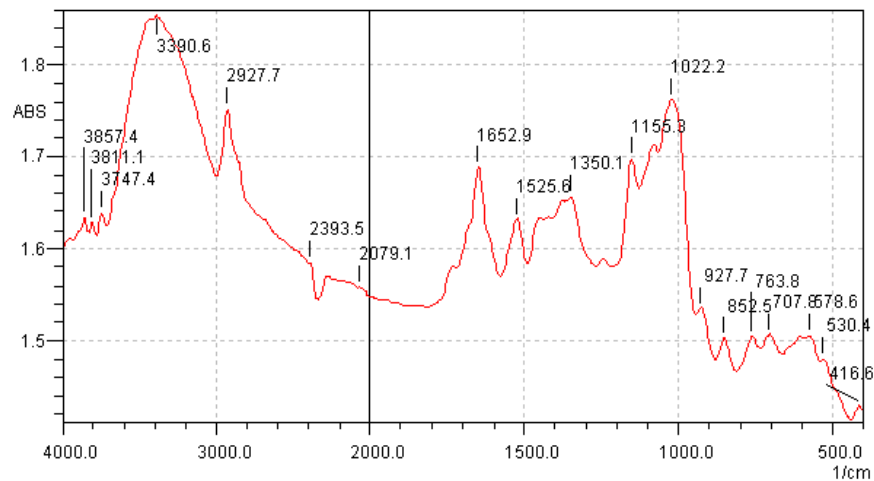


Figure 4.1: FTIR Spectrum of the unmodified maize tassels

The results from FTIR-spectrum of the maize tassels indicated the presence of functional groups such as -NH , -OH and -C=O . The broad band 3390.6 cm^{-1} are attributed to either -OH or -NH groups while the band at 1652.6 cm^{-1} could be due to a carbonyl functional group (Stuart, 1996; Nurul *et al.*, 2013). Such functional groups could be derivitized to improve flocculation properties of the maize tassels material. The parent material was chlorinated to enable further derivatization of this product.

4.2.2 Characterization of chlorinated maize tassels

A sample of the chlorinated material was analyzed using the using FTIR and the results obtained are as presented in figure 4.2.

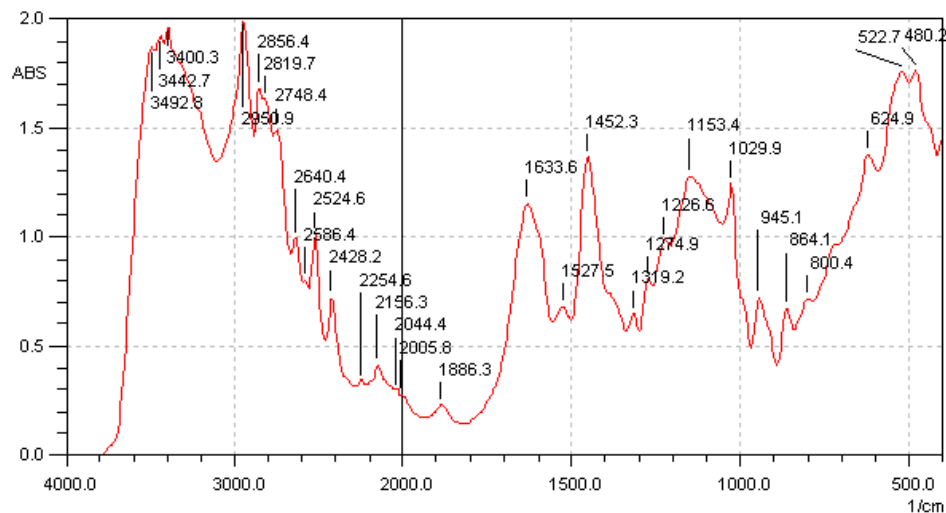


Figure 4.2: FTIR Spectrum of the chlorinated maize tassels

From figure 4.2, there was a shift of the peaks at 3390.6 cm^{-1} to 3400.3 cm^{-1} . This could be attributed by the fact that initial peak at 3390.6 cm^{-1} could have been contributed by the -OH group which changes upon chlorination. A new peak at 624.9 cm^{-1} appears indicating the presence of the -C-Cl stretch. This peak was absent in the parent maize tassels. This implies that a chloro group was introduced into the maize tassels. The chloro group was then condensed with a tertiary amine.

4.2.3 Characterization of the quaternized maize tassels

The chlorinated maize tassels were reacted with triethanolamine for the quaternisation process of the chlorocellulose to occur. The resulting FTIR spectrum obtained is as presented in figure 4.3.

