JIMMA UNIVERSITY

COLLEGE OF PUBLIC HEALTH AND MEDICAL SCIENCES

DEPARTEMENT OF ENVIRONMENTAL HEALTH SCIENCE AND TECHNOLOGY

REMOVAL OF DISINFECTION BY-PRODUCT PRECURSORS FROM NATURAL
WATER USING COAGULATION AND SUBSEQUENT ADSORPTION

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DECLARATION

The undersigned agrees to accept responsibility for the scientific, ethical and technical conduct of the research project and for provision of required progress reports as per terms and conditions of Jimma University College of public health and medical science in effect at the time of grants is forwarded as a result of this application.

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Abstract

A critical task in drinking water treatment is the removal of natural organic matter (NOM), particularly during the rainy season when a lot of organic matter is transported by run of the water bodies. In order to increase the NOM removal; synthetic chemical coagulants were used as coagulants. However, they have been associated with Alzheimer and are carcinogenic. The application of natural coagulants (green compounds) has become a responsibility to guarantee the health of the population.

The aim of this study was to evaluate the removal efficiency of disinfection by-product precursors by coagulation and activated carbon adsorption. Coagulation was studied by *Moringa stenopetala* and activated carbon adsorption was tested with *Vachellia abyssinica*.

The experimental procedure employs first treating the raw water sample with *Moringa stenopetala* and filtering the coagulated supernatant water. Then this filtered supernatant was prepared for activated carbon adsorption test and any removal improvement by activated carbon adsorption over that of coagulation was assessed. The dose of the coagulant was selected as 10,20,30,40 and 50mg/L and that of the adsorbent dose was selected as 0.01, 0.02, 0.04, 0.1 and 0.2g.

The finding shows that there is afraction of DBP precursor that was not amenable under coagulation, especially at higher coagulant doses indicating that part of the very reactive component of DBP precursors or SUVA to form disininfection by-product wasn't removed sufficiently resulting high THMFP in the coagulation treated samples. On the other hand subsequent application of activated carbon adsorption improved the removal efficiency on the DOC and SUVA concentration over that of coagulation with avery minimal concentration of THMFP.

Key words: Coagulation, Adsorption, NOM, DOC, SUVA, THMFP, *Moringa stenopetala, Vachellia abyssinica.*

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Abbreviations and Acronyms

ASTM   American standard for testing materials

AC   Activated carbon

COD   Chemical oxygen demand

CBP   Chlorination by-products

DBPs   Disinfection by-products

DBPP   Disinfection by-product precursors

DBPFP   Disinfection by-product formation potential

DOC   Dissolved organic carbon

DON   Dissolved organic nitrogen

EPA   Environmental Protection Authority

GAC   Granular activated carbon

HAAs   Haloacetic acids

KHP   Potassium hydrogen phathlate

MOH   Ministry of health

MDGs   Millennium development goals

MWCOs Molecular weight cutoffs

MF   Microfiltration membrane

MW   Molecular weight

NOMs   Natural organic matters

NF   Nanofiltration membrane

PAC   Powdered activated carbon

RO   Reverse osmosis

SUVA   Specific ultraviolet absorbance

STHMFP   Specific trihalomethane formation potential

NTU   Nephelometer Turbidity Unit

TTHM   Total trihalomethane

THMFPrb   Reactivity-based test for trihalomethane formation potential

THMFPdb   Dose-based test for trihalomethane formation potential

THMs   Trihalomethanes

THMFP   Trihalomethane formation potential

TOC   Total organic carbon

TOX   Total organic halogens

UVA   Ultraviolet absorbance

USEPA   United States Environmental Protection Agency

UF   Ultra filtration membrane

WHO   World Health Organization

Table of Contents   Pages

List of Tables   Pages

List of Figures   Pages

CHAPTER ONE: INTRODUCTION

1.2. Background of the Study

Natural organic matter (NOM) is a term used to describe the complex matrix of organic material present in natural waters and a relation exists between its characteristics and treatability (Owen et al., 1995). Molecular weight distribution of NOM is one of important parameters in characterizing NOM (Amy et al., 1992). In water treatement process each unit process may exhibit different removal efficiencies for a specific Molecular weight fraction of NOM **(**Jacangelo et al., 1995).

Ultraviolet absorbance is a useful surrogate measurement of selected organic constituents in natural water, may exhibit strong correlation with organic carbon content and disinfection by-product precursors (Najm, 1994). Furthermore, studies show that parameters like DOC, TOC UVA, and SUVA are good indicators of NOM and should be used to estimate the disinfection by-product formation potential (Chang et al.,2001). However, Dissolved organic carbon (DOC) rather than Total organic carbon (TOC) is a good indicator of disinfection by-product formation potential, because TOC provides the gross concentration of organic carbon only. However, DOC can provide information about nature and reactivity of precursors (Najm et al., 1994).

A number of approaches exist for reducing DBP formation including catchment management, altering the disinfection process and/or removal of precursors (Singer, 1999).While the second option is desirable, evidence suggests that changing disinfectant produces alternative DBP which also pose a health risk (Andrzejewski et al., 2005). Further, the capability to reduce disinfectant doses is limited by the need to supply adequate disinfection and this is limited option over longer period; Meanwhile, precursor removal does not generate alternative DBPs, and often utilizes existing technology. Hence, much research practice is focused on this area (Singer, 1999).The reduction of NOM by various methods including coagulation, oxidation, ion exchange, adsorption, membrane filtration has been revealed by several studies (Chadwick and Amy, 1983).

Coagulation is effective in removing turbidity and reducing organic disinfection by-product precursors. In the coagulation the effect of high dosage are readily apparent because of formation of hydrolyzed species (Babcok and Singer, 1979). A better DOC removal by coagulation is found in water with higher specific UV absorbance. The source water with low DOC was required to employ the alternative treatement process to meet the drinking water standards (Edzwald, 1993 and USEPA, 1998). Coagulation is the standard NOM removal process at water treatement works (Singer, 1999),however, the coagulation process is only effective in removing large organic precursors, so the conventional treatement methods have limited efficiency in eliminating small precursors, which have high formation potential of disinfection by-product precursors(Chang et al.,2001)

Hence, efficient work interms of treatability is limited and this make connection between the understanding of DBP formation and strategies to control their formation difficult. Further, the selection and operation of treatement technologies for target DBP precursors removal rather than bulk DOC remains uncertain (Singer, 1999). Therefore, as part of this our aim in this study was to understand whether combination of treatement for removal of DBP precursors is feasible by testing NOM surrogates. The treatments' selected were coagulation and adsorption.

1.2. Statement of the problem

Although one of the eight goals of the millennium development (MDGs) is to reduce by half the population without sustainable access to safe drinking water and basic sanitation, this compromise is so far from being achieved, due to the lack of commitment of different governments (Garcia, 2011). According to the world water council (2010) report, 1200 million peoples do not have access to safe drinking water and 2600 million are living without adequate sanitation. Many water sources in developing countries are contaminated with industrial and agricultural activities as a result of lack of education of the population and poor enforcement of the regulations concerning water use and waste disposal.

The drinking water crises could become the worst crisis of humankind in the future due to the increment in the population, changes of life style, and increasing industrial and agricultural needs; all of these are demanding constantly more water. Aquatic ecosystem are also being affected by pollution and reduction of habitat due to continuous dumping of wastes (Garcia, 2011).

The health consequences of the inadequate water and sanitation services include an estimated 4 billion cases of diarrhea and 2.2 million deaths per year, mostly among young children in developing countries. In addition to this, waterborne diarrheal diseases lead to decreased food intake and nutrient absorption, malnutrition, reduced resistance to infection and impaired physical growth and cognitive development (Lantagne et al., 2008).

Since1970s, the discovery of haloforms such as chloroform formation during chlorine disinfection of drinking water and the result of regulations on DBPs and interest in NOM removal has initiated extensive research in to the formation of chemical DBPs and many water treatment plants in developed countries have started to measure the concentration of NOM in their finished waters and promulgation of the rules has substantially increased these efforts in other countries too. Because of the increased-cost of NOM and DBPs determination, it was decided to study the traditional analysis of NOM parameters as a surrogate measure to detect the organic constituents in raw water and the extent to which optimized coagulation can increase NOM removal. Most waters contain NOMs which should be removed; they include precursor compounds that form health-related DBPs when chlorine and other chemicals are used for disinfection and oxidation. For these reasons, considerable attention is being directed at the removal of NOM by modifying coagulation in conventional water treatment plants (Vaezi et al., 2005; Mitch et al., 2009).

Environmental scientists are increasingly emphasizing on the geochemical and ecological roles of organic matters in aquatic ecosystems, because these organic matters in aqueous systems often controls geochemical processes by acting as a proton donor or acceptor and as a pH buffer, by affecting the transport and degradation of pollutants, and by participating in mineral dissolution and precipitation reactions. Organic matters may also control the depth of the photic zone in surface waters, influence the availability of nutrients, and serve as a carbon substrate for microbial mediated reactions. In addition, these reactive substances are potential precursors for DBPs formation resulting from water treatment practices and dissolved organic carbon (DOC) comprises the vast majority of the organic matter in most water samples (Weishaar et al.,2003).

