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Application of modified lignocellulosic materials as green flocculants for brewery wastewater treatment

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**APPLICATION OF MODIFIED LIGNOCELLULOSIC MATERIALS AS
GREEN FLOCCULANTS FOR BREWERY WASTEWATER
TREATMENT**

James Joseph Mwesiga

**A Dissertation Submitted in Partial Fulfillment of the Requirements for the Degree of
Master's in Environmental Science and Engineering of the Nelson Mandela African
Institution of Science and Technology**

Arusha, Tanzania

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ABSTRACT

Coagulation–flocculation technique is usually used in wastewater treatment by employing conventional inorganic materials such as alum and ferric chloride. Due to environmental challenges associated with the use of inorganic flocculants, biopolymers are gaining ground as alternative water treatment materials. In the present study, native cellulose and hemicelluloses isolated from sugarcane bagasse were used in the removal of turbidity and biological oxygen demand (BOD) from industrial wastewater. Isolated native cellulose was modified to regenerated cellulose. Also, native cellulose, regenerated cellulose and hemicellulose were carboxymethylated using sodium monochloroacetic acid. Functional groups on the isolated, regenerated, and carboxymethylated biopolymers were examined using Fourier transform infrared spectroscopy (FT-IR) and Carbon (C), Hydrogen (H), Nitrogen (N), Sulfur (S) and Oxygen (O) (CHNS/O) analysis. The degree of substitution for regenerated and carboxymethylated cellulosic materials were measured using recommended standard methods. Carboxymethyl cellulose (CMC) with 1.3 degree of substitution reduced turbidity and BOD by 62.2 and 64%, respectively. Carboxymethyl regenerated-cellulose (CMC-II) at 1.1 degree of substitution reduced turbidity and BOD by 55.6 and 60%, respectively. Carboxymethyl hemicellulose (CMH) with 1.4 degree of substitution was capable of reducing turbidity and BOD by 45.7 and 47%, respectively. Carboxymethylcellulose and hemicellulose have rarely been used in the treatment of brewery wastewater. In the present study, these two novel materials showed a good prospect for application in water and wastewater treatment.

Keywords: Green flocculants; brewery wastewater; industrial wastewater; lignocellulosic materials; cellulose carboxymethylation.

DECLARATION

I, James Joseph Mwesiga, do hereby declare to the Senate of the Nelson Mandela African Institution of Science and Technology that this dissertation is my own original work and that it has neither been submitted nor being concurrently submitted for degree award in any other institution.

James Joseph Mwesiga

Name and signature of candidate

Date

The above declaration is confirmed

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Name and signature of supervisor 1

Date

Professor Elena Kalmykova

Name and signature of supervisor 2

Date

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CERTIFICATION

The undersigned certifies that they have read and hereby recommend for acceptance by the Nelson Mandela African Institution of Science and Technology a dissertation entitled; *“Application of modified lignocellulosic materials as green flocculants for brewery wastewater treatment”* in partial fulfillment of the requirements for the degree of Master’s in Environmental Science and Engineering of the Nelson Mandela African Institution of Science and Technology.

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DEDICATION

I dedicate this work in the lovely memory of my late father, Mr. Joseph Rwezaura Kasilingi.

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LIST OF ABBREVIATIONS AND SYMBOLS

1 MCA	Carboxymethylation process using 2 g of Na-chloroacetate
2 MCA	Carboxymethylation process using 4 g of Na-chloroacetate
3 MCA	Carboxymethylation process using 6 g of Na-chloroacetate
AGU	Anhydrous sugar unit
BOD	Biological oxygen demand
CMC	Carboxymethyl cellulose
CMC-II	Carboxymethyl regenerated cellulose/carboxymethyl cellulose-II
CMH	Carboxymethyl hemicelluloses
COD	Chemical oxygen demand
DNA	Deoxyribonucleic acid
DS	Degree of substitution
FT – IR	Fourier transforms infrared spectroscopy
KOH	Potassium hydroxide
MCA	Sodium chloroacetate (Na-chloroacetate), carboxymethylation agent
NaOH	Sodium hydroxide
RC	Regenerated cellulose
RNA	Ribonucleic acid
rpm	Revolution per minute
TDS	Total dissolved solids
TSS	Total suspended solids

CHAPTER ONE

INTRODUCTION

1.1 Background of the Problem

Recently, wastewater management has become a world problem due to industrialization, population increase and urbanization. Globally, industrialization has led to the discharge of a large volume of wastewater, that if not well managed might cause negative impacts to human as well as ecosystem health (Wang & Yang, 2016). The release of untreated and partially treated wastewater from industries increases the extent of organic and inorganic pollution of aquatic ecosystems (Miao *et al.*, 2015).

In many African countries, industries do release untreated wastewater to the natural receiving environment. In Tanzania, for example, industries usually claim that the available wastewater treatment technologies are expensive (Mashauri *et al.*, 2000). Moreover, most industries prefer treatment techniques that would give monetary benefits to their enterprise (Shete & Shinkar, 2013). Nevertheless, most industries might opt to release untreated wastewater to the environment mainly because of: a) Disposal challenges of the sludge obtained after treatment, b) Poor environmental policy on the emerging contaminants discharging standards e.g. pharmaceutical wastewater, and c) Lack of enforcement of existing laws and policies (Ashfaq *et al.*, 2017).

Before wastewater effluents are discharged to the natural environment, physico-chemical and biological conditions should be monitored. Contaminant levels being monitored must comply with both international and local regulatory guidelines. Environmental contaminants of concern in industrial wastewater include, but are not limited to: a) Chemical oxygen demand (COD), b) Total dissolved solids (TDS), c) Turbidity, d) High biological oxygen demand (BOD), e) High total suspended solids (TSS), f) Heavy metals, and g) Various organic constituents (Akpor & Muchie, 2011).

Coagulation and flocculation are the most applied processes in the treatment of industrial wastewater to achieve removal of BOD, TSS, TDS, turbidity and many other contaminants due to its simplicity and effectiveness's (Teh *et al.*, 2016). Conventional coagulants or flocculants used are aluminum sulfate (alum), ferrous chloride and ferric chloride. Unfortunately, these conventional treatment practices are linked to many disadvantages e.g. causing of diseases, secondary pollution and are non-biodegradable (Tzoupanos & Zouboulis,

2008). Thus, the search for alternative methods to replace inorganic chemical methods is of paramount importance.

In the present study, cellulose and hemicellulose materials from sugarcane bagasse were chemically modified to carboxymethyl cellulose (CMC), carboxymethyl cellulose-II (CMC-II) and carboxymethyl hemicelluloses (CMH), respectively; and were applied in the treatment of brewery wastewater.

1.2 Statement of the Problem

The applications of inorganic coagulants/flocculants in wastewater treatment are not advisable by most researchers. The reason behind that is because most of the researched inorganic flocculants are associated with environmental, ecological and economic challenges. For example, alum-based coagulants have been linked to the development of Alzheimer's disease and senile dementia disease (Sinha & Mathur, 2016). Also, both iron and alum based inorganic coagulants have been reported to be insufficient in removing heavy metals and emerging organic contaminants such as pesticides, pharmaceutical products, personal care products and plasticizers (Adeleye *et al.*, 2016; Tang *et al.*, 2016). Furthermore, it was found that iron-based coagulants e.g. ferric chloride (FeCl_3) have the effect of worsening the effluent color after treatment, hence secondary pollution (Xu *et al.*, 2016). Not only that but also, all inorganic coagulants are non-biodegradable leading to land pollution (Freitas *et al.*, 2015). Consequently, special attention has shifted towards using biodegradable polymers that are more eco-friendly and less hazardous (Kumar & Christopher, 2017).

1.3 Rationale of the Study

The global rapid growth in industrialization has caused an increase in industrial pollution through discharging untreated wastewater to the environment (Belhaj *et al.*, 2015). Coagulation-flocculation technique based on the use of inorganic coagulants is one of the best available techniques used in the treatment of industrial wastewater. Various studies have reported the downside of these techniques including the development of large quantities of biodegradable sludge as well as their inability to remove heavy metals and emerging organic contaminants (Khan & Malik, 2014; Ashfaq *et al.*, 2017). Thus, there is a great need to develop novel and alternative coagulants i.e., organic flocculants to address these and other eco-socio-economic challenges. Organic flocculants have been reported to be bio-degradable; could be a proper replacement of the conventional chemicals used in the coagulation-flocculation processes (Freitas *et al.*, 2015). Furthermore, precursors of organic flocculants

have functional groups that can be substituted or modified with other functional groups that would interact with specific pollutants in a wastewater treatment system (Pettignano *et al.*, 2019).

1.4 Research Objectives

1.4.1 General Objective

The general objective of this study was to investigate the application of carboxymethylcellulose, carboxymethyl cellulose-II and carboxymethyl hemicelluloses as possible green flocculants in treating brewery wastewater.

1.4.2 Specific Objectives

The specific objectives of the present study were:

- (i) To extract, modify and characterize the extracted and modified glycans (cellulose-II, carboxymethyl cellulose, carboxymethyl hemicelluloses and carboxymethyl regenerated cellulose-II).
- (ii) To apply carboxymethyl hemicelluloses, carboxymethyl cellulose, and carboxymethyl cellulose-II as flocculants for BOD and turbidity removal from brewery wastewater.

1.5 Research Questions

- (i) How are the characteristics of extracted and modified bio-molecules similar to the bio-molecules found in literature data?
- (ii) How efficient are carboxymethyl hemicelluloses, carboxymethyl cellulose, and carboxymethyl cellulose-II in removing biological oxygen demand and turbidity from brewery wastewater?

1.6 Significance of the Study

The results of this research could be useful to the society, industry, policy making authorities and even the academia to emphasize a shift from conventional inorganic wastewater treatment technologies to greener alternatives. The present study was set to investigate the synthesis and possible application of modified bio-molecules (CMC, CMC-II, and CMH) as green flocculants from low-cost sugarcane bagasse waste materials.

The synthesized and modified flocculants were utilized in treating brewery wastewater and the study focused on: a) Turbidity and removal efficiency of the synthesized and modified bio-flocculants, b) A possibility of minimizing secondary environmental toxicity, and c) The cost-effectiveness of the produced materials in comparison to conventional inorganic coagulants. These materials indicated a good performance in removing BOD and turbidity from brewery wastewater. Due to the organic nature of the materials, the present study proposes the same to be used to replace conventional coagulants for reasons of conserving both environmental and human health.

1.7 Delineation of the Study

The present study aimed at the application of modified biopolymers as green flocculants for brewery wastewater treatment. This was achieved by, first, isolating hemicelluloses and native cellulose from sugarcane bagasse that was collected from TPC Sugar Factory in Moshi, Tanzania. This was followed by modification of isolated native cellulose to regenerated cellulose. Furthermore, the solubility of hemicellulose, native cellulose and regenerated cellulose was enhanced by modification of the hydroxyl functional groups using monochloroacetic acid. The effectiveness of the modification process was confirmed by using Attenuated Total Reflection Fourier transform infrared spectroscopy (ATR FT-IR) and Carbon (C), Hydrogen (H), Nitrogen (N), Sulfur (S) and Oxygen (O) elemental analyzer (CHNS/O).