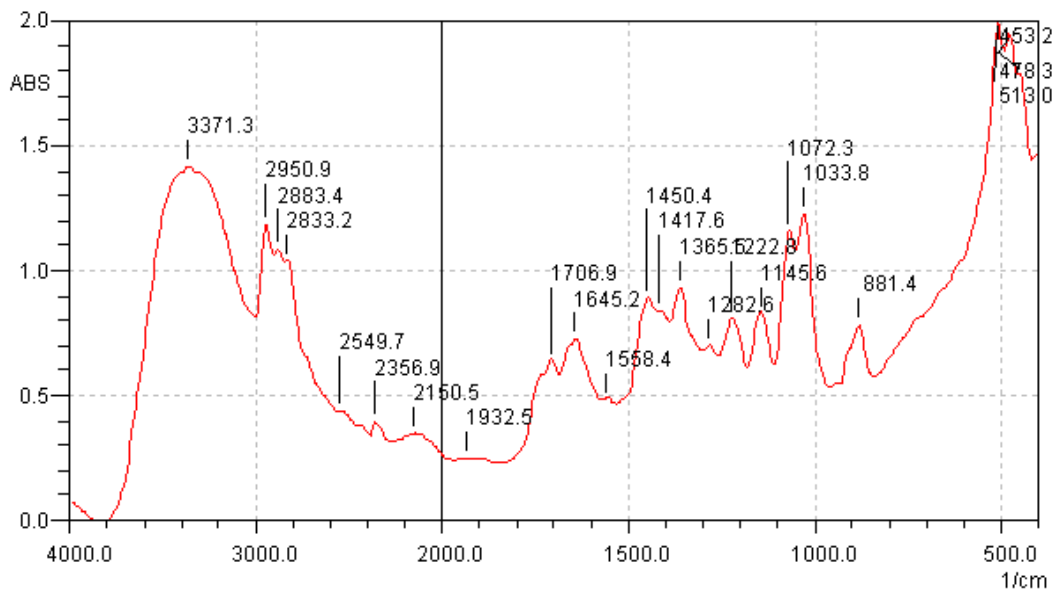


Figure 4.3: FTIR Spectrum of the quaternised maize tassels (QMT)

From figure 4.3, the peak at 624.9 cm^{-1} disappeared showing that the $-\text{C-Cl}$ group had also disappeared due to the chloro group being replaced by an amine group. A shift of the peak from 3400.3 cm^{-1} to 3371.3 cm^{-1} was also observed which suggests the presence of an amine group,

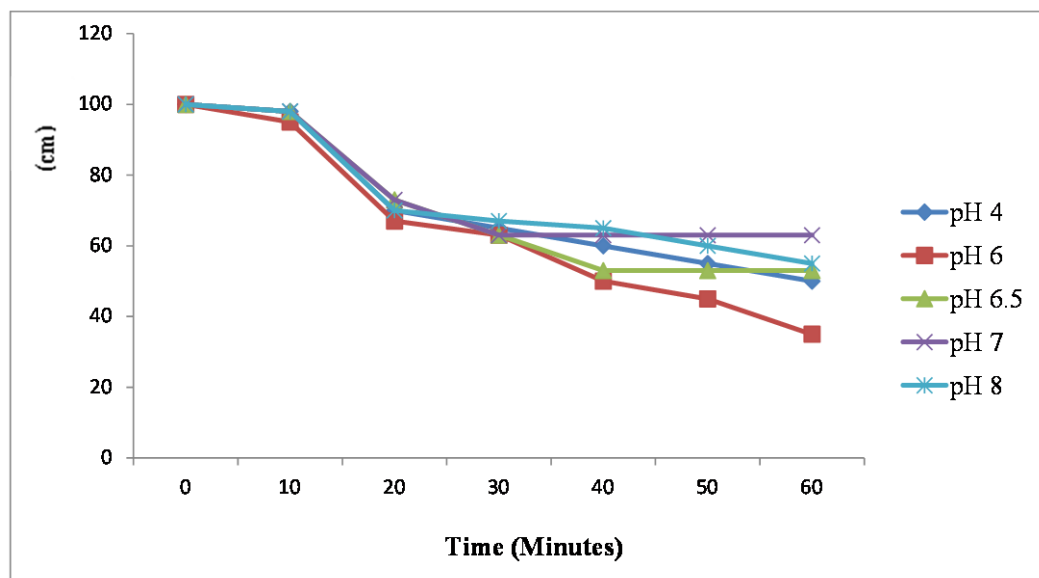
$-\text{NH}_4^+$ or its derivatives and this is shown by the appearance of a peak at 2356 cm^{-1} . A new peak at 1365.5 cm^{-1} can be attributed to the presence of the amide functional group, which is a characteristic of charged $-\text{NH}_4^+$ functional groups (Kacurakova *et al.*, 1994). The peak at 1645.2 cm^{-1} was due to the $-\text{NH}$ group (Carden and Morris, 2000). The above results show that there was the presence of cationic sites, which can interact with colloidal particles in water for effective clarification (Weber, 1986). This confirms that the modification was successful and the material was applied for flocculation experiments.