1.3. Research questions

To address the development of this thesis the following research questions were posed for possible answers.

- ➢ What treatement methods can remove disinfection byproduct precursors in water to the required level?
- ➢ What are the possible success variables to achieve the treatement goals?

1.4. Significance of the study

The significance of this research is to improve the removal efficiency of DBP Precursors from natural water through combination of affordable treatement techniques that can be produced from local available materials and contributing equity and overall quality of life, especially among rural and pre-urban marginalized communities. The work may also offer improved capabilities of monitoring DBP precursors from drinking water systemically by providing knowledge and skill for interested individual who wants to investigate further study about the nature and characteristics of NOMs and the way of monitoring them.

1.5. Hypothesis

Activated carbon adsorption can further reduce disinfection by-product precursor's concentration in water when applied subsequent to Coagulation.

1.6. Scope of the study

The scope of this study includes preparation of raw materials and investigating their potential in removing DBP precursors from natural water when applied subsequently. Various variables of DBP precursors were assessed in order to quantify the removal efficiency. The assessed variables include: THMFP, DOC, SUVA and UVA along with other variables of interest required for treatement objectives.

CHAPTER TWO: LITERATURE REVIEW

2.1. Natural Organic Matters (NOMs)

NOM is a term used to describe the complex matrix of organic matter or a complex mixture of pedogenic (soil derived) and anthropogenic (water column) material derived from the contact of water with dead and living organic matter in the hydrological cycle that occurs universally in aquatic and terrestrial environment and a relationship is found to exist between its characteristics and treatability (Roe,2011;Ashery et al.,2010; Parsons et al.,2004). It can also be defined as all withering material from plants and animals and their degradation products, all containing carbon with the exception of carbon dioxide (CO_2), carbonates; carbide and metal cyanides.

NOM fractions can be separated into two broad categories as humic and non-humic or hydrophobic (water repelling) and hydrophilic (water absorbing).The hydrophobic fractions are aromatic compounds and are composed of primarily humic substances formed by decaying of vegetation matter and are quite resistant to biodegradation yet it is reactive to oxidants, such as chlorine, and these characteristics of the aromatic hydrophobic humic material tend to form higher THM levels, while the water absorbing or hydrophilic fractions of organic matter are composed of primarily fulvic material, Carbohydrates and sugars, and are a relatively poor THM precursor (Kordel et al., 1997 and Garcia,2011).
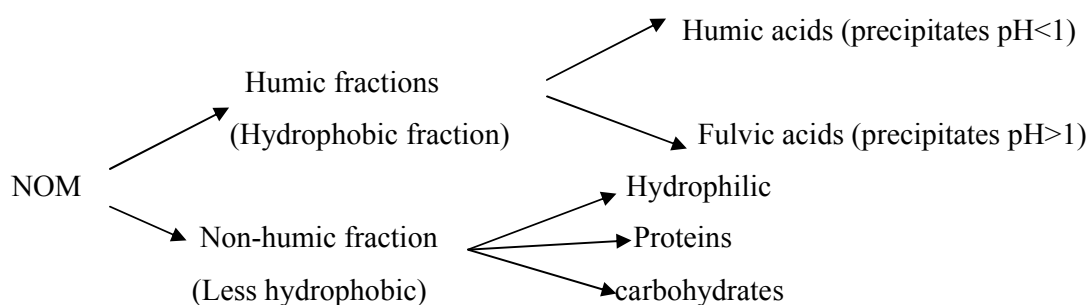

Figure 1.Classification of Natural organic matter (Garcia, 2011)

2.2. The Origins of Natural Organic Matters (NOMs)

Although the origin of NOM is not well-known:- (Reckhow, 2006; Roche and Benanou, 2007), distinguished two different origins of organic matter as *Allochthonous* and *Autochthonous* or aquagenic and pedogenic and they may vary over time within the same body of water. *Autochthonous* result directly from biological activity via photosynthesis and the metabolic activities of algae and micro-organisms or of indirect origin, from the degradation of aquatic plants by organisms living in the medium or compounds that are created within the water body.

However, *Allochthonous* result from lixiviation or washing of floors and percolation of water containing vegetal debris as well as products from the degradation of ground vegetal and animal biomass or compounds that can originate from either the soil or from upstream water bodies; they are called aquagenic if originating from any water body or pedogenic if originating from soil, woody & non-woody plants, and depend on vegetation, soil, and hydrology (Veum,2006 and Timofeyev,2004) also found that, the autochthonous precursors are generally more liable in nature, and are rapidly cycled through the microbial loop and generally constitute a small proportion of the total organic carbon pool compared to allochthonous, they also confirmed that the aquatic environment contains a wide range of dissolved or colloidal organic matter (DOM), which is a product of the decomposition of plant and animal organics than the terrestrial environment.

2.3. Impacts of Natural Organic Matters

Natural organic matter (NOM) in drinking water source is of primary concern, as it acts as precursor in the formation of potentially harmful disinfection by-products (DBPs) amongst which the trihalomethanes (THMs) and haloacetic acids (HAAs), products of chlorination, are considered to be dominant on a mass-basis in natural waters (Yee et al.,2009) and these disinfection byproducts (DBPs) have received considerable interest because of their possible association with cancer, particularly bladder and rectal cancer in drinking water.

More recently, the interest has shifted from cancer to reproductive outcomes because-mothers exposed to water with increased trihalomethanes concentrations have been shown to be at greater risk for a variety of pregnancy related complications including birth defects, stillbirths, spontaneous abortions, and fetal growth retardation (Wright et al., 2012).

As cited by (Reckhow, 2006) the basic premise of disinfection byproduct formation was first published by Rook (1977). He proposed that as long as chlorine and organic Precursors are present in solution, they react to form trihalomethanes (THMs).

Chlorine + Precursors =THMs.
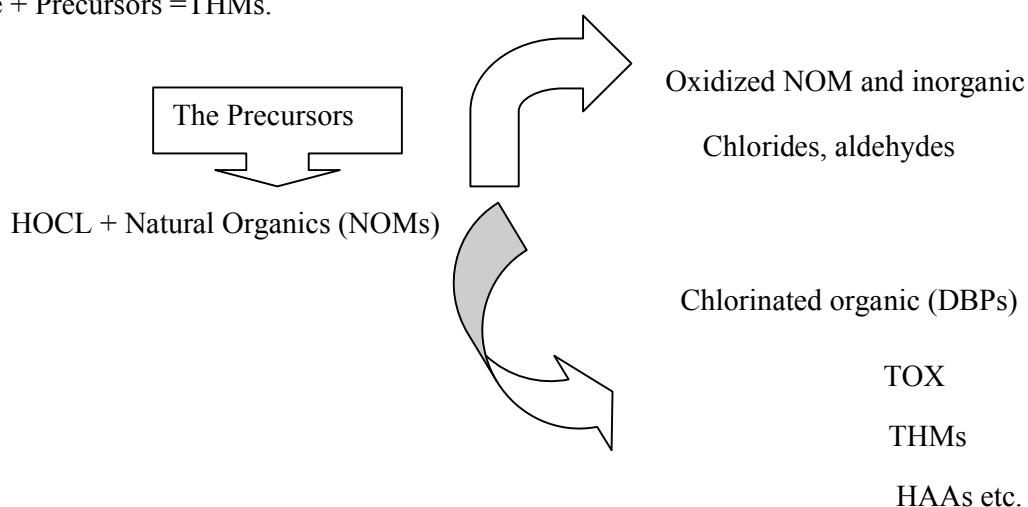
Figure 2. Formation of disinfection byproducts (Reckhow, 2006)

The chemical structure of NOM and associated DBP precursors vary with many environmental and chemical parameters, including the source of the organic material, age of the organic material, diagenetic history, soil type, season, molecular size, pH of the source waters, and so forth. The abundance of these chemical structures determines the speed and extent to which THM forms on treatment, as well as they carry information about the source and diagenetic history of the NOM. In addition, the intrinsic chemical structure of the NOM, the speed and extent of formation of THM during chlorination depend on a number of physical and chemical parameters such as the chlorine dose, the duration of the reaction, the presence of bromide and ammonium, the NOM concentration, and the temperature and pH at which the reaction is conducted contribute to the amount of THM formed (Fujii et al., 1998).

Generally, according to *(*Consonery et al., 2004**)** a wide variety of water quality and treatment conditions can affect byproduct formation. Some conditions that can affect the relation between precursors and disinfection byproduct formation are:

Residence time-Systems with longer residence time will likely have higher disinfection byproducts than those with lower residence times at equal precursor concentration.

Disinfectant concentration-All things being equal, a lower disinfectant residual will result in lower disinfection byproduct formation.

Alkalinity-Water systems with high alkalinity concentrations have lower precursor removal requirements. Thus, two systems with identical raw water precursor concentration but large difference in alkalinity may have a considerable difference in precursor removal.