The last part of this study was the application of CMH, CMC and CMC-II as the green flocculants for removing turbidity and BOD from brewery wastewater. To this end, the present study has successfully applied waste material as agents in the flocculation-coagulation process.

CHAPTER TWO

LITERATURE REVIEW

2.1 Worldview of the Industrialization Impacts

The global population now stands at approximately 7.7 billion; it is estimated that it will increase to between 9.6 billion in 2050 and 12.3 billion in 2100 (Lutz & Samir, 2010). In East Africa, the population is about 400 million and in Tanzania it is about 60 million (Worldometers, 2021). Population growth is a known driver of industrial growth due to the increase in product demand and the creation of more jobs (Zhou, 2009; He *et al.*, 2016).

Likewise, the increase in industrialization is accompanied by the increase of industrial wastewater that is generated as a by-product in industrial processes. This wastewater, if not well managed, might cause negative impacts on the natural and pristine environs of the world (Wang & Yang, 2016). Industrial wastewater categories depend on many factors some of which are: The type of source industry and the kinds of associated pollutants. Examples may include: Winery wastewater, oil refinery wastewater, pulp and paper production wastewater, pharmaceutical wastewater, agrochemical wastewater, textile wastewater and food processing wastewater (Vymazal, 2009). Regardless of their source and content, industrial wastewater must be well treated before being released to the receiving environs or before the water is considered safe for secondary uses (Sarkar *et al.*, 2006).

2.2 Brewery Wastewater

Brewery wastewater is usually produced from production and cleaning (washing) units. It consists of salts, starch, proteins, muddy and hence it's rich in turbidity and biological oxygen demands (Feng *et al.*, 2008). In Africa, Tanzania ranks 8th in brewery industry, howbeit, it only has two large and one small brewery plants (Nassary & Nasolwa, 2019). Despite having few brewery plants in Tanzania, wastewater generated must be monitored and treated before being discharged to the nearby environments. The brewery industry uses large quantities of clean water to generate a bulky amount of wastewater. The wastewater generated from brewery activities may sometimes contain hazardous chemicals creating a need for wastewater to be treated before being discharged to the environment (Enitan *et al.*, 2015). There are various methods available for brewery wastewater treatment. Choice of a suitable method depends on the wastewater characteristics and purpose of treatment (Simate *et al.*, 2012). In the present study, the raw brewery wastewater was collected from Tanzania Breweries

Limited, at the Arusha plant on which the treatment efficiency of modified glycans was studied.

2.3 Wastewater Treatment

Various wastewater treatment technologies have been adopted based on cost-effectiveness and treatment effectiveness to meet stipulated standards to avoid discharging of untreated effluents to the environment (Mulchandani & Westerhoff, 2016). Depending on the types of pollutants generated by industrial engagements, various conventional methods and techniques are available for managing such wastewaters. Some of the available methods are adsorption, constructed wetlands, photo-degradation, evaporation, electro-precipitation, membrane separation, ion exchange membrane and coagulation-flocculation technologies (Yargıç *et al.*, 2015). Various studies have been conducted on some of these methods for wastewater treatment that came out with good results. For example, the adsorption – destruction technique was applied in the treatment of hexamine-containing industrial wastewater. The treatment process that was based on adsorption and catalytic oxidation was capable of reducing hexamine in the form of total organic carbon by 57% (Zamani *et al.*, 2014).

Moreover, the adsorption technique was also coupled with ion-imprinted polymeric technology hence found to be very useful for the extraction of specific ions from the wastewaters (Rajabi *et al.*, 2013; Shamsipur *et al.*, 2013). But also, various studies have reports on the use of catalytic photo-degradation technique for wastewater treatment e.g., citric acid was used to prepare graphene quantum dots as a catalyst for photo-degradation of cationic dye-based organic pollutants (Roushani *et al.*, 2015). Similarly, electro precipitation technique has been reported by some studies to be a very effective method for wastewater treatment (Boye *et al.*, 2005). For example, chromium and some organic pollutants were removed from tannery wastewater by effective utilization of electro-precipitation based on an electrochemical membrane batch reactor (Kongjao *et al.*, 2007).

Similarly, membrane separation technique is widely applied for wastewater treatment due to its simplicity and low energy cost (Ravanchi *et al.*, 2009). On the other hand, a membrane separation method was coupled with the adsorption technique for the effective treatment of palm oil wastewater effluents (Azmi & Yunus, 2014). However, the coagulation-flocculation processes based on chemical enhancement techniques are widely applied for wastewater treatment especially for those wastewaters that are not amenable to biological processes (Semerjian & Ayoub, 2003).

Coagulation-flocculation techniques are mostly opted for the treatment of industrial wastewater due to their low cost and ease of operation (Liang *et al.*, 2014). Figure 1 describes how the coagulation-flocculation techniques are applied in industrial wastewater treatment. The coagulation-flocculation processes in industrial wastewater treatment are applied as pre-treatment, post-treatment or main treatment processes due to their flexibility and multipurpose applicability (Szyguła *et al.*, 2009).

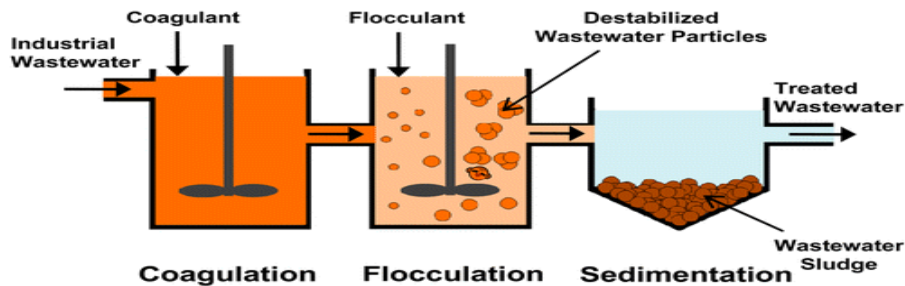


Figure 1: Coagulation-flocculation process (Teh *et al.*, 2016)

Conventionally, the technique usually employs the use of metal coagulants that are divided into two categories: a) Aluminum coagulants i.e. aluminum chloride (AlCl_3), alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$), and sodium aluminate (NaAlO_2) and b) Iron coagulants i.e. ferric chloride sulfate (ClFeO_4S), ferrous sulfate (FeSO_4), ferric chloride (FeCl_3) and ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$) (Teh *et al.*, 2016). On the other hand, iron coagulants are the best inorganic coagulants compared to aluminum coagulants due to their low toxicity and high efficient (Ghafari *et al.*, 2009).

However, some literatures have reports of the drawbacks and challenges associated with the use of inorganic coagulants. The use of aluminum coagulants i.e., alum have been reported to result into health many concerns. For example, if used in high doses in treating wastewater the residual aluminum ions may lead to the development of Alzheimer's disease (Renault *et al.*, 2009; Sinha & Mathur, 2016).

Moreover, it is well known that wastewater treatment using conventional inorganic coagulants results in the production of a large volume of sludge that acts as a secondary pollutant requiring costly management and disposal. Hence, it poses a difficulty in handling and disposal to the environment, the non-biodegradability problem (Ahmad *et al.*, 2016). It has been reported that this treatment method is ineffective to remove emerging contaminants such as pharmaceuticals and pesticides (Adeleye *et al.*, 2016). Also, conventional aluminum and iron-based coagulants have shown poor performance in removing heavy metals from industrial

wastewater (Tang *et al.*, 2016). Iron-based coagulants especially ferric coagulants have limited applicability due to its tendency of exacerbating effluent color (Xu *et al.*, 2016).

Ultimately, alternative coagulants/flocculants have to be used in coagulation-flocculation processes to remove the stated shortcomings of inorganic coagulants. The organic raw materials (biopolymers) either in their natural or modified state might be a good approach towards green wastewater treatment.

2.4 Biopolymeric Applications

There is a variety of naturally occurring polymers available for different applications. Biopolymers are derivative of polysaccharides i.e. amylopectin, polynucleotides i.e. DNA and RNA, polyphenols, proteins and special polymers from fungi, bacteria, plants and animals (Kaplan, 1998). Biopolymers contain varieties of functional groups such as the amylopectin structure (Fig. 2), which are available for modification that also offer many features to make them more useful. Biopolymers have attracted great attention in the scientific community due to their unique advantages that consist of excellent biodegradability, cost-effectiveness, availability and eco-friendliness (Mousa *et al.*, 2016).

Recently, biopolymers are being applied in different areas of science and technology. For example, proteins i.e. collagen, silk and albumin are widely used in biomedical research due to their biocompatibility (Reddy *et al.*, 2015). Moreover, proteins (enzymes) and starch (amylopectin) were physically modified under hydrostatic pressure and temperature to be used in food industry with improved shelf life (Knorr *et al.*, 2006). Polysaccharides i.e., amylose, gear gum and pectin are being modified to increase their hydrophobicity to be used as polymer-drug conjugates and matrix agents in medical and pharmaceutical fields (Vandamme *et al.*, 2002).

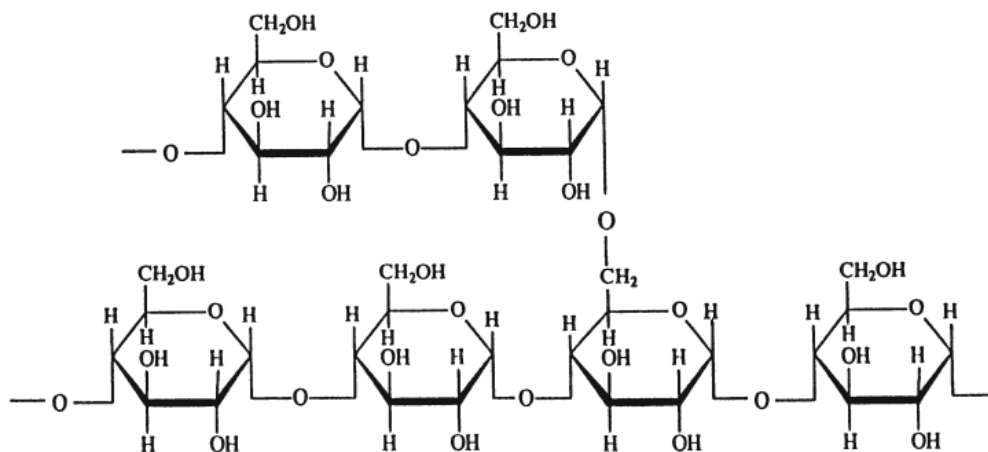


Figure 2: Amylopectin structure (Kaplan, 1998)

Furthermore, polysaccharides such as agar and carrageenan from red algae have very useful practical application as gelling and stabilizing agents in food technology (Usov, 2011). Moreover, the water-insoluble polysaccharides i.e., chitin and cellulose can be modified to water-soluble chitosan and cellulose derivatives, respectively. Increasingly, these modified polysaccharides are being used in water and wastewater treatment as the green flocculants (Kanmani *et al.*, 2017).

2.4.1 Chitosan and its Applications

Chitosan is a linear homopolysaccharide of D-glucosamine and N-acetyl D-glucosamine originated from deacetylation of chitin (Kurita, 2006). Chitosan is a biopolymer obtained by alkaline deacetylation of chitin, another biopolymer and the second most abundant biomass after cellulose (Renault *et al.*, 2009). The main sources of chitin include insects, crustaceans (crabs and shrimps), and fungi. The presence of numerous amino groups on its chemical structure as illustrated on Fig. 3 makes chitosan easy to solubilize.