4.3 Optimization studies

4.3.1 pH optimization

Kinetics of clarification describes the rate of electrostatic interaction between the polyelectrolyte and the surface of the colloidal material. This governs the formation of multilayer assemblies (Barker *et al.*, 2000) which contributes to the formation of flocs which result to agglomeration. The agglomerated material settles to the bottom due to attraction by gravitational force. As the material settles, the liquid starts to clear from the top. The effect of settling time on the clarification of synthetic water samples was monitored by recording the displacement of the settling material from the meniscus of the water in the jar. It was carried out using synthetic samples buffered at varied pH values of 4.0, 6.0, 6.5, 7.0 and 8.0 as reported in figure 4.4.

Figure 4.4: Settling of suspended material at different pH values



The figure shows that the suspended material settled within the first 30 minutes of the experiment. However, the most settled materials were yielded at pH 6.0. This could be due to the fact that some quaternary polycations lose their cationic nature at

pH higher than 6.5 as reported by Badawy and Rabea (2001). At lower pH values, the presence of positively charged protons offers a competition to the colloidal material.

4.3.2 Determining optimal settling time

Further clarification experiments were done at a pH value of 6.0. To establish the settling rates, three samples containing 100 ml of the synthetic water (pH 6.0) of turbidity (53.8 NTU) were treated with three different quaternised maize tassels (QMT) reagents (3.0 ml, 3.5 ml and 4.0 ml) and the results obtained were presented as shown in figure 4.5.

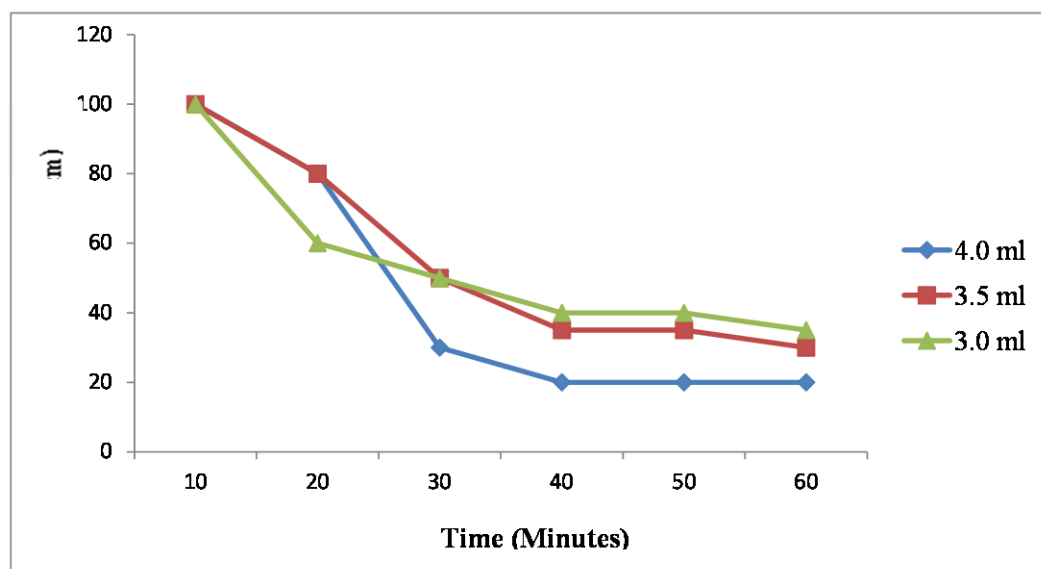


Figure 4.5: Settling of suspended material at pH 6 with different QMT dosages
The results showed that the rate of settlement of suspended particles in the synthetic turbid waters was fast such that the suspended matter settled within the first 20-30 minutes. It was also observed that the rate of settling was proportional to dosage. This is because at a high dosage of 4.0 ml, there was a high number of the