Chlorine application points-All things being equal, if chlorine is applied prior to coagulation, the water system would likely have higher byproducts than a similar system where chlorine is applied later in the treatement

Temperature-Because of the strong effect of temperature on disinfection byproduct formation, there can be strong seasonal variation between precursor and byproduct formation. Thus the warm water byproduct level can be much greater than those for cold water at a constant precursor concentration**.**

2.4. Reduction Mechanisms for NOMs and their Precursors

Several methods have been recently developed to treat serious contamination problems with drinking water, and especially to increase the removal efficiency of DOC and reducing the formation of DBPs. The first option includes catchment management, altering the disinfection process, and removal of precursors, while the second option suggests that changing disinfectant produces alternative DBPs which also pose health risk, and it has limited option over the longer term, meanwhile precursor removal does not generate alternative DBPs *(*Cheng and Chi,2003;Bond et al.,2009*)*. According to **(**MOH,2001**)**,the concentrations of trace organic compounds in water can be reduced by processes covered in several water supply element by:

- Good management of the raw water resource: stopping nutrients and other contaminants getting into the raw water, careful selection of the abstraction method

from lakes/reservoirs, use of algaecides in time to stop algal blooms, destratifying lakes or reservoirs before layers with no oxygen develop.

- Conventional coagulation/flocculation/sedimentation, dissolved air flotation, direct filtration.

- Oxidation of the organic substances: chlorine, chlorine dioxide, ozone, potassium permanganate.

- Aeration/air stripping: blowing air through the water spraying the water into air.

- Adsorption by activated carbon: powdered activated carbon – usually added before coagulation granular activated carbon – used as a bed on top of a rapid sand filter, or in its own separate contact tank (contactor).

However, the reduction of NOM by coagulation, oxidation, adsorption, and membrane filtration has been revealed as the best ones in several studies (Chang et al., 2004).

2.4.1. Membrane Filtration

In potable water treatment, there is much interest in the use of membranes as total treatment systems for the removal of DBP precursors, particles, and microorganisms, with the potential use of free chlorine as a post-disinfectant. The major deterrent to more widespread use of membranes is the requirement for often extensive pretreatment. Membranes within the category of nanofilters (NF), in particular, have great potential in this endeavor based on their molecular weight cutoff (MWCO) (Siddiqui et al., 1999), and they are now well-established in the water industry as an alternative to traditional media filters, because they can be used in conjunction with coagulation, adsorption, and oxidation processes or combined with one another to produce high quality drinking water without chemical addition (Chaulk and Sheppard, 2011).

According to (Chaulk and Sheppard, 2011), the four main types of membrane processes are: Microfiltration (MF), Ultra filtration (UF), Nanofiltration (NF), and Reverse osmosis (RO) and each is defined by its ability to remove species that fall into a given size range. Microfiltration (MF) can remove turbidity (particulates and bacteria), but no dissolved compounds unless associated with colloids, however, Ultra filtration (UF) can remove them, depending on the molecular weight cut off (MWCO) of the membrane.

On the other hand, Nanofiltration (NF) can remove NOM and hardness almost completely and it has been also proven that NF is reliable for the removal of organic and inorganic compounds with lower operating pressures than Reverse osmosis (RO) and lower molecular weight cut-off (MWCO) than UF (Matilainen, 2007). However, many of these technologies may be cost prohibitive in developing countries. If that is the case, it cannot be emphasized enough that proper disinfection should be maintained (Christman, 1990).

2.4.2. Oxidation

Chlorine, potassium permanganate, ozone, and oxygen are some examples of oxidants used in the water treatment industry, and these technologies can partially oxidize NOM molecules that are precursors to a given DBP to molecules that are not precursors to that DBP. Therefore, some DBP precursors are partially destroyed by oxidation while others are created. If the destruction of organic precursors for a given DBP exceeds the creation of new organic precursors for that DBP, then oxidation may be considered a precursor removal process for that DBP (USEPA, 1999).However, some oxidation processes, such as Ozonation, do not remove organic matter but instead break it down into smaller, more bio-degradable compounds which can lead to an increase in disinfection by-products, such as THMs if there is no subsequent removal stage (USEPA, 2010). Several factors, such as reactivity of the oxidant with the target compound, the rate of reactivity, the oxidant demand to achieve a desired degree of treatment, the extent of incidental stripping associated with the oxidant dispersion, and other treatment variables such as pH and temperature can influence the effectiveness of the oxidation process (Molva, 2004)

2.4.3. Coagulation

The production of potable water from most raw water sources usually entails the use of a coagulation /flocculation stage to remove turbidity in the form of suspended and colloidal material, and this process is believed to play a major role in surface water treatment by reducing turbidity, bacteria, algae, color, organic compounds and clay particles (Bina et al.,2009) and it involves reaction between coagulant chemicals, NOM molecules and the surface of particles, and is thought to occur via four primary mechanisms such as enmeshment, adsorption, charge neutralization/destabilization, complexation/precipitation (Pernitsky,2003) .

Coagulation has traditionally been used to remove turbidity from drinking water supplies and its major components include chemical feed systems; mixing equipment; basins for rapid mix, flocculation, settling, and filtration; filter media; sludge handling equipment; and filter backwash facilities (USEPA, 1999). However, the main role of the coagulant is to destabilize the particles, form ligands binding the particles together, and form hydroxide precipitate that will collect aggregate called *flocs* and adsorb certain dissolved molecules and after clarification, the water may go through several additional treatment steps, mainly to eliminate dissolved micro-pollution. These may include: Ozonation, Adsorption onto activated carbon (Roche and Benanou, 2007).An indigenous water treatment method using natural coagulants like *Moringa oleifera* seeds in the form of a water-soluble extract in suspension, results in an effective natural clarification agent for highly turbid and untreated pathogenic surface water. Efficient reduction (80.0% to 99.5%) of high turbidity produces an aesthetically clear supernatant, concurrently accompanied by 90.00% to 99.99% bacterial reduction (Michael Lea, 2010).

According to (Michael Lea,2010) application of this low-cost Moringa oleifera protocol is recommended for simplified, point-of-use, low-risk water treatment where rural and peri-urban people living in extreme poverty are presently drinking highly turbid and microbiologically contaminated water. To treat surface water, the equivalent weight of seed powder required to make up a crude extract solution is dependent upon the turbidity.

Table 1.Moringa Oliefera dosage ranges (Seed powder) (Michael Lea, 2010)

Raw water turbidity(NTU)	Dosage range(seeds/liter)	Dose(mg/liter)
<50 NTU(low)	1 seed/4 liters	50mg/liter
50-100 NTU(medium)	1 seed/2liters	100mg/liter
150-250 NTU(high)	1 seed/liter	200mg/liter
>250 NTU(extreme)	2seeds/liter	400mg/liter

2.4.4. Activated Carbon Adsorption

Activated carbon (AC) is a generic term for a family of highly carbonaceous materials none of which can be characterized by a structural formula (Verla et al.,2012).In water treatment, adsorption onto activated carbon is a very good process for eliminating a wide range of organic compounds, notably many of those responsible for unwanted tastes and odors. In addition to eliminating a wide range of organic pollutants, activated carbon has a capacity to absorb more or less effectively any type of molecule (wide spectrum) (Roche and Benanou,2007).In recent years, a considerable number of studies have focused on low cost alternative materials for the production of activated carbons from agricultural wastes such as, cherry stones *(*Calvete et al.,2010) and the use of low cost wastes and agricultural by-products to produce activated carbon has been shown to provide economic solution *(*Rajeshwar et al.,2012**)**.However, while using activated carbon adsorption,NOM competes for adsorption sites on activated carbon, decreasing the removal of other micro pollutant, so activated carbon should be considered as an additional treatement for the removal of NOM (Matilainen, 2007).

Direct activated carbon adsorption is not recommendable since the sorption capacity is quickly reduced by pore blocking caused by the large molecules. GAC adsorption of NOM may be suitable as post treatment for other processes (coagulation, Ozonation etc.) that have removed or changed the large sized-molecules to the extent that the residuals may be sufficiently small to arrive at sites in the finer pores. Granular activated carbon (GAC) is not used as the only NOM removing process, but is used as filter medium in Ozonation/Biofiltration plants (Odegaard et al., 2010).The American standard for testing materials (ASTM,2008) recommends that, the sample weights of activated carbon should have to be adjusted depending on the concentration of adsorbable constituents in the water as follows.

Table 2.Sample volumes and Carbon weights for determining adsorbable constituents (ASTM, 2008)

DOC Concentration, mg/L	Sample Volume, mL	Suggested Carbon Weights
≤10	500	1.0,2.5,5.0,7.5,10,25,50mg
>10;100	100	0.01,0.02,0.04,0.10,0.20,0.40,1.0,2.0,and 4.0g
>100	100	0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, and 10.0 g

2.5. Treatement combination (multi-barrier approach)

Most of the treatment technologies to be considered will have subject to some limitations on their effectiveness due to the diverse nature of NOM and combinations of treatment technologies may prove to offer significant benefit over their individual performance in terms of treatement efficiency and achieving treatment goals. For example, activated carbon adsorption is most effective for the portion of NOM composed of smaller sized organic compounds without charged functional groups, and conversely, enhanced coagulation is generally considered to be most effective for the portion of NOM composed of large organic molecules with negatively charged functional groups (Roy, 2009).