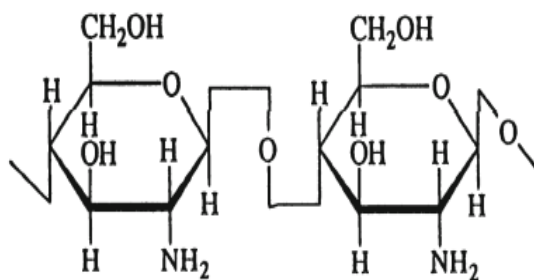


Figure 3: Chitosan structure (Kaplan, 1998)

Due to its solubility and degree of substitutions chitosan is widely preferred for industrial applications compared to cellulose and other native biomolecules (Roberts, 1992; Rinaudo, 2006). Chitosan is very useful in agriculture as it is used as a growth promoter and stimulates plant immunity (Abdel-Mawgoud *et al.*, 2010; Boonlertnirun *et al.*, 2017). Moreover, in pharmaceutical and medicinal fields, chitosan and chitin derivatives are utilized as excipients and drug carriers (Bansal *et al.*, 2011). This is due to the physico-chemical characteristics that allow them to easily release the drugs compared to their conventional commercial counterparts (Kato *et al.*, 2003). Also, the composite of chitosan and clay was successfully prepared and used as an adsorbent for wastewater treatment (Chang & Juang, 2004). Furthermore, another composite prepared from nano-hydroxyapatite and chitosan was applied for removing 92% Cd ions from wastewater (Salah *et al.*, 2014). Although chitosan has been extensively studied and used by researchers, cellulose has not received a similar level of attention (Kanmani *et al.*, 2017).

2.4.2 Cellulose in Research: A Background

Cellulose is a homopolysaccharide natural polymer consisting of a linear chain of several hundred to many thousands of β -(1, 4)-linked D-glucose units. Its sugar units are oriented in parallel direction linked through inter and intermolecular hydrogen bonds (Fig. 4) (Mousa *et al.*, 2016). Cellulose is the most abundant biopolymer and is the structural component of all vegetative plants and other living organisms i.e., acetobacter and algae (Fan *et al.*, 2012; Wang *et al.*, 2012). Cellulose is extracted to its pure native form by various methods and techniques such as alkaline extraction, acid hydrolysis, chlorination and bleaching (Morán *et al.*, 2008). For instance, nanocrystals of cellulose were extracted from *Pandanus tectorius* leaves by alkali and bleaching methods (Sheltami *et al.*, 2012). About 40 to 45% of dry substances in the biomass are the cellulosic materials. Globally, its production is around 11^{11} to 10^{12} tons per year (Holtzapple & Benjamin, 2003; Zhao *et al.*, 2007). Most of the properties of cellulose depend on its crystallinity and the degree of polymerization that ranges from 500 to 15 000 (Hall *et al.*, 2010).

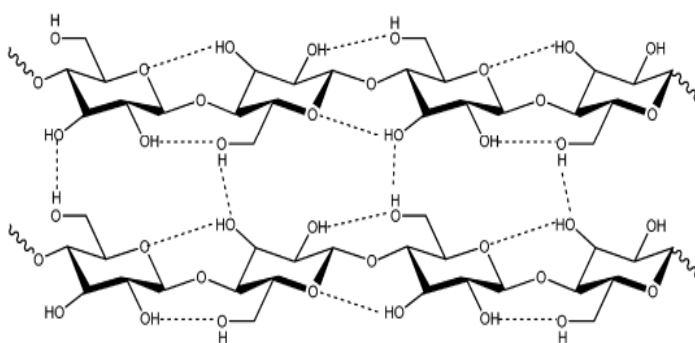


Figure 4: Cellulose structure (Wang *et al.*, 2012)

Cellulose is odorless, insoluble in either dilute alkali, acid or in water. It can be broken down to glucose monomers by treating it with strong alkali and acid, a process aided by heat. Even though the insolubility of cellulose in various solvents makes it easier to be obtained from lignocellulosic materials, this property hinders its application in various fields (Ghebreselassie, 2013). Cellulose that results from both the crystalline and amorphous cellulosic residues through the crystalline region is the most abundant one (Andersson *et al.*, 2003). The crystallinity results of nuclear magnetic resonance (NMR) and x-ray diffraction (XRD) portray that cellulose exists in four amorphous forms which are: Cellulose I, II, III, and IV.

Additionally, cellulose I which is described as a native form of cellulose exists as monoclinic cellulose (I_{α}) and triclinic cellulose (I_{β}). Triclinic cellulose (I_{β}) is mostly found in microorganisms while monoclinic cellulose (I_{α}) is found in higher plants (Mittal *et al.*, 2011).

When native cellulose is treated with dry liquid ammonia, cellulose III₁ is obtained as a product. But, when regenerated cellulose or cellulose II for liquid ammonia treatment, the reaction might be reversible hence the polymorph produced is termed as cellulose III₂. Nevertheless, when cellulose (III₁ or III₂) is heated, they lead to the production of cellulose (IV₁ or IV₂), through a reversible reaction. Furthermore, cellulose II is obtained by alkali treatment while regenerated cellulose is obtained by the mercerization process both of which form a perpendicular orientation of microfibrils (Zugenmaier, 2008). The overall description of cellulose polymorphs is provided in Fig. 5.

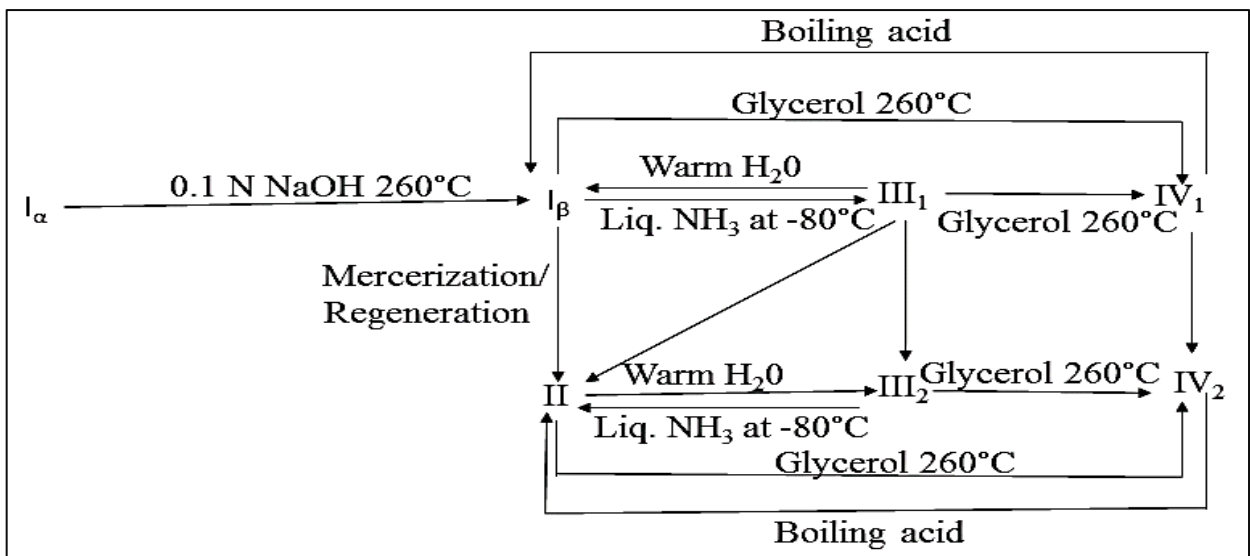


Figure 5: Cellulose polymorphs conversions (Zugenmaier, 2008)

Of recent, the use of cellulose and its derivatives (cellulosic biomolecules) for wastewater treatment has become a topic of intense research (Singha & Guleria, 2014). Hyperbranched polyethyleneimine-grafted cellulose demonstrated good performance as a natural flocculant at a relatively low dosage of 3 g/L and a wide pH range, with high removal efficiencies (Zhang *et al.*, 2018). Similarly, the modified cellulose nanocrystals grafted with N, N (dimethylamine) ethyl methacrylate, 4-Vinylpyridine and polyamine demonstrated the best performance on the flocculation of organic colloids of industrial wastewater effluents (Zhou, 2015). Moreover, carboxymethyl cellulose that was prepared from native cellulose, was effectively used as a coagulant in the treatment of industrial effluents that actively reduced various types of parameters such as conductivity, TDS, COD and turbidity at the lowest dose of 70 mg/L at a neutral pH (Ali *et al.*, 2013). Not only native cellulose but also cellulose-II and hemicelluloses have recently shown some interesting applications in various fields of science and technology.

2.4.3 Regenerated Cellulose, its Derivatives and their Applications

Native cellulose has limited applications due to its strong inter and intra hydrogen bonding hence poor solubility in water and most other solvents (Li *et al.*, 2012). This tendency makes it difficult for chemical modification of cellulose, hence converting natural cellulose to regenerated cellulose which has improved properties was found to be much necessary (Pang *et al.*, 2014).

Regenerated cellulose has been pointed out by various researchers for having improved properties compared to native cellulose. This may be due to the perpendicular orientation of microfibrils in cellulose-II as compared to parallel orientations on native cellulose (Dinand *et al.*, 2002). Cellulose-II is produced from the mercerization of native cellulose under alkaline condition that result in the rotation of D-glucose residue about the glycosidic bond. Thus, reduced cohesion with an increased amorphous region with greater accessibility to alkali for increased reactivity in anionic reactions (Marks, 2015). Also, regenerated cellulose can be prepared from molten salt hydrates such as zinc chloride tetrahydrate ($\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$) and lithium bromide (LiBr) (Pang *et al.*, 2014).

There is reduced crystallinity or increased solubility of cellulose-II as compared to native cellulose, due to the location of hydroxyl groups in the equatorial position of glucopyranose rings (Liu *et al.*, 2015). The hydroxyl groups corresponds to (1-10) orientation of the respective miller index determined by X-Ray diffraction method, hence regenerated cellulose is more soluble than native cellulose under similar conditions (Yamane *et al.*, 2006).

Moreover, regenerated cellulose and its derivatives have important applications in science and technology. For example, the graphene composite fibers prepared through chemical modification of regenerated cellulose were found to have improved thermal and mechanical properties when applied as thermal insulation materials (Tian *et al.*, 2014). Furthermore, regenerated cellulose was recently modified to oxidized regenerated cellulose and used as bactericidal filler in food technology (Sezer *et al.*, 2016). Also, regenerated cellulose has been widely utilized as an emulsion stabilizing and rheology agent for oil-in-water dispersion system (Hu *et al.*, 2016).

Furthermore, the derivative of regenerated cellulose i.e., regenerated cellulose coated with diethylenetriamine was used as a membrane for ultrafiltration of wastewater containing heavy metals (Pb^{2+}) (Madaeni & Heidary, 2011). Thus, little information is available on the application of regenerated cellulose and its derivatives in various fields of science and technology. Therefore, in the present study, regenerated cellulose was carboxymethylated to

carboxymethyl regenerated cellulose and applied as green flocculants for brewery wastewater treatment.