polycations present in the water. These polyelectrolytes attached onto the colloids due to electrostatic attraction and since the polymeric chain is long, the mobility of the colloid-polymer particle is low. This promoted contact with other particles as the polymer chain protruded to form "bridges" with other similar particles. Therefore, there was particle agglomeration into flocs, which settled down due to their high density. The study therefore observed that 30 minutes were sufficient to carry out flocculation experiments. This time is within the standard flocculation time which is commonly 10-30 minutes. Similar results were observed by (Li, 2012) when he researched on use of starch-based cationic flocculants for harvesting microalgae.

4.3.3 Effect of pH on clarity

The effect of pH on the rate of clarification was monitored. This is because pH influences the charge of nitrogen containing organic compounds (Kairi and Kassim, 2013). The charge density of amino groups is influenced by pH and affects their dissociation constants (pK_a) and thus the interaction of the polycation and the suspended material (Sorlier *et al.*, 2001).

The jar test procedure was used with the test samples (250 ml) having a turbidity of 24 NTU and buffered at different pH environments of 4, 6 and 8. The turbidity of the supernatant samples drawn out of each jar and the water clarity was measured after 30 minutes using a calibrated Turbidimeter. The results are shown in figure 4.6.

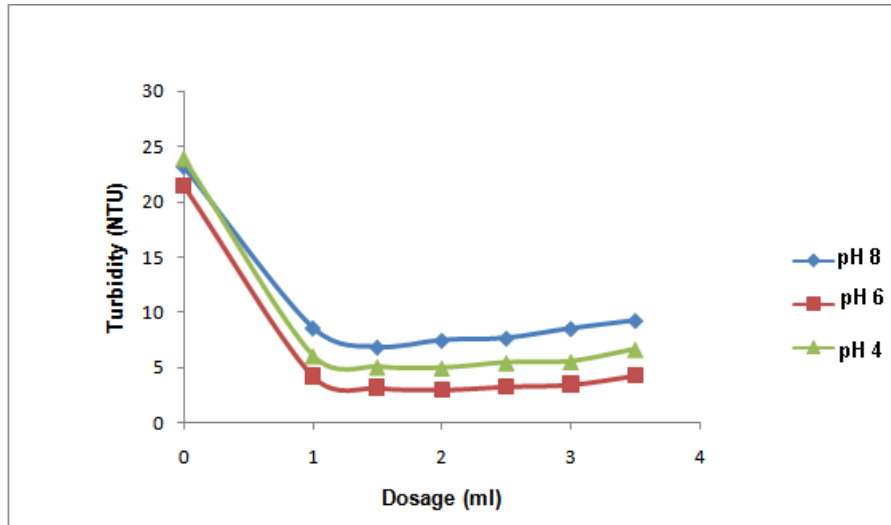


Figure 4.6: Jar test results of reduced turbidity using QMT at different pH values

The results show a clarification profile of general increase in clarity for all the three samples. However, pH 6 provided the best clarification as it had the lowest turbidity as compared to the rest. This can be attributed to the high flocculant activity of the polyelectrolyte because quaternary amine polyelectrolytes become highly cationic at that pH value. At this pH (6), there was increased neutralization of the particles by the flocculant and high bridging effect due to the spreading of its molecules (Xing *et al.*, 2013).

At pH 4, the environment has a high positive charge contributed by the protons of the acidic media offering a completion to attract negatively and neutral species in water. The presence of H^+ ions in solution lowered the negative surface charge of the particles because of the acidic nature of the solution, resulting to particles tending to self-aggregate (Sahu and Chaudhari, 2013).

At pH 8, the polyelectrolyte becomes negatively charged, and this restricts agglomeration to neutral species in the water only due to static electrical attraction (Shin *et al.*, 2006). The polyelectrolyte was effective in lowering water turbidity contributed by neutral species at pH 8. The best flocculation results were at pH 6, which is at the physiological pH of water, and further flocculation experiments were carried out at that pH value. Similar results were observed by (Zulkeflee *et al.*, 2012 ; Ramavandi, 2014).

4.3.4 Effect of dosage on clarity

The effect of reagent dose was investigated using water with a highly suspended mater. The jar test procedure was carried on waters having a turbidity of 12 NTU while varying dosages of the QMT. The turbidity of the supernatant samples drawn after 30 minutes were measured using a calibrated turbidimeter. The turbidity values obtained were plotted against the concentration as shown in figure 4.7.