Accordingly, coagulation is found suitable to treat a higher molecular weight (MW) fraction of NOM, and the remaining small MW organics after coagulation/sedimentation processes can be expected to be removed by GAC adsorption, resulting in an effective reduction of DBP precursors. Therefore, the GAC adsorption process, applied after coagulation has been proved to provide relatively lower trihalomethane formation potential (THMFP) in the treated water at the same level of THM and lower coagulant doses demand, because a large MW fraction of NOM can cause pore blockage of activated carbon and result in the decrease of effective adsorption sites. Thus, the water treated by coagulation followed by adsorption process should provide safer drinking-water quality with regard to DBP formation (Chang et al, 2004).

Multi-barrier approaches are any combination of technologies used together, either simultaneously or sequentially for water treatment, and have to be tested according to manufacturers or implementers recommendation for the normal house hold use in the target context. Some examples of such combination include coagulation/disinfection, filtration/disinfection and/or filtration/membrane technology. These combination systems might also be commercial products in the form of granules, powders or tablets containing a chemical coagulant such as an iron or aluminum salt and a disinfectant such as chlorine (WHO, 2011).

When added to water, these chemicals coagulate and flocculate impurities to promote their rapid and efficient sedimentation and also deliver the chemical disinfectant to inactivate microbes. To use these combined coagulant–flocculants–disinfectant products, they are added to specified volumes of water, allowed to react for floc formation, usually with brief mixing to promote coagulation– flocculation, then allowed to remain unmixed for the floc to settle; the clarified supernatant water is then decanted off, usually through a cloth or other fine mesh medium to strain out remaining particles. The recovered supernatant is then stored for a period of time to allow for additional chemical reactions and disinfection to occur before the water is consumed (WHO, 2011).

2.6. Surrogate Parameters of NOM Precursors.

Simple NOM characterization included total organic carbon (TOC), dissolved organic carbon (DOC), and dissolved organic nitrogen (DON) (Mitch et al., 2009). However, the quantity and reactivity of NOM in a water sample will not be characterized by these parameters only, instead it is determined by the characteristics of the water source and its watershed as stated by (Chaulk and Sheppard, 2011).The smaller water bodies have been observed to have higher NOM content than larger ones, and moving water bodies like rivers have been observed to have more variable NOM content than more stagnant ones. However, wetlands, coniferous forests, and heathers in the watershed have all been identified as being correlated with elevated NOM levels, and human activities that impact the drainage pattern and land cover of the watershed have also been shown to increase the amount of NOM in some water sources**.**

This difference in source, quantity and quality of NOM leads to a conclusion that there is no direct analytical procedure for the characterization of NOM in water, because its composition is obviously influenced by the soil chemistry and hydrology of the catchment from which the water is derived(Lamsal,1997).But, some researchers like (Wattanachira et al.,2004;Parsons et al.,2004) believe that NOM can be characterized by bulk water parameters such as DOC, UV-254nm, SUVA or can be fractionated into either charge or size fractions to some parameters or they can be also characterized by their trihalomethane formation potential(THMFP) along with pH,turbidity,and alkalinity.

2.6.1. Total organic carbon (TOC) and dissolved organic carbon (DOC)

The total organic carbon (TOC) concentration of water is generally an indicator of the amount of THM precursor present (Mishra and Dixit, 2013).Although TOC is a direct measure of water's organic carbon content; it is not necessarily a consistent measure of DBP precursor concentrations. One explanation for this observation is that TOC does not provide an indication of the aromaticity, aliphatic nature, functional group chemistry, or chemical bonding associated with natural organic molecules. The reactivity of chemical bonds and functional groups is likely to be a significant factor in explaining why different waters with the same TOC concentration will form different DBP concentrations under identical disinfection conditions and bromide levels (USEPA, 1999).

However, DOC is the most commonly used surrogate measure of DBP precursor concentrations because DOC is operationally defined as that portion of TOC which passes through a 0.45 μm membrane filter. Therefore, DOC measures the amount of organic carbon dissolved in given water and the dissolved phase organics may be more reactive than particulate phase organics (USEPA,1999*).*Nonetheless, concentration and composition of dissolved organic matter (DOM) in freshwater systems is of concern due to its role in the formation of disinfection byproducts (DBPs) during drinking water treatment. Reactions between chlorine and dissolved organic carbon (DOC) form a suite of compounds with potential human health impacts, including increased risk of cancers and birth defects (Pellerin et al.,2010*).*Dissolved organic carbon (DOC) present in natural water forms a variety of disinfection byproducts when chlorinated during treatment. Some of these byproducts are known to be carcinogenic, and the final concentrations are regulated in finished drinking water (Bergamaschi et al., 1998)

2.6.2. UV absorbance and Specific ultraviolet absorbance

UV absorbance reflects the bulk concentration of precursors in water, however, the nature and reactivity of the precursor is best assessed using a parameter called specific UV absorbance (SUVA) *(USEPA*, 2010).Specific UV absorbance (SUVA) is defined as the UV absorbance of a water sample at a given wavelength normalized for dissolved organic carbon (DOC) concentration SUVA, has shown to be a useful parameter for estimating the dissolved aromatic carbon content in aquatic systems (Weishaar et al.,2003).

2.6.3. Disinfection byproduct formation potential (DBFP)

Trihalomethanes formation (THMFP) test is a measure of the potential of the water samples to form THM after the addition of chlorine (Yee et al., 2009**).**The THMFP test is therefore likely to be reasonably representative of the informal chlorination procedures used by individual water users. In these cases, drinking water is saturated with chlorine before use, either in jerry cans or from a container of chlorine tablets suspended in the well (Stuart et al., 1998).Several tests for the capacity of natural waters to form DBP are currently in use. The two main tests that are in use to determine the THMFP of the tested waters are:

- The dose based test (THMFPdb), in which a fixed amount of chlorine is added to the sample.
- The second type of test was the reactivity-based test (THMFPrb), in which the chlorine demand is calculated to determine chlorine dose (Fujii et al., 1998).

Dissolved organic material can react with chlorine during water disinfection for potable supply to form trihalomethanes (THMs, haloforms). For effective disinfection an excess of chlorine over the sample consumption is needed and this free chlorine can react with organic compounds present in the water during storage or distribution of the treated water.

The THM compounds most commonly formed are chloroform, bromodichloromethane, chlorodibromomethane, and bromoform. Owing to its high reactivity, chlorine reacts very rapidly with many natural organic compounds present in raw water (Stuart et al., 1998*).* There is concern that the reuse of renovated water with an enhanced organic load may lead to increased haloform production during chlorination. However, there is some evidence that polar high molecular weight natural organic material, such as humic acids, rather than

anthropogenic organic compounds are the preferred precursors. The type and relative amounts of chlorination by-products vary with chlorine concentration, the concentration of organic precursor compounds, pH, temperature, and contact time (Stuart etal., 1998).

Bromide, often present in raw water, from either natural or anthropogenic sources has an important effect on the speciation of any THMs produced. During chlorination, bromide is oxidized by chlorine to bromine and chlorination and bromination become competitive reactions. Bromine appears to be more effective as a halogen-substituting agent and, if bromine acts as an oxidant, it will be reduced to the bromide ion, which may then be re-oxidized by chlorine. This results in high bromine incorporation into the THMs and may account for the mutagenic activity of chlorinated waters which cannot be solely ascribed to chloroform (Stuart et al., 1998)

2.6.4. Equations and Predictive models

Numerous researchers have attempted to develop equations to predict the formation of THMs and HAAs based on water quality parameters TOC, DOC, UV_{254nm}, bromide, and operational conditions (chlorine dose, retention time),and many of these models performed very well (R^2 > 0.9).However, none have been universally adopted by the water industry because many of them were developed in laboratories under controlled conditions, and limited by a small sample size, and/or were specific to the water supplies evaluated (Chaulk and Sheppard, 2011).

According to (Wattanachira et al., 2004),the correlation section was used to demonstrate the correlation and regression among surrogate parameters for NOM so as to allow one parameter such as UVA to be used as a surrogate for another parameter such THMs and its levels were divided into four categories, as the correlation coefficient (R^2)> 0.9 was considered a good correlation, $0.7 < R^2 < 0.9$ a moderate correlation, $0.5 < R^2 < 0.7$ a fair correlation, and $R^2 < 0.5$ considerably poor correlations ,and the regression analysis will not performed for this; hence, the slope and intercept for the equation were not accepted.