2.4.4 Hemicelluloses and their Applications

Hemicelluloses are the group of polysaccharides i.e., xylan, xyloglucan, glucoman and mannans found in plant cell walls together with cellulose and lignin (lignocellulosic) (Scheller & Ulvskov, 2010). Hemicellulose, unlike cellulose, consists of glycans that have an amorphous structure with a low degree of polymerization (80 – 200). Moreover, hemicelluloses contain monomers of hexoses (mannose, glucose and galactose), pentoses (arabinose and xylose), and hexuronic acids (glucuronic acid) (Werner *et al.*, 2014). The sugar unit which occurs in large proportion in the secondary cell wall is the one that determines the name of the hemicellulose. For example, the primary cell wall of hardwood contains 15 – 30 % of xylan hence named glucuronoxylans (Gírio *et al.*, 2010; Scheller & Ulvskov, 2010). Various methods and techniques are available for the extraction of hemicelluloses from lignocellulosic materials. These methods include water, alkali, ultrasonic, microwave-assisted and steam explosion extractions (Peng *et al.*, 2012). Recently, researchers have shown great interest in the use and application of hemicelluloses and their derivative in various fields (Yao *et al.*, 2017).

The hydrolysates (monomers) of hemicelluloses i.e. mannose, glucose, xylose, arabinose and galactose can be altered to biofuel (bioethanol) and other useful chemicals such as furfural, xylitol and levulinic acid (Carvalho *et al.*, 2006). Furthermore, it can be chemically modified to other biopolymers and still find important applications. Modified biopolymers of hemicelluloses are used as gelling, coatings, adhesives, viscosity-enhancing in food, pharmacy and other related industries uses (Ebringerová, 2005). Usually, the free and available hydroxyl functional group in hemicellulose structure i.e., those indicated in Fig. 6 are the promising site for chemical modifications.

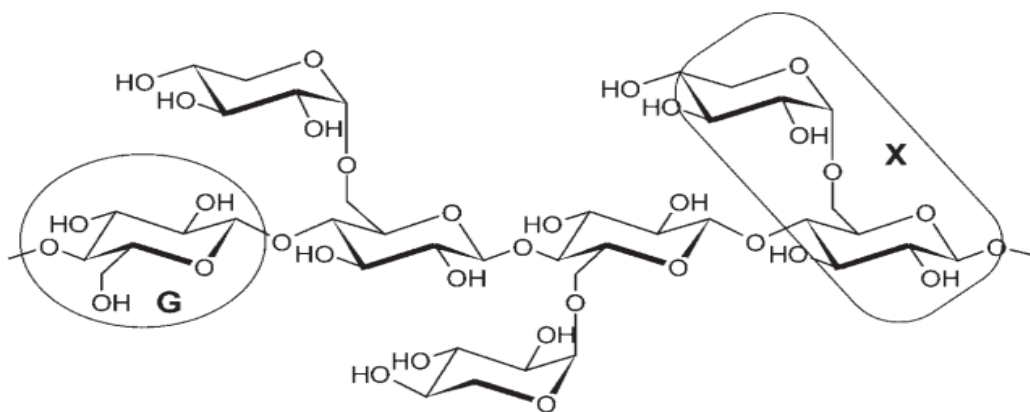


Figure 6: Primary structure of hemicelluloses D-xylo- D-glucan (XG) (Ebringerová, 2005)

In the present study, isolated hemicelluloses, regenerated cellulose as well as native cellulose were carboxymethylated to their respective derivatives and used as flocculants for brewery wastewater treatment.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Site

The present study was based on treating wastewater that was obtained from Tanzania Breweries Ltd (TBL), Arusha Plant, Tanzania. Currently, the Company's principal activities are; the production, distribution and sale of non-alcoholic malt beverages, malt beer, and alcoholic fruit beverages in Tanzania and nearby countries. The extraction and subsequent modification of bio-molecules (CMC, CMC-II and CMH) was carried out at the NM-AIST laboratories and some characterization of modified bio-molecules was done at the University of Dar es Salaam in the Chemistry Laboratory.

3.2 Precursor Materials

In the present study, sugarcane bagasse was used as the main precursor for obtaining native cellulose and hemicellulose. It was used because it has good lignocellulosic composition for cellulose and hemicellulose ranging from 40 to 50% and 25 to 35%, respectively (Sun *et al.*, 2004). Sugarcane bagasse was collected from the TPC Sugar Factory in Kilimanjaro, Tanzania.

3.3 Chemicals and Reagents

The selection of chemicals and reagents to be used in this study was based on their availability and took into account the possible negative impacts to human health and the environment. All the chemicals and reagents used in the present study i.e., sodium monochloroacetic acid ($\text{Cl-CH}_2\text{COONa}$), isopropyl alcohol ($\text{CH}_3\text{CHOHCH}_3$), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), hydrochloric (HCl), potassium hydroxide (KOH), sulfuric acid (H_2SO_4), and sodium hydroxide (NaOH) were of analytical grade.

3.4 Methods

3.4.1 Preparation of Holocellulose from Sugarcane Bagasse

The collected sugarcane bagasse was pretreated by washing following drying in an oven at 45°C for 48 hours before being ground and sieved. Holocellulose material was prepared from treating ground sugarcane bagasse (15 g) of 250 μm pore size with sodium chlorite (4.5 g) in which the mixture was acidified using dilute acetic acid to a pH of 3.8. The mixture was

inserted in the water bath for 4 hours with a simultaneous addition of 4.5 g of sodium chlorite after every hour at a constant agitation at a temperature of 75 °C for delignification process (Siqueira *et al.*, 2013).

3.4.2 Preparation of Native Cellulose and Hemicelluloses

Native cellulose was obtained by isolating hemicelluloses from holocellulose using 10% potassium hydroxide (KOH) at a ratio of 1:20 holocellulose against KOH, respectively for 10 hours with constant agitation at room temperature. The alkaline hemicelluloses were then filtered to remain with alkaline residues of native cellulose which was neutralized with few drops of 10% hydrochloric acid (HCl) and freeze-dried (Peng *et al.*, 2010). In addition, neutralized hemicellulose solution was dialyzed using a dialysis membrane to remove potassium chloride (KCl) and concentrated with hand air dryer before being subjected to alcohol precipitation. Isopropyl alcohol was used as the precipitating agent to obtain hemicellulose precipitates from neutralized hemicellulose-containing solution. Moreover, a 2:1 (v/v) ratio of isopropyl alcohol to hemicellulose solution was used. The hemicellulose precipitates were obtained following a 12-hour sedimentation (Zhang *et al.*, 2018). Finally, the isopropyl alcohol was removed by decantation followed by freeze-drying to remove residual alcohol.

3.5 Material Modifications

The freeze-dried isolated cellulose and hemicellulose were carboxymethylated, while some of the cellulose was regenerated before being carboxymethylated.

3.5.1 Preparation of Regenerated Cellulose

The regenerated cellulose was prepared via a green modification process that involved the addition of 2 g of native cellulose in a SCHOTT DURAN[®] laboratory glass bottle (100 mL). In the same bottle appropriate amount of solution-mixture of urea, sodium hydroxide and distilled water in the ratio of 12:7:81(v/v), respectively were added. The dissolved mixture was re-crystallized using a water solution of 0.5 M of sulfuric acid to form regenerated cellulose crystals. The regenerated cellulose crystals were separated from mixture through centrifugation process under 1000 rpm for 10 minutes (Qi *et al.*, 2009).

3.5.2 Preparation of Carboxymethyl Cellulose, Regenerated Cellulose and Hemicelluloses

In the present study, the carboxymethylation process was accomplished by varying the ratio of sodium monochloroacetic acid against a constant concentration of the initial glycan type (Petzold *et al.*, 2005). Approximately, 2 g of cellulose, regenerated cellulose, and hemicelluloses were separately put into three different SCHOTT DURAN[®] laboratory glass bottles (50 mL). Into each bottle 10 mL of 25% sodium hydroxide was added drop-wise while stirring for 30 minutes; then about 40 mL of isopropyl alcohol was added and the mixture and agitated for 30 minutes at room temperature (23°C). Furthermore, 2 g of sodium monochloroacetic acid was added in each bottle before raising the temperature to 65°C for 71 minutes, to mark the end of 1:1 sodium monochloroacetic acid against glycan concentration's first experiment. Finally, after the stated time of 1:1 first experiment, another 2 g of sodium monochloroacetic acid was added to account for 2:1 sodium monochloroacetic acid against glycan concentration's second experiment. The same procedure was repeated for 3:1 of the third experiment. Eventually, the carboxymethylated glycans were filtered and the residual suspended in 150 mL of methanol (CH₃OH) for 12 hours. Lastly, the mixture was neutralized with diluted acetic acid and filtered, freeze-dried, and finally activated in an oven at a temperature of 70°C for 7 hours (Ali *et al.*, 2013).

3.6 Determination of the Degree of Substitution

3.6.1 Determination of Degree of Substitution for Carboxymethyl Cellulose and Regenerated Cellulose

For carboxymethyl cellulose and regenerated cellulose, into 250 mL beakers, 5 g of each CMC and CMC-II was added separately. Thereafter, 150 mL of HNO₃ – methanol (1:1) v/v was added in all beakers followed by shaking. This mixture was then left to stand for 3 hours. Excess acid in the mixtures was removed by a 70% solution of methanol, and all neutralized samples were freeze-dried for 12 hours. In separate clean 250 mL conical flasks, 1.2 g of each freeze-dried sample was added followed by 120 mL of deionized water and 18 mL of 1 M NaOH. The mixture was then titrated against 1 M HCl. Finally, the DS of CMC and CMC-II were determined using Equations 1 and 2 adopted from Candido and Gonçalves (2016) and (Toğrul & Arslan, 2003):

$$DS = (0.162 * A) - (0.058 * A) \quad (1)$$

$$A = \frac{[(B * C) - (D * E)]}{F} \quad (2)$$

where A is an equivalent weight (g) of sodium hydroxide required per gram of CMC or CMC-II, B is volume of NaOH (mL), C is molarity of NaOH (M), D is volume of HCl solution (mL), E is molarity of HCl (M) and F is the weight of CMC or CMC-II.

3.6.2 Determination of Degree of Substitution for Carboxymethyl Hemicelluloses

(i) Purity of Carboxymethyl Hemicelluloses

About 0.3 g of modified carboxymethyl hemicelluloses (CMH) was added in a beaker (250 mL) containing 6 mL of distilled water followed with gentle stirring. In the same flask, 6 mL of 1 N hydrochloric acid (HCl) was added and the mixture was agitated for about 10 minutes for its complete dissolution. Also, three drops of phenolphthalein indicator were added while stirring until the red color formed. Furthermore, 50 mL of 95% ethanol was put in portions in the same mixture while stirring. In the meantime, another 100 mL of ethanol was added, while stirring and mixture was left for 15 minutes to settle. After that stated time the supernatant was filtered and discarded (Ren *et al.*, 2008). The remaining precipitates were washed up four times with 80% ethanol, and finally with 95% ethanol then dried in an oven at 105°C for 4 hours and re-weighed.