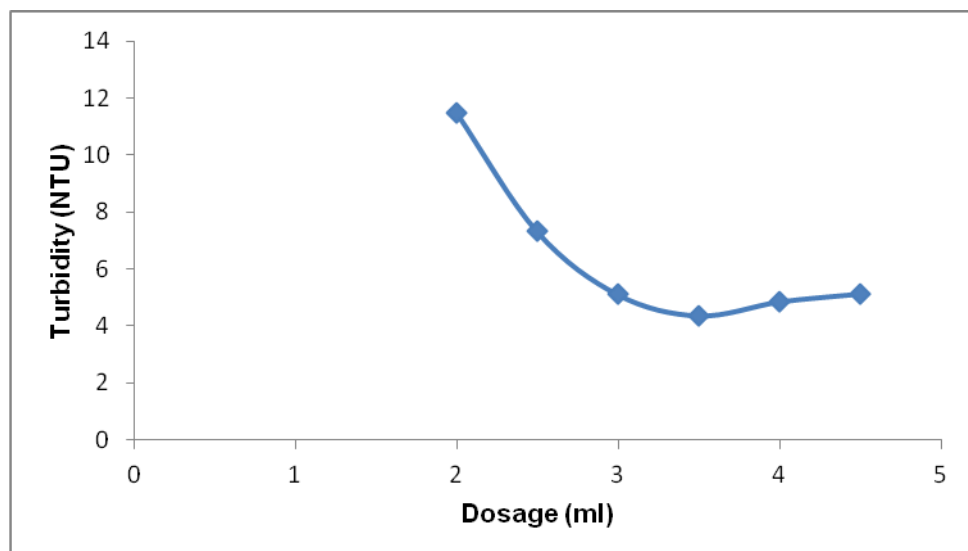


Figure 4.7: Effect of flocculent dosage on clarity of water

The results show a general decrease in turbidity with increase in the dosage of the QMT reagent. The lowest turbidity of 4.36 NTU was achieved at a dosage of 3.5 ml of the modified clarifying reagent at the pH of 6.0. This is because as the QMT encounters a colloidal particle, its positive sites are attracted to the particle surface reducing the repulsive forces between the colloidal particles, the remainder of the molecule remain extended into the solution forming bridges with other similar particles. This causes agglomeration of the colloidal particles into flocs, which then settle by gravity due to increased density of the resultant particle. When the flocculating reagent has completely neutralized the anionic charges of the particles, the turbidity level of the synthetic water reaches its minimum and this is the optimal QMT dosage.

Further increase in the clarifying reagent had no effect on the change in the turbidity of this synthetic water sample. The negative charges on the agglomerated colloidal particles cause repulsion between themselves as they collide with each other and prevent Van der Waals interactions contributing to the observation (Cayre *et al.*, 2003). Therefore, the clarifying dosage at 3.5 ml was the most effective dosage of the flocculant when the turbidity of water was 12 NTU.

4.3.5 Effect of high turbidity on clarification

More experiments were carried using high turbid water samples (50 to 150 NTU) while the synthetic water was buffered at different pH values. The results obtained were as provided in figure 4.8.