Table 3.Disinfection byproduct formation models **(**Chaulk and Sheppard, 2011; Sadiq and Rodriguez, 2004**)**

Source	Data type	Equation
Minear and Morrow(1983) Morrow and Minear(1987)	Laboratory	$TTHM\ (\mu mol/L) = -3.91 + (Br\ \text{-})^{0.15} + 0.23\ log(D) + 0.24\ pH + 10^{0.009T} + 0.26\ NVTOC$
Amy et al.(1987) Chowdhury et al(1991)	Laboratory	$TTHM\ (\mu mol/L) = 0.0031(UV \cdot TOC)^{0.44}\ D^{0.409}\ t^{0.265}\ T^{1.06}\ (pH - 2.6)^{0.715}\ (Br + 1)^{0.036}$
Chang et al (1996)	Laboratory	$TTHM\ (\mu g/L) = 12.7(TOC)^{0.291}\ t^{0.271}\ D^{-0.072}$
Amy et al (1998)	Laboratory	$TTHM\ (\mu g/L) = 0.00412(DOC)^{1.1}\ D^{0.152}\ Br^{0.068}\ T^{0.61}\ pH^{1.60}\ t^{0.26}$
Rodriguez(2000)	Field Laboratory	$TTHM\ (\mu g/L) = 1.392(DOC)^{1.092}\ pH^{0.531}\ T^{0.255}$ $TTHM\ (\mu g/L) = 0.044(DOC)^{1.030}\ t^{0.262}\ pH^{1.149}\ D^{0.277}\ T^{0.968}$
Rathbun(1996)	Laboratory	$TTHM(\mu g/L)=14.6(pH\text{-}3.8)^{1.01}(D)^{0.206}(UV)^{0.849}(t)^{0.306}$
Chang.et.al(1996)	Laboratory	$TTHM(\mu g/L)=12.7(TOC)^{0.291}(t)^{0.271}(D)^{-0.072}$
Urano.et.al(1983)	Laboratory	$TTHM(\mu g/L)=0.00082(pH\text{-}2.8)(TOC)(D)^{0.25}(t)0.36$

**D = Chlorine dose (mg/L), t = reaction time (h), T = temperature (C^0), TTHM = total trihalomethane (μg/L), NVTOC=non-volatile total organic carbon.

In some cases, modeling is aimed at identifying the significance of diverse operational and water quality parameters controlling the formation of DBPs or at investigating the kinetics for their formation. Predictive modeling for DBPs consists of establishing empirical and mechanistic relationships of water quality and operational parameters with the prevailing levels of DBPs at various stages after the water treatment. The studies in the last two decades has been aimed principally at linking DBP concentrations (mainly THMs) with dissolved organic matter (TOC or DOC), (UV-254), pH, temperature (T), bromide ion (Br-), chlorine dose (D) and reaction time of residual chlorine (t). Longer reaction time generally leads to higher consumption of residual disinfectant and results in more formation of DBPs. This is one of the major reasons for the generally higher DBP concentrations observed in the extremities of water distribution systems compared to the finished water at treatment plants (Sadiq and Rodriguez, 2004).

However, recent research suggests that some chlorinated DBPs such as HAAs may degrade in extremities of distribution systems. The pH effects on DBP formation vary for different by-products. For example, in general THM formation increases with an increase in pH but the effects are reversed for HAA. Temperature has a positive effect on DBP formation potential, and increases the rate of reaction. Classically, models are used to identify the relative significance of water quality (NOM indicators, bromine, pH, etc.) and operational variables (disinfectant dose, water temperature, contact time, etc.) responsible for the formation of DBPs (Sadiq and Rodriguez, 2004)

CHAPTER THREE: OBJECTIVE OF THE STUDY

3.1. General Objective

To evaluate the effectiveness of Coagulation and activated carbon adsorption in removal of Disinfection by-product precursor's from natural water.

3.2. Specific Objectives

To assess the effect of Moringa stenopetala dosages on DBP precursors and turbidity removal

To evaluate the effectiveness of activated carbon adsorption for reducing DBP precursors

To predict the THMFP of coagulation and activated carbon adsorption treated water samples

CHAPTER FOUR: METHODS AND MATERIALS

4.1. Experimental Procedures.

The main focus of this work was evaluating and investigating appropriate methods for DBP precursor's removal with minimal generation of by-products. The methods evaluated are subsequent effects of coagulation and adsorption on disinfection by-product precursor's removal using *Moringa stenopetala* coagulant and *Vachellia abyssinica* adsorbent. According to the procedure; first the effect/influence of coagulation on the removal efficiency of DBP precursors was studied. Later these studies were extended to include subsequent effect of activated carbon adsorption. The generalized simple schematic layout of the procedure is shown in Fig.3 below.
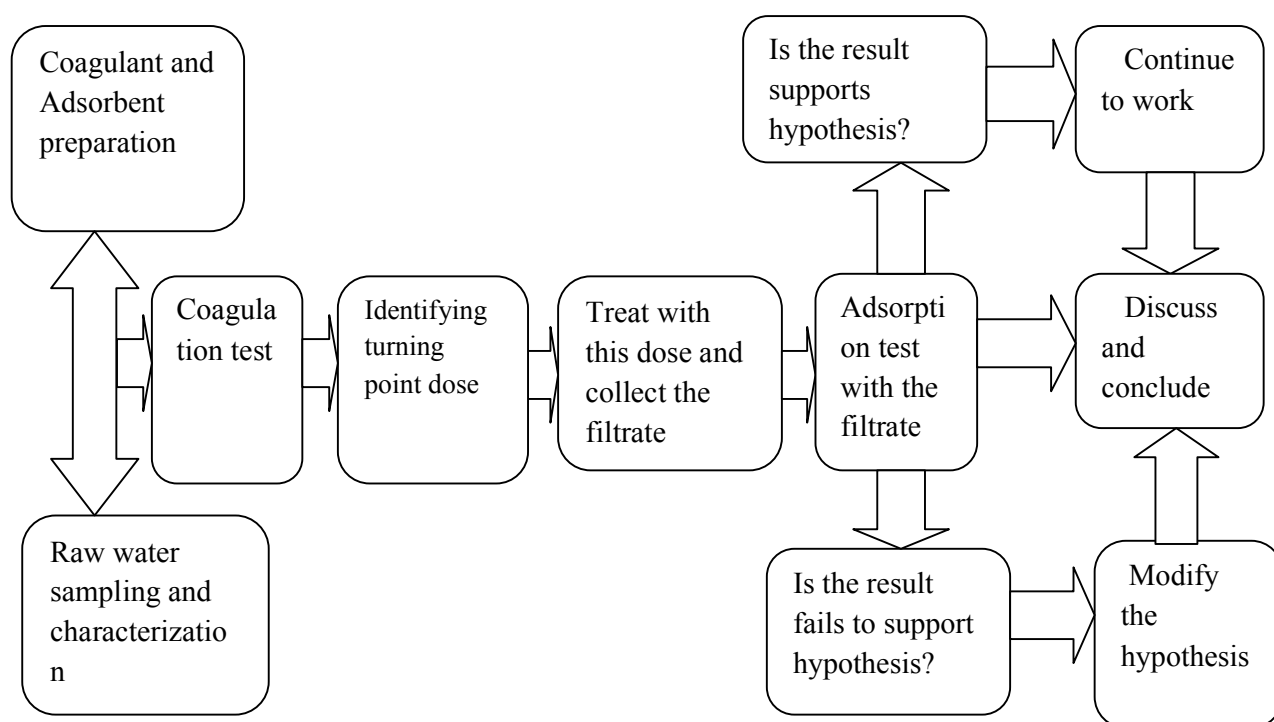

Figure 3.Simple schematic layout of the experimental process

It is clear from the Figure that the water sample for adsorption test was collected from the filtrate/supernatant of a coagulant dose that indicated point of diminishing return for coagulation study and the filtrate was prepared for subsequent adsorption test.

4.2. Sampling Procedure and Analytical Methods

Water samples were collected from surface source, particularly in rivers for study purpose and added 1mL of phosphoric acid (H_3PO_4) was added for preservation and stored with polyethylene bottles. Then the water sample was characterized for DOC, SUVA, and UVA along with pH, turbidity and alkalinity both in raw and treated samples.

Turbidity and pH were directly measured by turbidity meter and pH meter respectively, and alkalinity was determined by standard titration method. However, DOC and UVA are measured according to (USEPA, 2005) standard procedure, using DR 5000 spectrophotometer at 254 nm absorbance.

THMFP was estimated by model equation to predict THMs formation based on water quality parameters and Laboratory controlled conditions:

$$TTHM = 14.6(pH)^{1.01}(D)^{0.206}(UV)^{0.849}(t)^{0.306} \text{ ----------------------------- (1)}$$

Where: TTHM = total trihalomethane (µg/L), D = Chlorine dose (mg/L), UV = ultraviolet absorbance (cm^{-1}), t = reaction time (168hr) and pH of 3 (Sadiq and Rodriguez, 2004; Fujii et al., 1998)

The chlorine dose (D) of each sample prior to TTHM prediction was determined based on inorganic and organic demand of each samples by the formula:

$$[Cl_2] = \{3 \times [DOC] + 7.6 \times [NH_3]\} \text{ ------------------------------------ (2)}$$

Ammonia concentration of each sample was determined by direct Nesslerization method. The procedure employs direct Nesslerization of each water sample, reacting 25mL of each sample with 1mL Nessler reagent for 1 minute, then measurement of solution color against a blank on a spectrophotometer at 425 nm (Fujii et al., 1998; Ngatia, 2010).