(ii) Degree of Substitution

The acidometric titration method was used for the determination of the degree of substitution for CMH. In this manner, 0.1 g of CMH was weighed and added into a conical flask (100 mL) next to the addition of 25 mL distilled water and mixture agitated for 10 minutes. Then 0.05 M NaOH was added drop-wise in the same flask until the pH of the solution reached 8. Then 0.05 M H₂SO₄ was used to titrate the solution until the pH dropped to 3.74. Thereafter, Equations (3 - 5) were employed for the quantification of the degree of substitution:

$$a = \frac{m'}{m} \quad (3)$$

$$B = \frac{2 * M * V}{a * m} \quad (4)$$

$$DS = \frac{0.132 * B}{1 - 0.08 * B} \quad (5)$$

where: a is purity of CMH used, m' is mass of CMH after purification, m is mass of CMH before purification, M is molarity of H_2SO_4 used, V is volume (mL) of H_2SO_4 used during titration and B is mmol/g of H_2SO_4 consumed per gram of CMH.

3.7 Material Characterization

3.7.1 Fourier Transform Infrared Spectroscopy

The characterization of glycans before and after modification was analyzed based on the functional group identification via attenuated total reflection Fourier transform infrared spectroscopy (ATR FT-IR) technique. The Infrared Spectroscopy (Bruker Alpha) model with the resolution of 2 cm^{-1} and spectral range from 500 to 4000 cm^{-1} was used to analyze the samples. Before the analysis, the ATR crystal was cleaned using a smooth tissue dipped in acetone, then the background was allowed to run for 2-4 minutes. Finally, a small amount of the sample was placed on the ATR crystal, and the anvil was allowed to contact the sample for measurements.

3.7.2 Elemental Analysis

The elemental analysis for the determination of carbon (C), hydrogen (H), and oxygen (O) before and after carboxymethylation of cellulose, hemicellulose and regenerated cellulose was carried out using Thermo scientific Flash 2000 elemental analyzer (CHNS/O) with a thermal conductivity detector (TCD). Helium was used as the carrier gas and oxygen was used as the combustion gas during the analysis of carbon and hydrogen.

3.8 Solubility Test

Onto three clean glass plates, a small amount of carboxymethylated glycans (CMH, CMC, and CMC-II) under different modification ratios was separately added. Thereafter, about 2 to 3 drops of distilled water were added onto each plate (Khiari *et al.*, 2010).

3.9 Application of Carboxymethyl Glycans for Industrial Wastewater Treatment

Approximately, 10 L of raw wastewater was sampled, transported and stored according to standard methods and protocols (American Public Health Association [APHA], 2017). The physical characteristics i.e., pH, conductivity, total dissolved solids (TDS), dissolved oxygen (DO) and temperature were determined on-site using the HI-9829 multi-parameter (Hanna Instruments, Italy). Turbidity was also determined on site using a HIS3703 microprocessor

turbidimeter, while biological oxygen demand (BOD) was quantified in the laboratory using the OxiTop BOD device at room temperature.

3.9.1 Turbidity and Biological Oxygen Demand Removal Efficiency Experiments

Wastewater was neutralized from a pH of 11.94 to 7.00 using 0.5 M HCl. The neutralized raw wastewater (100 mL) was added into a 200 mL beaker then separated into different smaller beakers. Thereafter, carboxymethyl cellulose, regenerated cellulose and hemicelluloses were added to account for the concentration of 70 to 130 mg/L. Furthermore, the mixture of wastewater and modified glycan in a beaker was fast stirred at 600 rpm for 5 minutes then slowly stirred at 200 rpm for another 15 minutes (Hassan *et al.*, 2009). Analysis for the turbidity and biological oxygen demand was conducted after 30 minutes of settling. Respective removal efficiencies were calculated using Equation (6). It should, however, be noted that analysis was carried out only by varying flocculant concentrations at a constant pH accompanied by stirring and followed by a settling time (Pérez *et al.*, 2007).

$$\text{Removal efficiency (\%)} = \frac{p_i - P_f}{p_i} \times 100 \quad (6)$$

where: p_i is the initial concentration in mg/L and P_f is final concentration after treatment also in mg/L for BOD and NTU for turbidity.

3.9.2 Why Turbidity and Biological Oxygen Demand?

Turbidity and BOD were chosen as the endpoints to test the efficiency of the modified glycans because of the three main factors: a) The availability of the instruments to be used during the experiments at the NM-AIST laboratory, b) Turbidity and BOD are among the primary indicators of the extent of wastewater pollution, and c) Time limitations. Although the present study focused on turbidity and BOD, there is a need to extend it to other environmental pollution indicators. As such, this has been recommended in Chapter 5.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Brewery Wastewater Characterization

From the results presented in Table 1, wastewater was significantly loaded with contaminants; it needed to be treated before being discharged to the receiving environment. This was evidenced through the observations of biological oxygen demand and pH that was higher than those recommended by the Tanzania Bureau of Standards (TBS).

Table 1: Characterization of sampled brewery wastewater Tanzania Bureau of Standards (2006)

S/N	Parameter	Measured value	Unit	Permissible discharge Limit
1.	pH	11.94	NIL	6.50 – 9.0
2.	EC	0.054	μ /cm	Not available
3.	TDS	11.70	mg/L	1200
4.	Temperature	34.70	$^{\circ}$ C	25 – 35
5.	Turbidity	112	NTU	300
6.	DO	3.00	mg/L	30
7.	BOD	1950	mg/L	30

4.2 Characteristics of Native Cellulose and Hemicelluloses

The lignin materials were removed from sugarcane bagasse through a pretreatment process to obtain holocellulose. The native cellulose was obtained by successful isolation of hemicelluloses from holocellulose by a method stated in the experimental part above. Successful isolation of both native cellulose and hemicelluloses was confirmed by the FTIR technique (Łojewska *et al.*, 2005; Peng *et al.*, 2010) (Fig. 7). The hydroxyl (—OH) functional group occurs in hemicelluloses as a flat curve band with absorbance ranging from 3375.90 to 3364.25 cm^{-1} while in cellulose it occurs as a pointed curve band on the absorbance of 3330.25 cm^{-1} . The band at 892.41 cm^{-1} in the hemicellulose spectra is associated with the presence of xylose residuals which is missing in the cellulose spectra. The strongest peak at the absorbance of 1600.67 cm^{-1} which is seen in hemicelluloses spectra and slightly seen in cellulose spectra is due to the adsorbed water molecule. Hence hemicellulose molecules due to their chemistry adsorbed more water molecules compared to cellulose molecules (Olsson & Salmén, 2004).

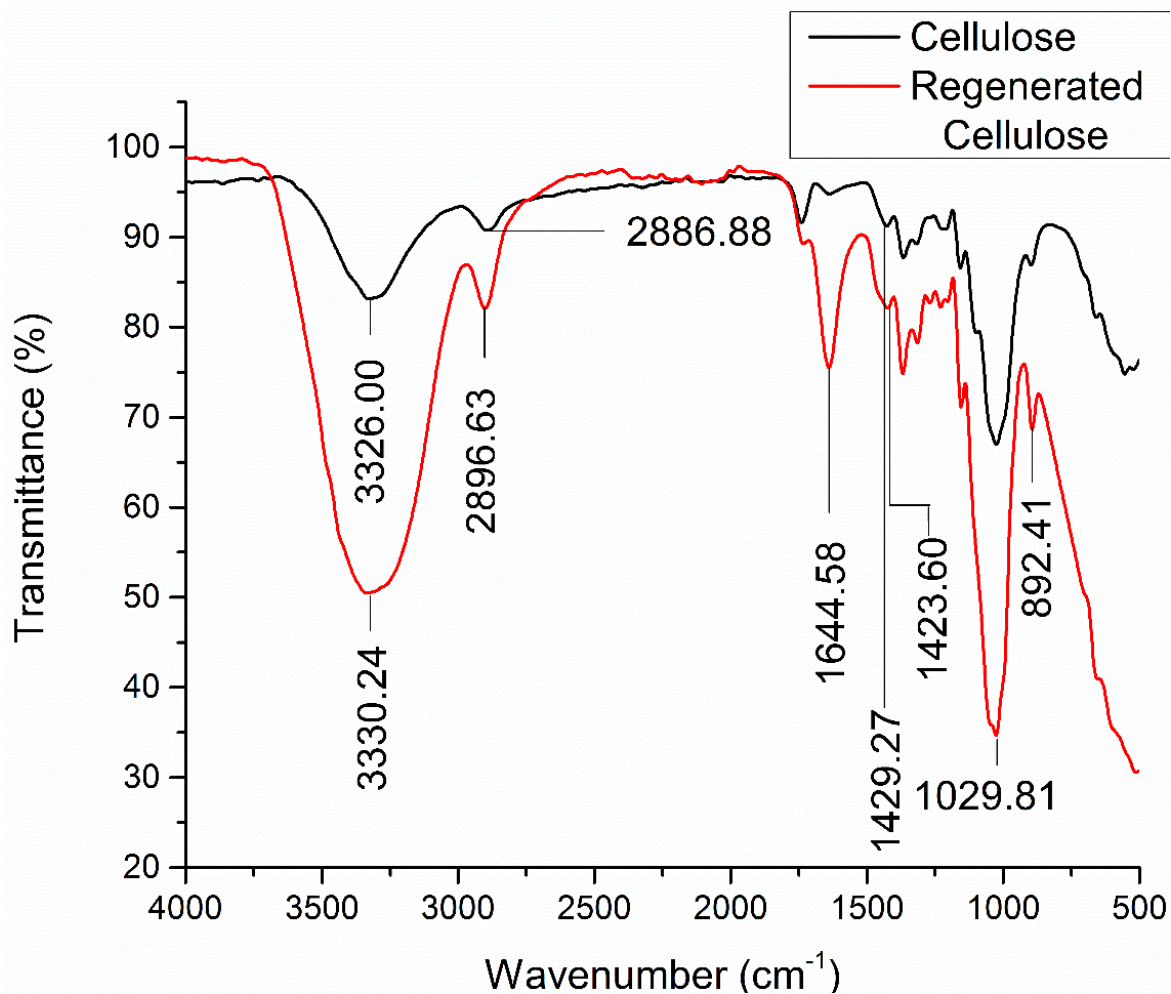


Figure 7: Fourier Transmission-Infra Red spectra of native cellulose (black line) and hemicelluloses (red line)

4.3 Effects of Material Modifications

4.3.1 Characterization of Regenerated Cellulose against Native Cellulose

Hydrogen bonds resulted from native cellulose were probably of intramolecular hydrogen bonding due to the parallel orientation of glucose molecules (Lee *et al.*, 2013). It follows, therefore, that a few hydroxy functional groups were exposed causing absorption of infrared radiations at lower absorbance with low transmittance (Hishikawa *et al.*, 2017). Hydrogen bonds that resulted from regenerated cellulose had inter-hydrogen bonds due to anti-parallel orientation of glucose molecules (Koochaki *et al.*, 2020). Henceforth, the highest number of hydroxy functional groups were highly exposed at infrared radiations with high absorbance and transmittance range compared to those of native cellulose (Zhang *et al.*, 2005).