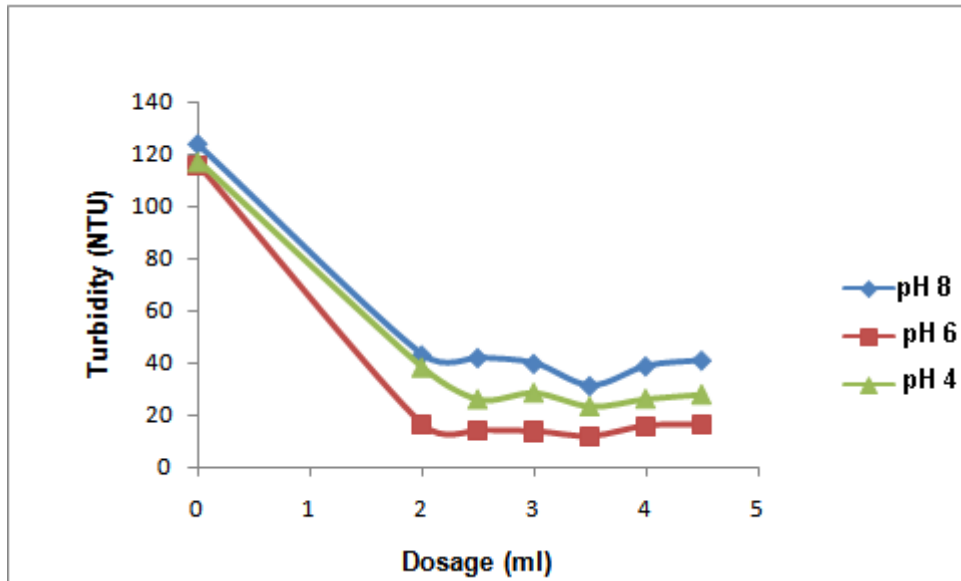


Figure 4.8: Effect of QMT dosage at different pH values on highly turbid waters

It was observed that good clarification was achieved at pH value of 6 which favors the presence of lower positively or even negatively charged species when the turbidity was low. This suggests that even at high turbidity, flocculation is due to heterocoagulation caused by charge neutralization of supermolecular layers that provide an effective aggregation of the particles since the charges of the particle are not neutralized (Lim-Seok, 1994). The study therefore observed that the modified material was an effective flocculant at pH 6 hence suitable for use on environmental water samples at varying dosages of the flocculant. This demonstrates that concentration of the interacting species is the driving force in the flocculation as they interact in certain stoichiometric ratios (Knoll *et al.*, 1982; Tillmann *et al.*, 1989).

When the dosage is increased, the clarity of turbid water can be made to suitable levels. The suspended matter and the quaternized product were interacting in specific stoichiometric ratios. The results show that as the dosage increases, the clarity of water increases to a value of 20 NTU after which no more clarification was observed. This is because the charge on the flocculating reagent is completely neutralized and has no effect on the suspended matter in the water, which remains at a turbidity level of 20 NTU despite addition of more reagents. This is attributed to the fact that suspended particles are destabilized by the electrostatic repulsion among themselves even when they are already bound with the quaternary maize tassels resulting into increase in turbidity as reported by Weber (1986).

4.4 Application of the QMT on raw water samples

The environmental water samples were collected from a swampy field in Wangige, Kiambu County in Kenya. The water sample had an initial turbidity of 25.14 NTU at a temperature of 24.0°C and a pH of 7. The samples were treated with 3.0, 3.5 and 4.0 ml of the QMT dosage using the jar test procedure, and the turbidity of their supernatant samples was drawn and measured at intervals of 10 minutes during the 30 minutes settling time. The results obtained are shown in figure 4.9.

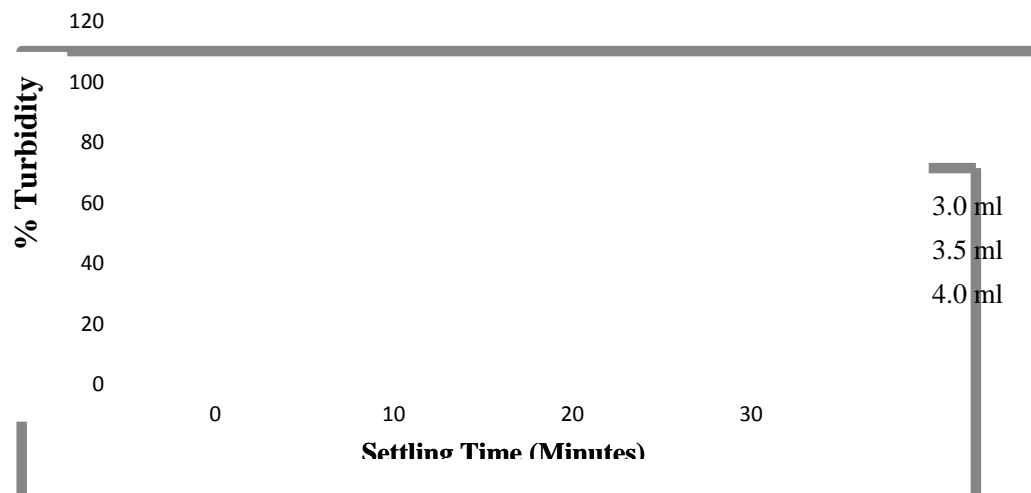


Figure 4.9: Treatment of raw water sample

The results showed that the turbidity of the raw water sample was increasingly being lowered to below 50% with the increase in dosage of the flocculant. This meant that the modified material was an effective flocculent suitable for use on environmental water samples. It also demonstrated that concentration of the interacting species enhances the flocculation process as they interact in certain stoichiometric ratios (Knoll *et al.*, 1982; Tillmann *et al.*, 1989). Therefore, the results are in agreement with the results obtained using the synthetic water; that concentration of the QMT is the driving force in the clarification process.