Potassium hydrogen phthalate ($C_8H_5O_4K$) and ammonium chloride (NH_4Cl) solutions were used for standardization and calibration of spectrophotometer instrument for DOC and ammonia measurements, respectively (USEPA, 1995).

4.3. Coagulation test using moringa stenopetala

The mature fruits of *Moringa stenopetala halakko* were collected from Arbaminch, Ethiopia and prepared according to (Michael Lea, 2010) standard procedure. The fruit pods cracked and the seeds were plucked out, then dried and grinded to 0.5 mesh size and this fine powder was directly used as coagulant. The doses of the coagulant for the treatement were selected as 10, 20, 30, 40 and 50 mg/L. Then, in accordance with (ASTM,2008) standard procedure the multiple stirrers of jar test apparatus at the flash mix speed of approximately 120 rpm for 20 minutes was operated and settled for 1 hour. After settling the supernatant of treated water samples from each jar was collected for turbidity measurement and the coagulated supernatant of treated water samples was filtered through $0.7\mu m$ filter to determined, DOC, SUVA, UV_{254nm} and STHMFP.

4.4. Adsorbent preparation and Subsequent adsorption test

The *Vachellia abyssinica* (adsorbent) was collected, crushed in to small peices, washed with water and dried under sunlight. The dried material was carbonized in furnace electrically heated at $500^{0}C$ for 4h, cooled to room temperature. Finally, the carbonized sample was immersed in 50% phosphoric acid (H_3PO_4) solution and leached with distilled water to pH =6 and dried at $110^{0}C$ for 12hr and sieved to 0.5 mesh size (Nageswara et al., 2011; Jagtoyen et al., 1993; Rajeshwar et al., 2012**)** and this powder is directly applied as follows.

The Adsorption experiment was conducted with a wide range of adsorbent/DOC concentration based on (ASTM, 2008) standard procedure. The activated carbon dosage was adjusted as 0.01, 0.02, 0.04, 0.10 and 0.20g in100mL of the water sample and the samples were allowed to be shacked on the water bath at 120rpm for 1 hour contact time, and filtered through $0.7\mu m$ filter for DOC, UVA, SUVA and STHMFP determination.

The water sample for adsorption test was obtained after pre-treating with 20mg/L Moringa stenopetala and the filtrate was prepared for adsorption study.

4.5. Data analysis and interpretation

The finding was quantitatively analyzed by statistical software, SPSS version.21.

4.6. Data quality management

To avoid any positive error carbon free reagent water was used. For Spectrophotometric measurements, blank sample readings were checked every time after each sample where a non-zero for a blank indicated need for cell cleaning, or variation in the spectrophotometer response caused by heating since it was being used over a long time.

4.7. Dissemination of the study

Final findings of the study were submitted to Jimma University, college of public health and medical science, department of environmental health science and technology.

4.8. Ethical Considerations

Ethical issue was considered in all steps of this research and academic honest was kept throughout the study.

4.9. Limitation of the Study

The significant impact of using natural coagulants as a pretreatment for adsorption has not been addressed and quantified because of limited capacity in providing solutions for this problem

4.10. Study area and period

The study was conducted in Jimma University, college of public health and medical science, department of Environmental health science and technology laboratory from September to April/2014.

CHAPTER FIVE: RESULTS AND DISSCUSSION

5.1. Characteristics of Raw water

Table 4.Presents average results of raw water characteristics. All measurements in this thesis were done with three replicates and mean value was taken for quantification.

Table 4.Characteristics of Raw water

Parameters	Mean	Standard deviation
PH	7.05	0.2
Alkalinity(mg/L) as $CaCo_3$	10.1	1.3
Turbidity(NTU)	27.25	0.95
Ammonia(mg/L)	1.4	0.55
DOC(mg/L)	36.63	2.0
$UV_{254nm}(cm^{-1})$	0.535	0.02
SUVA(L/mg-m)	1.392	0.007
Chlorine demand(mg/L)	128.58	7.9
TTHMFP(µg/L)	431.66	21.4
STHMFP(µg/mg)	11.220	0.235

As seen from Table 4.this source water has almost neutral pH (~ 7), low alkalinity (<60mg/L) and high DOC concentration (>10mg/L). From the table it is also observed that the source water has low SUVA values (< 2). Specific ultraviolet absorbance (SUVA) is defined as the UV absorbance of a water sample at a given wavelength normalized for DOC concentration and SUVA has shown to be a useful parameter for estimating the DOC content in aquatic systems (ASTM, 2008; USEPA, 2010).Analytical techniques to fractionate organic matter are very complex and expensive, and this makes it impossible to routinely monitor parameters to control coagulation at the drinking water plants, and the concept of SUVA was therefore developed as an indicator of the nature and reactivity of NOM and the effectiveness of coagulation in removing DBP precursors.

The SUVA (aromatic portion of DOC) was calculated from DOC and UVA:

$$SUVA = \frac{UVA}{DOC} \times 100 \text{ -- (3)}$$

SUVA values less than 2 indicate the organic matter of low molecular weight; SUVA values between 2 and 4 indicate a mixture of low and high molecular weight organics and SUVA values higher than 4 show the presence of high molecular weight (USEPA, 2010; Garcia, 2011; Weishaar et al., 2003).

5.2. Removal of disinfection by-product Precursors by Coagulation

In the coagulation study it is found that the results of variation in NOM precursors as a function of coagulant dose were presented in Table 5.

Table 5.Results of coagulation test

Parameters	Coagulant doses(mg/L)				
	10	20	30	40	50
Turbidity(NTU)	25.90±1.6	23.60±2.2	21.14±2.3	21.37±3.4	25.67±1.2
Ammonia(mg/L)	1.77±0.3	1.77±0.3	2.05±0.4	2.15±0.3	2.30±0.5
DOC(mg/L)	36.13±4.4	35.96±3.3	34.67±4.8	30.21±6.4	26.82±4.78
UV_{254nm}(cm$^{-1)}$	0.503±0.05	0.500±0.03	0.483±0.05	0.424±0.07	0.383±0.05
SUVA(L/mg-m)	1.390±0.00	1.389±0.0	1.390±0.01	1.392±0.02	1.395±0.02
Chlorine demand(mg/L)	122.97±12.3	121.19±10.23	119.72±14.2	105.18±11.2	97.93±13.9
TTHM(µg /L)	404.66±20.0	403.16±20.3	389.70±24.5	339.87±18.9	306.20±13.5
STHMFP(µg/mg)	11.187±0.00	11.156±0.03	11.172±0.01	11.250±0.03	11.420±0.08

The absorbance of Ultraviolet radiation at 254nm by natural water is a good indicator of the concentration of NOM (as DOC) in water. The results of this measurement as a function of Moringa stenopetala coagulant dose is presented in Fig 4.It can be seen that the DOC concentration decreases with as the coagulant dose increases.

The mean value of SUVA in this source water is 1.392 L/mg-m (Table 4.) and SUVA values of treated water as a function of coagulant dose are reported in Fig 5.

In Fig 6.Specific trihalomethane formation potential (STHMFP) is sketched as a function of coagulant dose. As shown there the decrease in STHMFP appears to track the removal of UV absorbing substances and they were reduced at lower dose of Moringa stenopetala dose.
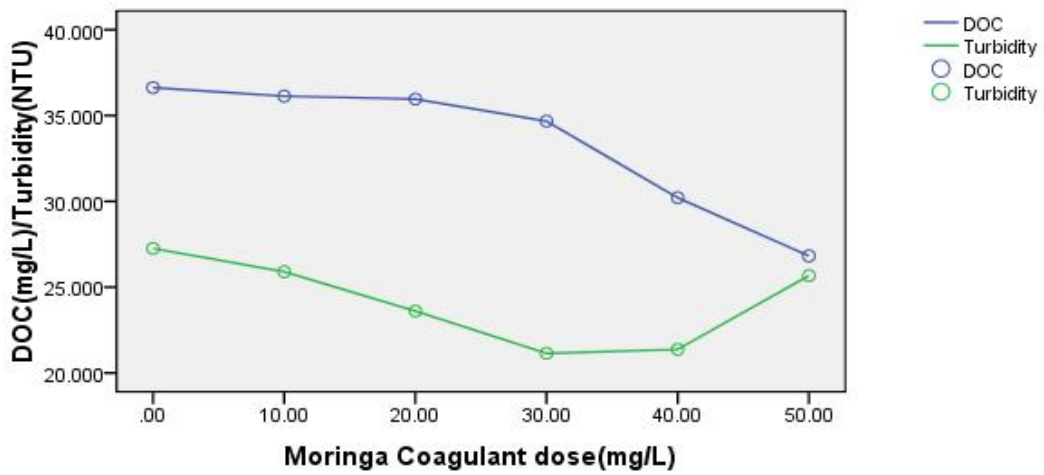
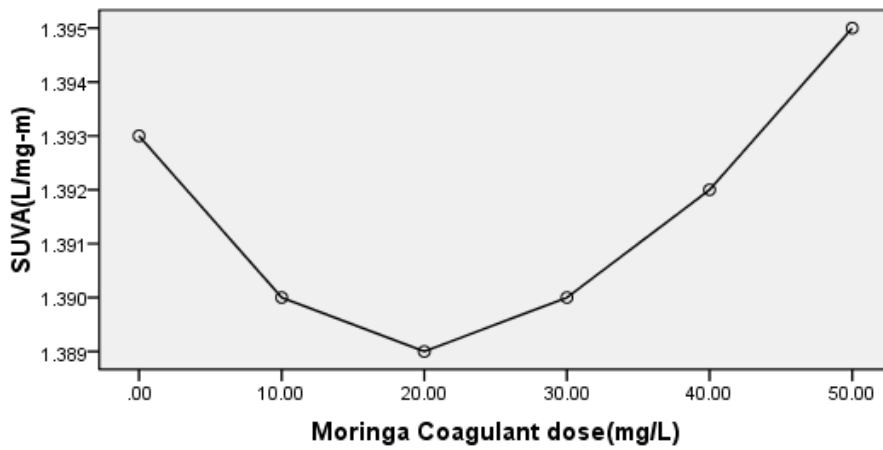Figure 4.Residual DOC and Turbidity remaining as a function Moringa stenopetala doses