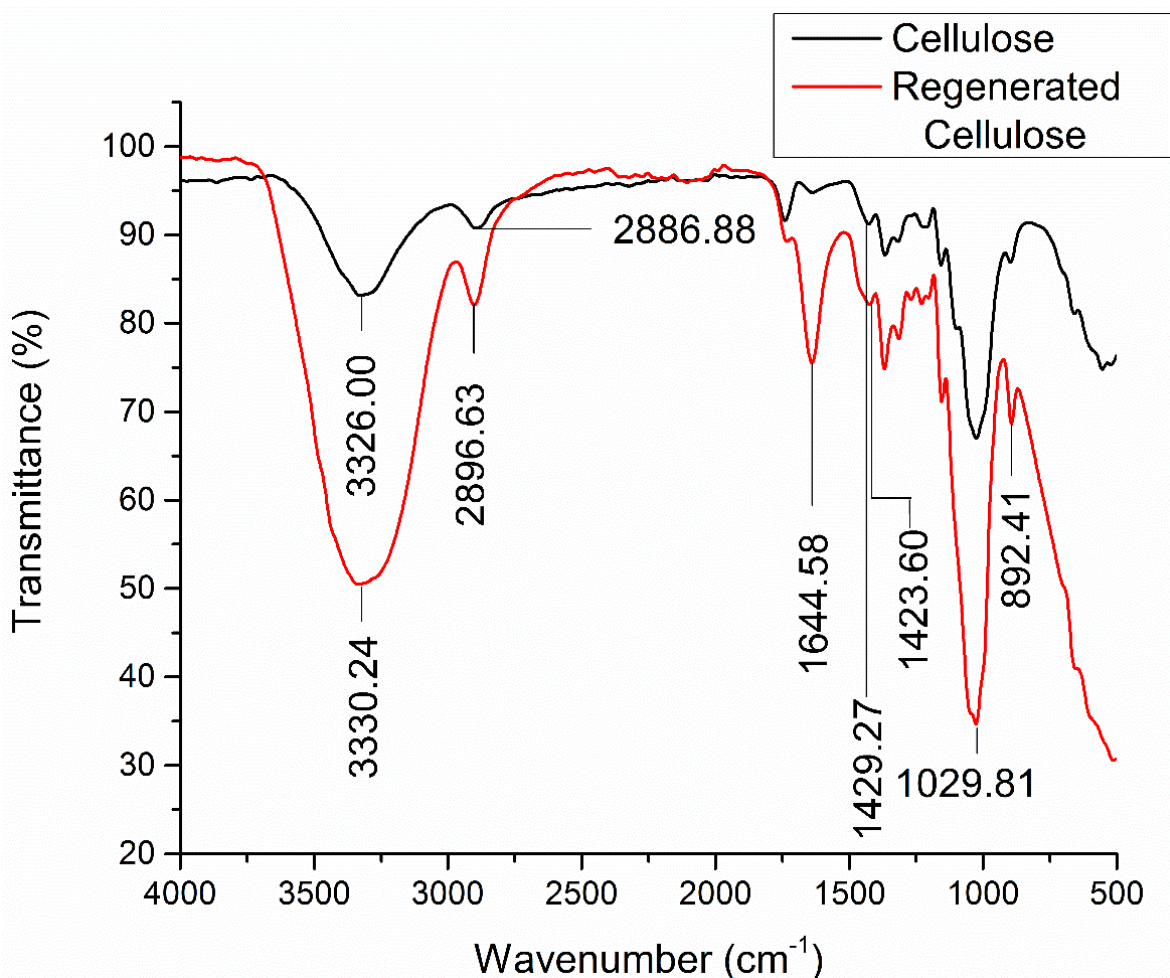


Figure 8: Fourier Transmission-Infra Red spectra of regenerated cellulose (red line) against native cellulose (black line)

The FT-IR spectrum results observed in Fig. 8 demonstrated the presence of a band of hydroxyl (—OH) functional groups in regenerated cellulose at an absorbance of 3330.24 cm^{-1} with high transmittance range compared with the OH-band of native cellulose that had the absorbance of 3326.00 cm^{-1} and lower transmittance (Marchessault & Liang, 1960; Hishikawa *et al.*, 2017). Likewise, in Fig. 8, the absorbance of CH_2 bending peak shifted from 1429.27 cm^{-1} in native cellulose to 1423.60 in regenerated cellulose which indicated the cleavage of hydrogen bonding in $\text{C}_6\text{-OH}$ (Lan *et al.*, 2011). The strength of intensities around band signals (2896.63 , 1423.60 , 1029.81 and 892.41 cm^{-1}) in Fig. 8 were almost similar in both native and regenerated cellulose. Conversely, the band intensity at signal 1644.58 cm^{-1} indicates the presence of adsorbed water was stronger in regenerated cellulose than in native cellulose and this was probably due to the amorphous nature of the regenerated cellulose (Nakamura *et al.*, 1981; Mohan *et al.*, 2011).

4.3.2 Effect of Concentration of Sodium Monochloroacetic Acid on Carboxymethylation

Results of the carboxymethylation process of glycans (cellulose, regenerated cellulose and hemicelluloses) are demonstrated in Fig. 9, 10 and 11, respectively. The presence of an adsorption band at a wavelength of 1740 cm^{-1} in cellulose observed in Fig. 9 was indicative that the carboxymethylation process was successful.

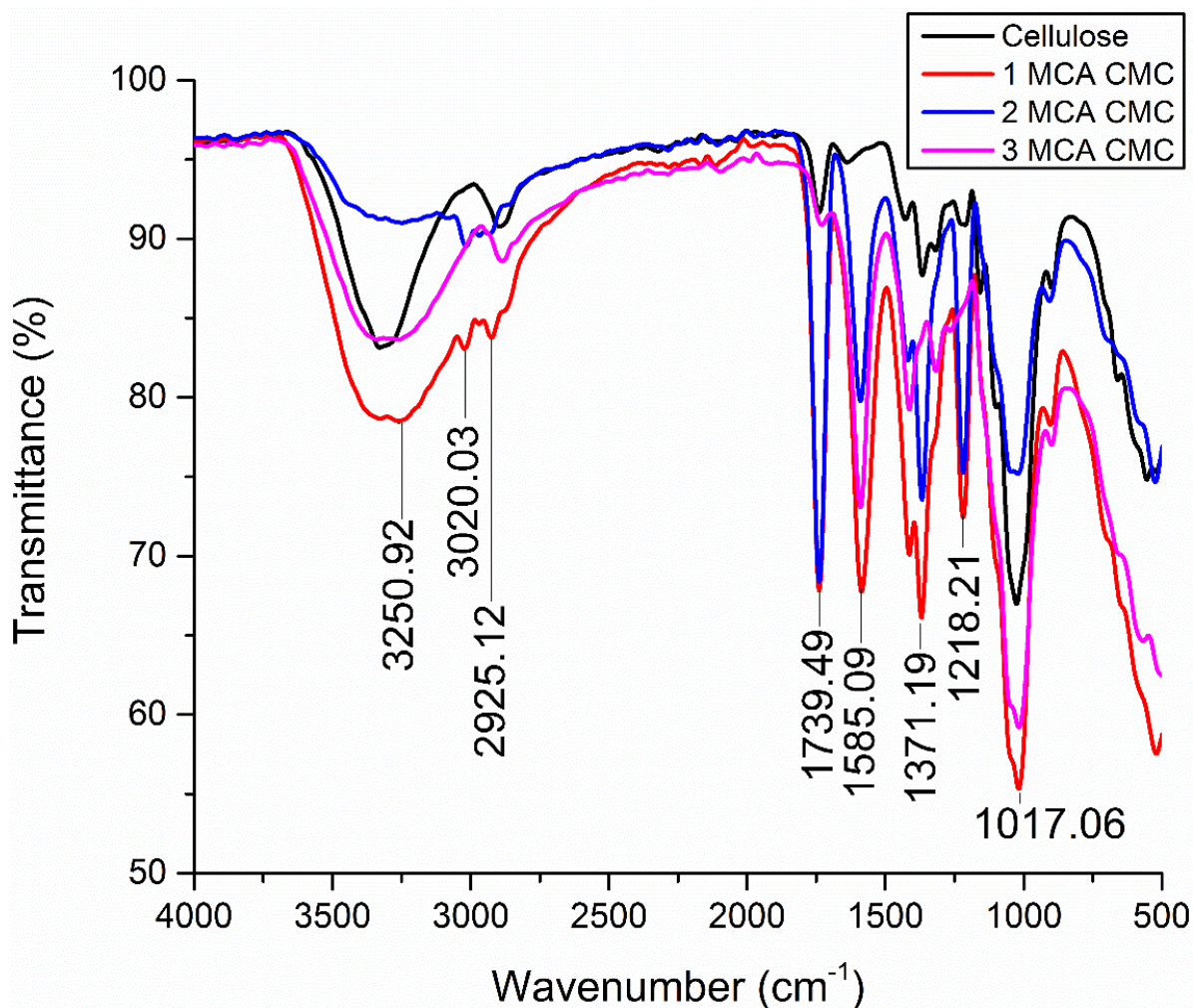


Figure 9: Fourier Transmission-Infra Red spectra for carboxymethylation of native cellulose

The intensification of transmittance around the absorbance of 1740 cm^{-1} prevailed the carboxymethylation of cellulose and hemicelluloses in Fig. 9 and 10, respectively. The intensification of the same band increased with the increase in the concentration of sodium monochloroacetic acid in the ratio of 1:2 (blue), which was also observed by other authors (Petzold *et al.*, 2005).