4.5 Analysis of the sludge

The clarification process results into formation of a floc which settled and is hereafter referred to as sludge. A sample of the sludge was analysed by FTIR and the resulting spectrum is as recorded in figure 4.10.

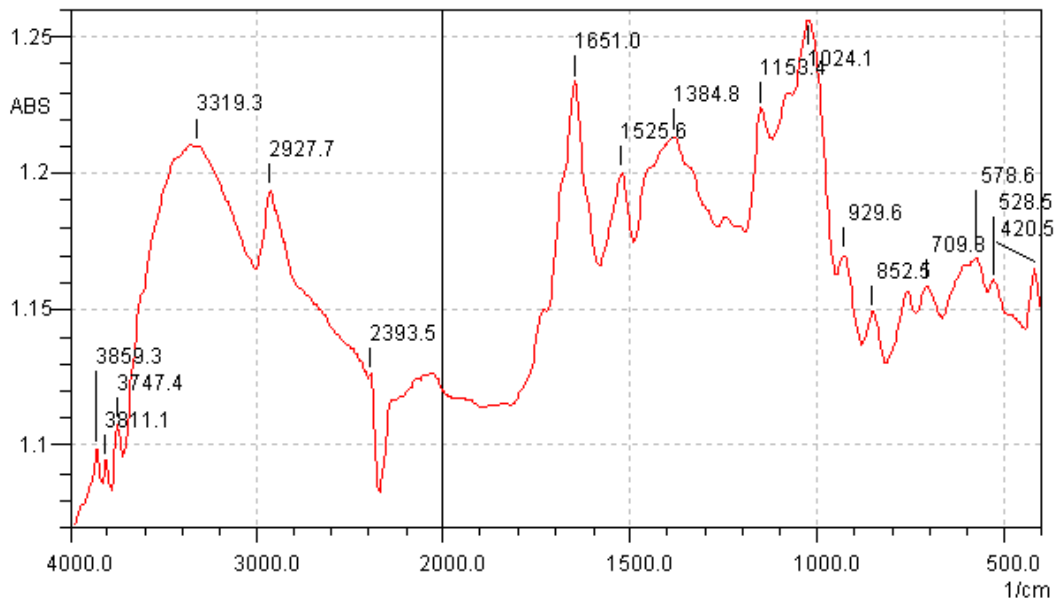


Figure 4.10: FTIR Spectrum of the settled sludge after clarification

The results showed presence of free O-H groups at the peaks 3859 cm^{-1} and 3811 cm^{-1} . The peak at 1384.8 cm^{-1} was attributed to the presence of NH_4^+ . This shows that the charged species was still in the sludge, confirming that the QMT was co-precipitated with the settling flocs during clarification process. This may be due to formation of an irreversible adsorption of a polyelectrolyte layer on the surface of those suspended particles forming a strong bond (Barker *et al.*, 2000). The bond is based on the formation of layer-by-layer assemblies leading to the formation of supermolecular layers by a self-assembly process (Knoll *et al.*, 1982; Tillmann *et al.*, 1989). This implies that the polycation settles with the agglomerated matter as sludge. The resulting sludge formed during flocculation process was treated with hydrochloric acid and the results obtained are presented in figure 4.11.