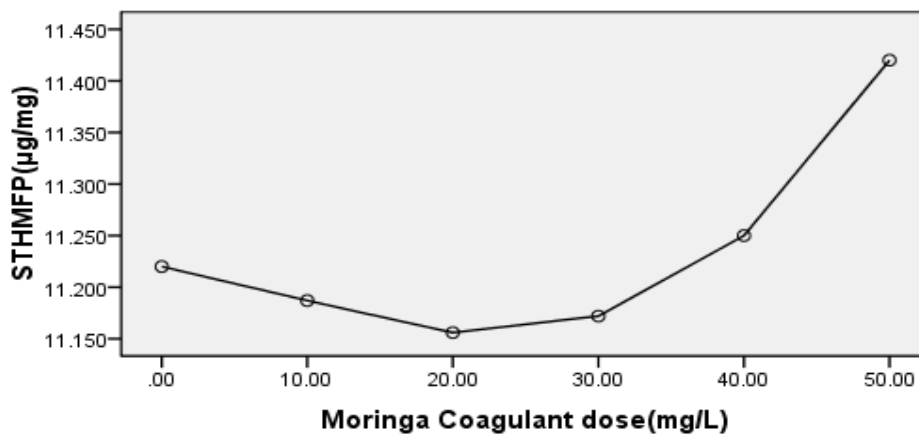Figure 5.The SUVA remaining as a function of Moringa stenopetala dose

Figure 6. STHMFP as a function of Moringa stenopetala dose

The initial dose of Moringa stenopetala (10mg/L) reduced the turbidity concentration only by 4.94% as shown in Fig 4.As the Moringa stenopetala dose increased further, the reduction in DOC and turbidity also increased gradually and maximum removal of turbidity (22.4%) was observed at 30mg/L and was the point of diminishing return for turbidity. However, no point of diminishing return was observed for DOC within the whole range of coagulant dose. This is fairly consistent with the finding suggested by (Mesdihigana et al, 2005) the concentration of coagulant added to remove organic matter should be proportional to the bulk concentration of organic matter present in water. The improvement observed on the performance of DOC removal at higher coagulant dose is due to higher removal of transphilic and hydrophilic acid fractions and this being explained its higher charge density. This tells us that coagulation is a charge driven process and the electrical character of NOM was noted as the key defining factor in the efficacy of coagulation (Bond et al, 2009)

The increase in turbidity for doses above 30mg/L is due to destabilization of destabilized colloidal particles. which are associated with higher residual turbidity occurred or it is common that the particles are destabilized by small amounts of hydrolyzing particles and that optimum destabilization corresponds with neutralization of the particles size and large amount of coagulants cause charge reversal so that the particles become positively charged as far as natural coagulants considered (Vara,2012).Another most likely explanation for this observation is formation of insoluble colloidal particles and humate precipitates (as DOC is converted to non-settling particulate forms) in the sub micrometer size range. Adsorption of NOM to the colloidal precipitates enhances their colloidal precipitates and thus increases the residual turbidity (Krasner et al., 1995; Edzwald et al., 1999 and Latterman et al., 1999).

An increase in SUVA concentration was observed as coagulant dose increases (Fig 5).The probable factor for this increase in SUVA in agreement with the study conducted by (Bina et al., 2009) is formation of high content of basic amine groups in natural coagulants like chitosan may also exhibit similar trends in moringa and results to increase SUVA concentration. As seen from the same graph, increasing the moringa dose doesn't decrease SUVA concentration. On the contrary it starts considerably to increase the SUVA concentration. This result is due the formation of a stable suspension that did not settle, conferring a high concentration of aromatic amine groups absorbing UV radiation to the water (Santos et al., 2010) and this stable suspension is due to formation of insoluble maters and this insoluble matters are active components for coagulation and they cannot dissolve in

water without salt (Okuada et al.,2003).It either forms a part of a salt dissolved in water or it is joined by electrostatic attraction to the surface of negatively charged particles reducing ammonia nitrogen association (Tiyan-yin et al., 2006).Another confirmation is that the SUVA values (1-1.5) coagulation is not effective in removing low UV absorbing fractions of NOM probably for those with smaller MW and more hydrophobic (Mesdagihinia et al.,2005;USEPA,2010;Weishaar et al, 2003).

Fig 6.shows STHMFP versus Coagulant dose, and it is evident that, use of DOC to predict THMFP could lead to considerable error in estimating THMFP, especially at higher DOC concentration. In addition, high correlation between DOC and THMFP would not be expected for samples from less homogeneous areas that contain diverse sources of NOM. However, SUVA (UVA/DOC× 100) and STHMFP (THMFP/DOC) provides an indication of the average potential of the organic carbon in a sample to form THMs, a measure of the potential THM precursors normalized to carbon (Fujii et al., 1998; USEPA, 1999).

In Fig.5 and Fig.6 it is observed that SUVA and STHMFP decrease rapidly up to 20mg/L and then, increase gradually with increased coagulant dose. However as Moringa dose increase to 50mg/L slightly increased concentration of SUVA and STHMFP in the treated water sample was observed. This results show that the benefit of using Moringa coagulant for SUVA values less than 2 is intangible at a higher dosage of the coagulant.

5.3. Subsequent Impact of Activated Carbon Adsorption on the Coagulation

As observed in Fig.5 and Fig.6 above coagulation was found to achieve the highest removal of SUVA and minimum STHMFP at 20mg/L indicating that 20mg/L was point of diminishing return for coagulation test. Therefore for subsequent adsorption test first 1L of the raw water sample was coagulated with 20mg/L *Moringa stenopetala* and 600ml of the supernatant was filtered and analyzed. This filtered supernatant was also treated with *Vachellia abyssinica* activated carbon adsorption and the result of subsequent impact of activated carbon adsorption over that of the coagulation is seen in table 6.

Table 6.Results of subsequent adsorption test

Parameters	Coagulation (20mg/L)	Activated carbon doses(g/100ml)				
		0.01	0.02	0.04	0.1	0.20
Ammonia(mg/L)	1.77±0.3	1.45±0.8	1.20±0.5	0.93±0.5	0.87±0.8	0.80±0.6
DOC(mg/L)	35.96±3.3	20.99±2	21.53±2	21.75±2.7	21.80±2.4	21.82±2.9
$UV_{254nm}(cm^{-1})$	0.500±0.03	0.295±0.03	0.293±0.03	0..291±0.03	0.287±0.03	0.288±0.04
SUVA(L/mg-m)	1.389±0.02	1.361±0.02	1.354±0.02	1.353±0.02	1.352±0.02	1.352±0.02
Chlorine demand(mg/L)	121.19±10.23	73.22±6.7	72.62±3.0	71.67±4.7	71.35±5.0	70.26±4.0
TTHM(μg/L)	403.16±20.3	235.8±12.6	235.07±11	234.32±15	231.04±10.5	229.83±8
STHMFP(μg/mg)	11.156±0.03	11.042±0.018	10.981±0.15	10.970±0.09	10.965±0.25	10.964±0.2