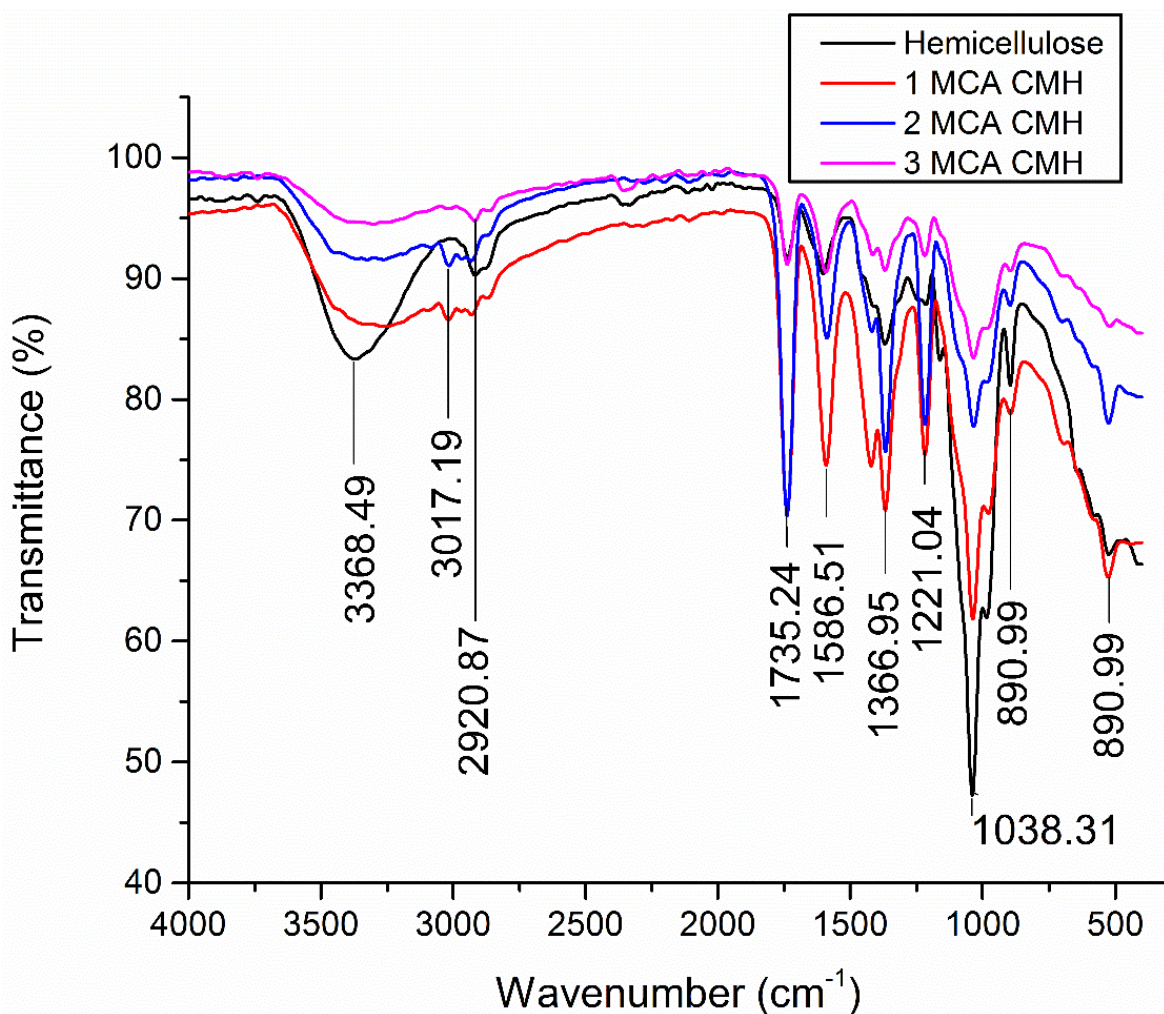


Figure 10: Fourier Transmission-Infra Red spectra for the carboxymethylation of hemicelluloses

Contrary to the polysaccharides, regenerated cellulose showed a different trend (Fig. 11). The trend indicated a decrease in the carboxymethylation process with an increase in the amount of sodium monochloroacetic acid. Thus, 1:1 (red) regenerated cellulose to sodium monochloroacetic acid was enough for the completion of the carboxymethylation reaction. Such a decrease in the transmittance in regenerated cellulose during the second stage of the addition of another 2 g of sodium monochloroacetic acid could be associated with the anti-parallel orientation of micro fibrils of regenerated cellulose. Therefore, OH-groups were plentifully available for substitution during the first step of esterification (Teh *et al.*, 2016).

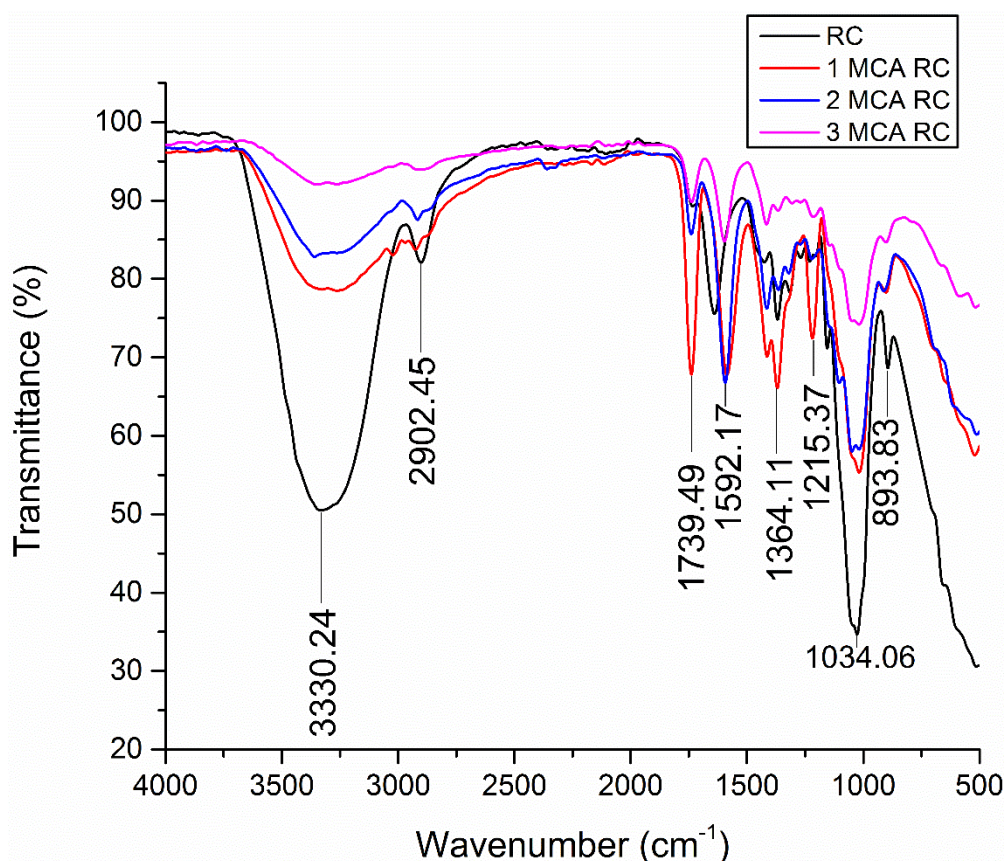


Figure 11: The Fourier Transmission Infra-Red spectra indicating the carboxymethylation of regenerated cellulose

4.3.3 Effect of Adsorbed Water

Polysaccharides including cellulose, regenerated cellulose, and hemicelluloses have a good ability to adsorb water molecules due to the availability of hydroxyl function groups (Fringant *et al.*, 1996). The FT-IR spectra in Fig. 10 indicated that carboxymethyl hemicelluloses had more amount of adsorbed water compared to carboxymethyl cellulose and regenerated cellulose. This was demonstrated by having intense absorbance at the wavelength of 1586.51 cm⁻¹ and a high transmittance range with a modification ratio of 1:1 hemicellulose mass to the mass of monochloroacetic acid (1 MCA). The carboxymethylation of hemicellulose increased its ability to bind more water molecules depending on the degree of substitution. At a high degree of substitution the ability to adsorb water decreased as it was observed in Fig. 10 (Postma, 2012). In the same way, regenerated cellulose was found to adsorb more water than to native cellulose (Fig. 8).

It is important to note that regenerated cellulose is extremely hydrophilic with a number of hydroxyl functional groups available to bind water molecules (Godbillot *et al.*, 2006). Moreover, carboxymethylation process on both cellulose and regenerated cellulose indicated an effect on the ability to adsorb water molecules. However, an increase in the concentration of

monochloroacetic acid in the carboxymethylation process of regenerated cellulose did not affect the increase in the amount of adsorbed water. The absorbance band at 1592.17 cm^{-1} on Fig. 8 signified the presence of limited OH functional groups for water to adsorb on CMC-2 (Guo *et al.*, 2016). Nonetheless, the increase in the amount of monochloroacetic acid caused an increase in the amount of adsorbed water molecules by the carboxymethyl cellulose. The carboxymethyl cellulose modified under 1:2 (cellulose and monochloroacetic acid) had absorbance band (1586.51cm^{-1}) with higher range of transmittance than the one modified under the 1:1 ratio (Berthold *et al.*, 1998). The present study found that an increase in the concentration of monochloroacetic acid during the carboxymethylation process had no effect on the increase of the amount of adsorbed water for CMH and CMC-II but it had an effect on carboxymethyl cellulose.

4.4 Elemental Composition

For the elemental composition, the results indicated an increase in oxygen concentration coupled with a simultaneous decrease in carbon and hydrogen concentration after carboxymethylation (Maity & Sa, 2014) (Table 2).

Table 2: Elemental analysis for cellulose, regenerated cellulose, and hemicellulose before and after carboxymethylation

S/N	Sample (glycan)	Carbon (%)	Hydrogen (%)	Oxygen (%)
1.	Cellulose	27.65	5.45	3.14
2.	2 MCA CMC	25.12	4.65	3.30
3.	Regenerated Cellulose	25.50	5.78	2.56
4.	1 MCA CMC-II	22.83	3.93	3.00
5.	Hemicellulose	31.37	4.55	3.23
6.	2 MCA CMH	28.00	4.16	3.36

The increase in oxygen in carboxymethylated glycans was probably attributed to the substitution reactions of $-\text{CH}_2\text{COONa}$ to the replaceable OH groups (Kaity & Ghosh, 2013). Comparatively, the decrease in carbon and hydrogen concentrations was probably because of the distortion of cellulose, regenerated cellulose, and hemicellulose chains i.e., stirring and formation of water molecules (Chakravorty *et al.*, 2016).

4.5 Degree of Substitution

Depending on the solvent, the concentration of functionalization reagent, contact time and the concentration of sodium hydroxide; usually the degrees of substitution of cellulose, regenerated cellulose and hemicelluloses ranges from 0.0 to 2.2 (Wach *et al.*, 2003). In the present study it was found that the degree of substitution of the cellulose, hemicellulose, and regenerated improved with increase in the concentration of monochloroacetic acid (MCA) and it ranged from 0.9 to 1.4 (Table 3).

Table 3: Degree of substitutions of polysaccharides

S/N	Ratio of monochloroacetic acid (MCA) to glycan (m/m)	Degree of substitution	Solubility
1	MCA CMC (1:1)	1.15	Soluble
2	MCA CMC (2:1)	1.30	Soluble
3	MCA CMC-II (1:1)	1.10	Soluble
4	MCA CMC-II (2:1)	0.90	Slightly soluble
5	MCA CMH (1:1)	1.22	Soluble
6	MCA CMH (2:1)	1.40	Soluble

The increase in the degree of substitution in respect of increasing concentration of monochloroacetic acid was observed. This might have been caused by the presence of a large number of acetate ions as compared to the available hydroxyl function groups in glycans to be substituted (Pushpamalar *et al.*, 2006). But among the three types of glycans (native cellulose, regenerated cellulose, and hemicelluloses); hemicelluloses were highly carboxymethylated. Therefore, carboxymethyl hemicelluloses had the highest degree of substitution of 1.4 that was obtained with 1:2 hemicellulose and monochloroacetic acid ratio, respectively. This was expected due to the anatomy of hemicellulose and the presence of wide varieties of monosaccharides on the hemicellulose structure with a hydroxyl function group available for chemical substitution (Sun, 2010).

When all other factors for carboxymethylation are kept constant, the degree of substitution of glycans increases with the increase of concentration of monochloroacetic acid. The degree of substitution keeps increasing until all the available free hydroxyl groups on glycans have been replaced with carboxymethyl groups (Joshi *et al.*, 2015; Casaburi *et al.*, 2018). However, the concentration of monochloroacetic acid used in carboxymethylation of regenerated cellulose was reduced because there was an increased amount of freely available hydroxyl groups in

regenerated cellulose compared to native cellulose (Dinand *et al.*, 2002; Yamane *et al.*, 2006; Marks, 2015).