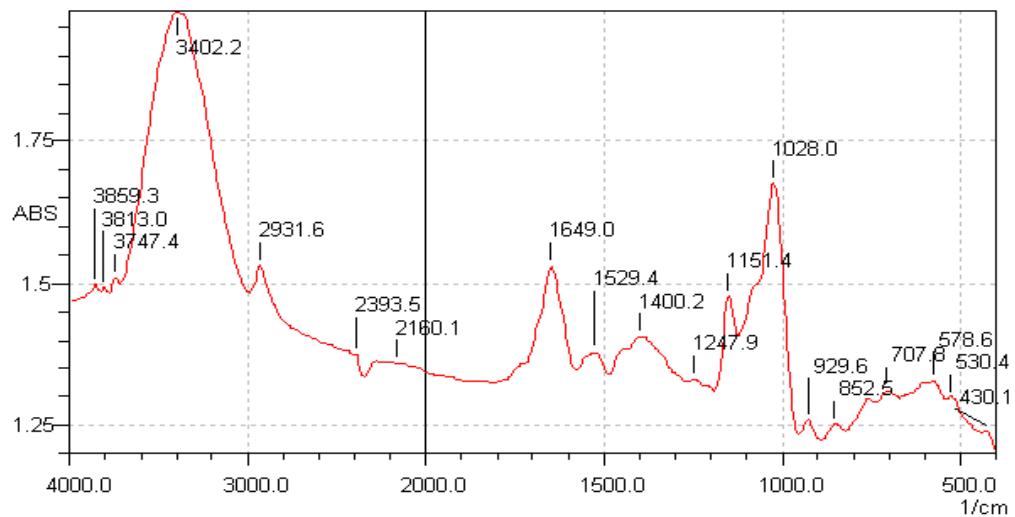


Figure 4.11: FTIR Spectrum of the sludge after treating it with hydrochloric acid

It was observed that the peak at 1384.8 cm^{-1} shifted to 1400.2 cm^{-1} . The shift could be due to the attachment of the chloride ion on the charged NH_4^+ group. This implies that the polycation was strongly attached to the sediments due to the strong bond of the layer-by-layer assemblies suggested by Knoll *et al.*, (1982).

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The following are the conclusions from this study;

- Maize tassels were successfully modified with triethanolamine, as confirmed by FTIR analysis.
- The polycationic had a settling time of 30 minutes in a sample whose turbidity was 53.8 NTU.
- An optimum dosage of 3.5 to 4 ml of the polycation lowered 250 ml of water with a turbidity of 12 NTU to 4.36 NTU in less than 30 minutes.
- The clarification process was found to be best at a pH value of 6.0.
- The turbidity of the raw water sample was lowered to below 50% when a dosage of 4.0 ml of the flocculant was used.
- The polyelectrolyte could be depleted from the solution as indicated by the FTIR analysis of the sludge.

This study therefore offers a solution to the problem of water pollution caused by suspended and colloidal matter through treatment with triethanolamine modified maize tassels.

5.2 Recommendations

From this work, modified maize tassels have shown the ability to agglomerate suspended particles in turbid waters. It is therefore recommended for remediation of turbid waters in water treatment processes. For further studies, maize tassels can be investigated on;

- Their antibacterial capabilities
- Their potential in removal of other species in water.

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APPENDICES

Appendix A: Effect of the flocculant dosage on turbidity levels

Jars	Dosage (ml)	Turbidity(NTU)
1	2.0	11.6
2	2.5	9.3
3	3.0	8.0
4	3.5	6.2
5	4.0	8.2
6	4.5	7.7

Appendix B: Effect of pH on clarification of low turbid waters

Jar s	Dosage e (ml)	Measured turbidity levels (NTU) after clarification		
		p 1	p 1	p 1
1	2.0	7.4	4.0	6.4
2	2.5	8.4	4.0	6.4
3	3.0	7.4	4.0	6.4
4	3.5	7.4	8.0	4.0
5	4.0	8.4	7.0	4.0
6	4.5	9.4	9.0	4.0

Appendix C: Effect of the flocculating reagent on clarification of high turbid waters

Jar s	Dosage (ml)	Measured turbidity levels(NTU) after clarification		
		pH 4	pH 6	pH 8
1	2.0	1.4	4.2	3.8
2	2.5	1.4	4.2	3.8
3	3.0	3.2	4.2	2.9
4	3.5	3.2	2.1	2.2
5	4.0	2.9	2.1	1.9
6	4.5	3.2	2.1	1.8

Appendix D: Effect of flocculant on settling rate at different pH values

Height of the clarified water from the meniscus at different pH values					
Time (minutes)	pH 4	pH 6	pH 6.5	pH 7	pH 8
0	100	100	100	100	100
10	98	95	98	98	98
20	70	67	73	73	70
30	65	63	63	63	67
40	60	50	53	63	65
50	55	45	53	63	60
60	50	35	53	63	55

Appendix E: Settling rate at pH 6 using different dosages

Time (minutes)	Height of the clarified water from the meniscus at different dosages		
	4 ml	3.5 ml	3 ml
10	100	100	100
20	80	80	60
30	30	50	50
40	20	35	40
50	20	35	40
60	20	30	35

Appendix F: Effect of the flocculating reagent on raw water sample

Settling time (minutes)	%turbidity of water when treated with different dosages of		
	3 ml	3.5 ml	4 ml
0	100	100	100
10	89	80	68
20	70	67	56
30	54	50	41

Appendix G: Synthesis of the quaternary maize tassels

Appendix H: Sample water with different turbidity levels after clarification