The results from Table 6.Show that subsequent application of activated carbon adsorption has further removed the DOC and SUVA concentration remaining after coagulation effectively, with highest removals occurring at higher carbon doses.
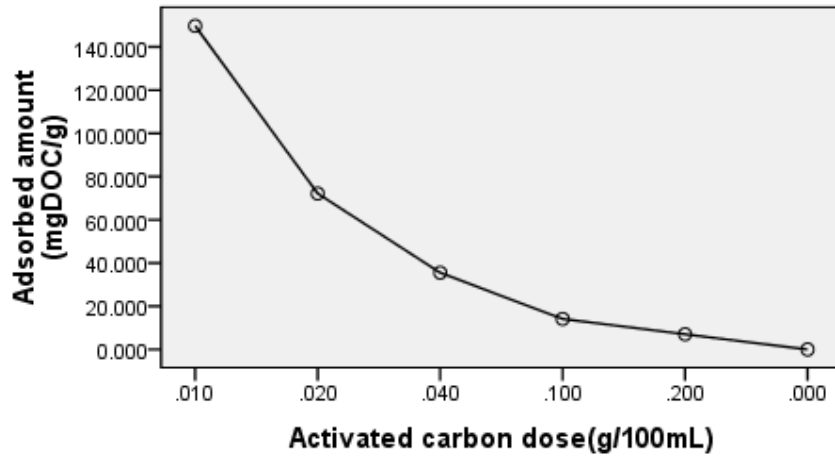
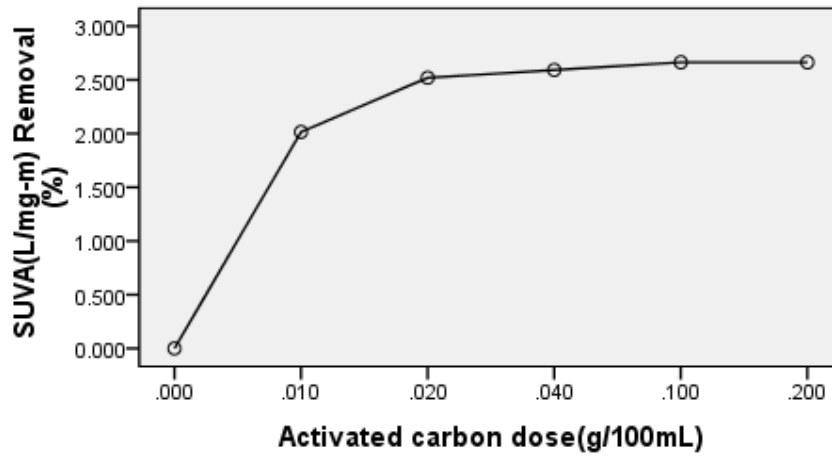Figure 7.Adsorbed amount of dissolved organic carbon (DOC) on activated carbon

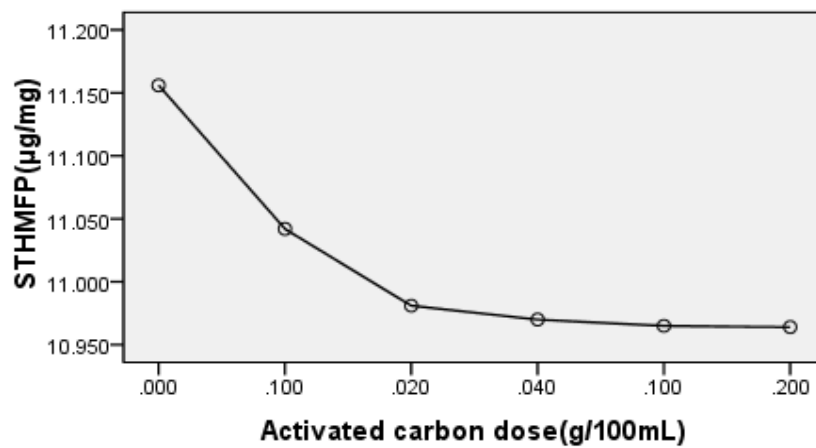Figure 8.Percent SUVA Removal as a function of activated carbon dose

Figure 9.STHMFP as a function of activated carbon dose

When assessed the nature of NOM precursors removed by subsequent adsorption comparing the rate of STHMFP in the coagulation treated and activated carbon treated supernatant,it was found that part of the very reactive component of NOM(i.e SUVA) to form THM wasn't removed sufficiently by coagulation .The residual SUVA and STHMFP in the coagulated water indicate that there is afraction of NOM that was not amenable under coagulation.This is in agreement with the observation made by (Bina et al.,2009) that at higher coagulant concentration,the removal of DOC becomes less sensetive due to destabilization process.On the other hand subsequent application of activated carbon adsorption has improved the removal efficiency on the DOC and SUVA concentration with minimal STHMFP formation potential.The lower DOC,SUVA and STHMFP observed would be the aresult of improved removal of activated carbon adsorption compared to coagulation.

Some researchers like (Babcock and Singer,1979) have indicated that coagulation is effective for organic disinfection by-product precursors.On the contrary (Crozes et al.,1995) suggested that anticipated maximum contaminant level could not met by enhanced coagulation.Recently (Singer and Bilyk,2002) used coagulation combined with ion resin to remove organic matters and disinfection by-product precursors from natural waters and indicated that the combination method was more effective as compared to coagulation alone despite the fact that lower coagulaant doses were used.This result implies that disinfection by-product precursors are better reduced by other mechanisims such as adsorption;hence activated carbon was introduced to reinforce coagulation treatement.

NOM and disinfection by-product precursors are adsorbed by activated carbon depending on concentration and nature of DOC.Because large fraction of NOM can cause pore blockage of activated carbon and result in the decrease of effective adsorption sites (Pelekani and Snoeyink,1999),the coagulation preceeding activated carbon adsorption can prevent the activated carbon from pore blockage by large MW organics .Further more the remaining small MW organics after coagulation/sedimentation process can be expected to be removed by activated carbon adsorption.Fig 7.presents the results of vachellia abyssinica activated carbon adsorption isotherm studies,indicating that per unit gram of DOC uptake decreases with increasing activated carbon(Adsorbent) dose).The plots in Fig 8.and Fig 9.reaffirms the fact that SUVA is greatly reduced with increased carbon dose and the predicted STHMFP was found to be 10.964µg/mg at carbon dose of 0.20g/100mL.

CHAPTER SIX: CONCLUSION AND RECCOMMENDATION

6.1. Conclusion

➢ A lower Moringa stenopetala dosage could reduce the SUVA by small amount. However, the coagulation has its limitation to reduce organics effectively at higher dosage due to destabilization occurred; resulting higher SUVA and STHMFP concentration in the treated water samples.

➢ The results further demonstrate that treated water by Moringa stenopetala coagulant might promote higher DBP formation potential if the dose adjustment was not done.

➢ Secondary treatments' like activated carbon adsorption can improve removal of organic precursors, beyond coagulation alone, thus low STHMFP was expected.

➢ The activated carbon adsorption provides lower STHMFP in the treated water samples.

➢ Thus, the water treated by coagulation followed by adsorption process may provide safe drinking water quality with regard to disinfection by-product formation.

➢ The combination of coagulation and activated carbon adsorption may therefore excellent at removing Organic precursors.

6.2. Recommendation

➢ Coagulant required for efficient removal of organic matter should be proportional to the bulk concentration of organic matter present in raw water, and it must be dosed based on organic matter concentration of the raw water but not on turbidity.

➢ Further study on the removal of organic substances by adsorption with activated carbon subsequent to coagulation should be conducted by quantifying disinfection by-product formed after disinfecting with chlorine or other oxidants.

➢ The influence of secondary compounds like (magnesium, iron, calcium and etc.), which are not responsible for by-product formation but has the influence on activated carbon adsorption capacity should be studied.

➢ The effect of operational parameters such as chlorination, pH, temperature and others should be quantified.

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Appendix

Standardizations and Calibrations

A. Organic Carbon Calibration: Organic carbon primary dilution solution(OC-PDS) was prepared by pouring 500mL of distilled water in 1L volumetric flask and carefully transferring 1.063g potassium hydrogen phthalate,$C_8H_5O_4K$ (equivalent to 0.5g organic carbon or 1.0mg$C_8H_5O_4K$ =0.471mg organic carbon) in to the distilled water and diluting to 1L mark. The standard calibration solution was prepared by transferring a series milliliters of organic carbon primary dilution solution representing 5mg,10mg,20mg,30mg,40mg and 50mg of organic carbon in 100mL of carbon free distilled water(1mL = 0.5mg organic carbon) and the spectrophotometer absorbance was read at 254nm

B. Direct Nesslerization Method: Stock ammonium solution was prepared by dissolving 3.819g anhydrous ammonium chloride (NH_4CL) with small quantity of distilled water in 1L volumetric flask and diluted to the mark(1mL=1.00mgN=1.22mgNH_3).The standard ammonium solution was prepared by diluting 10mL stock ammonium solution to 100mL with distilled water (1mL =10μgN = 12.2μgNH_3). A series of calibration solution representing 5μg, 10μg, 20μg, 30μg, 40μg and 50μg's were prepared by transferring a series of standard ammonium chloride solution to 50mL volumetric flask and diluting to the mark with carbon free distilled water and the standards were Nessrelized by adding 1mL Nessler reagent to each flask with a safety pipet, then stoppered and inverted several times and the spectrophotometer absorbance was read at 425nm,1 minute after adding Nessler reagent

$$mgNH_3= \frac{\underline{μgNH_3} \times 100}{ML \text{ of sample}}$$

C. Nessler Reagent Preparation: Nessler reagent was prepared by dissolving 20g mercuric iodide (HgI_2), 14g potassium iodide (KI) in small quantity of water and this mixture was added slowly, with stirring to a cool solution of 32g sodium hydroxide (NaOH) dissolved in 100mL distilled water, then diluted to 200mL and stored in rubber stoppered borosilicate glassware out of sunlight to maintain reagent stability.