4.6 Solubility Test

The carboxymethylated glycans used in the present study were mostly soluble in water, except for the carboxymethylated regenerated cellulose that was obtained under 2:1 ratio of monochloroacetic acid against regenerated cellulose (Table 3). This was probably due to its lowest degrees of substitution (0.9). The easily soluble carboxymethylated cellulose, regenerated cellulose, and hemicellulose with high degrees of substitution were taken to the next step of applications as flocculants for treating brewery wastewater (Khiari *et al.*, 2010).

4.7 Analysis of Materials' Removal Efficiencies

Raw brewery wastewater was treated using CMH, CMC and CMC-II for the assessment of effectiveness of modified glycans in removing biological oxygen demand (BOD) and turbidity.

4.7.1 Turbidity Removal

All the modified glycans (CMC, CMC-II and CMH) showed some ability to remove turbidity from wastewater of the brewery industry (Fig. 12).

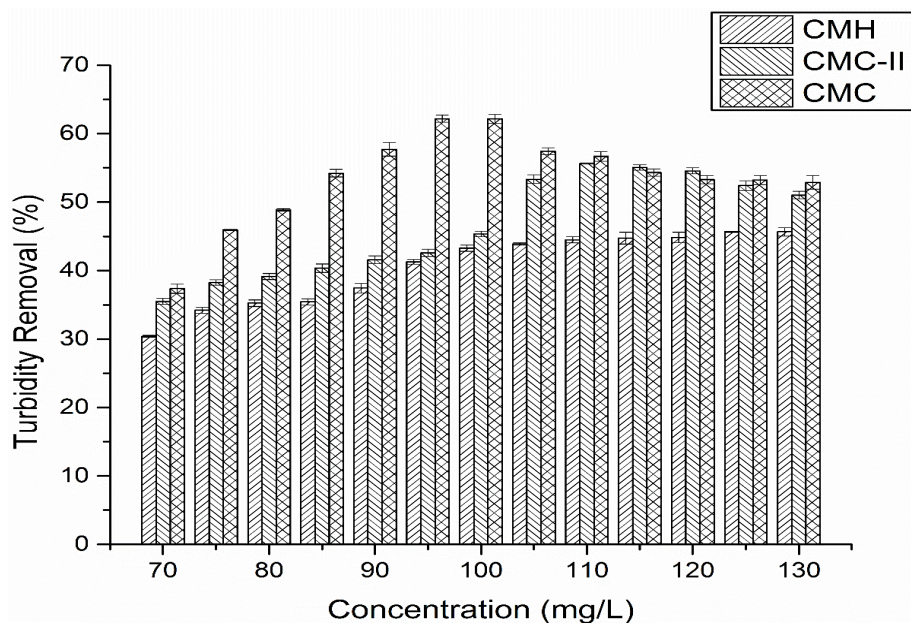


Figure 12: The dependence of turbidity removal efficiencies of modified glycans carboxymethyl hemicellulose (CMH), carboxymethyl regenerated cellulose (CMC-II), and carboxymethyl cellulose (CMC) from their concentration

The highest activity was demonstrated by CMC (max removal at ~62.19% under 95 – 100 mg/L dose). The CMC-II was characterized by less removal (~55.63% under 110 – 120 mg/L dose) of turbidity. Minimal activity was shown by CMH (~45.67% at a concentration equal to 130 mg/L). For a range of concentrations from 70 to 130 mg/L, carboxymethyl hemicelluloses (CMH) showed a linear behavior in which its activity towards reducing turbidity increased with the increase in its concentration. Concentrations greater than 110 and 100 mg/L for CMC-II and CMC, respectively, had the effect of reducing flocculating activity; high concentrations resulted in low efficiency of turbidity removal.

4.7.2 Biological Oxygen Demand Removal

The modified glycans were also researched on their ability to reduce biological oxygen demand (BOD) from wastewater, and their results are well summarized in Fig. 13.

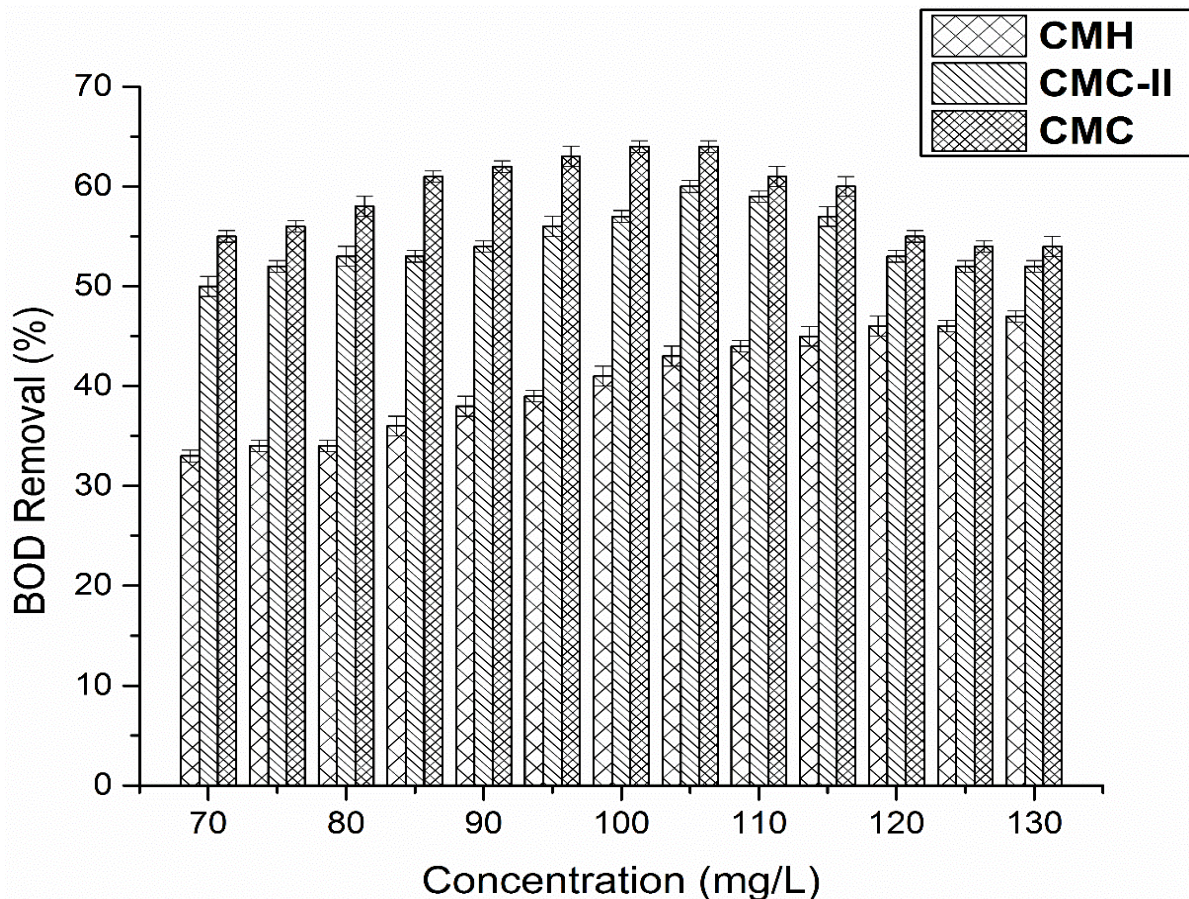


Figure 13: Biological Oxygen Demand (BOD) removal efficiency for modified glycans carboxymethyl hemicelluloses (CMH), carboxymethyl regenerated cellulose (CMC-II), and carboxymethyl cellulose (CMC) against their concentrations

Among the three types of carboxymethylated glycans, CMC and CMC-II showed higher BOD removal efficiencies than CMH for a selected range of concentration (70-130 mg/L). Initially, the increase in the concentration of CMC and CMC-II were proportional to the BOD removal

efficiency. As the concentration increased, however, CMC attained maximum BOD removal efficiency at 64% while CMC-II did so at 60%. Unlike CMC-II and CMC the increase of CMH concentrations also increased its BOD removal efficiency although at 130 mg/L the removal efficiency was only 47%. The trend of CMH concentrations against its BOD removal efficiency was different from other modified glycans probably due to its lower density and its powdery nature (amorphous) (Oun & Rhim, 2016). Depending on its various degrees of substitution, carboxymethyl hemicelluloses (CMH) could find application in different areas of science and technology such as heavy metal removal, food storages and rheology (Methacanon *et al.*, 2003; Peng *et al.*, 2010). In the present study, the degree of substitution of 1.40 was enough for CMH to form flocs in the brewery wastewater effluents

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Cellulose and hemicellulose were well isolated from sugarcane bagasse and cellulose was chemically modified to regenerated cellulose. Functional groups on the isolated native cellulose, hemicelluloses and regenerated cellulose were examined using Fourier Transform Infrared Spectroscopy.

Furthermore, native cellulose, hemicelluloses as well as regenerated cellulose, were all carboxymethylated using sodium monochloroacetic acid under a basic condition. The carboxymethylated glycans were pre-confirmed using water solubility test and through the determination of the degree of substitution. Further analysis such as Fourier Transform Infrared spectroscopy (FT-IR) as well as CHNS/O were conducted to confirm the added functional groups after the carboxymethylation process.

In the present study, the carboxymethylated cellulose, regenerated cellulose and hemicelluloses were all applied as flocculants for brewery wastewater treatment in a batch experimental set up. The CMC with 1.30 degree of substitution reduced turbidity and biological oxygen demand by 62.19% and 64%, respectively. Likewise, CMC-II with 1.10 degree of substitution reduced turbidity and biological oxygen demand by 55.63% and 60%, respectively. Finally, CMH that had 1.40 degrees of substitution was capable of reducing turbidity and biological oxygen demand by 45.67% and 47%, respectively.

In summary:

- (i) Novel materials were successfully synthesized and modified from sugarcane bagasse—materials plentifully available in Tanzania—at low or no cost.
- (ii) Materials were successfully carboxymethylated to increase the solubility of the flocculants.
- (iii) The isolated, regenerated, and carboxymethylated materials were successfully tested for their capacity to remove turbidity and BOD with good results.
- (iv) Overall, CMC attained the best removal efficiency for both turbidity and BOD.
- (v) On the hand, CMH had the poorest performance and needed higher dosage to remove turbidity and BOD.

5.2 Recommendations

Raw brewery wastewater treatment is a very crucial step before allowing the industrial effluents to interact with the surrounding environment. Many conventional technologies and methods are available for wastewater treatment. However, green technologies that apply renewable and readily available materials are much encouraged. In the present study, the use of organic flocculants in coagulation–flocculation process was demonstrated.

The present study therefore recommends the following:

- (i) Further analysis should be carried out using these or similar modified organic flocculants for removal of other water pollutants e.g., heavy metals, pharmaceuticals, pesticides, COD, etc.
- (ii) These modified glycans need to be further tested using different types of industrial wastewater. For the present study, only brewery wastewater was used.
- (iii) Also, the effectiveness of combining these modified glycans to use them as a single flocculant could be assessed.
- (iv) Since large quantities of agricultural waste rich in biomolecules are produced annually in Tanzania, these should be used precursors for green production of green flocculants.

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RESEARCH OUTPUTS

(1) **Research Article**

Mwesiga, J. J., Rwiza, M. J. & Kalmykova, E. N. (2021). Regeneration and carboxymethylation of cellulose and its derivatives: application assessment for brewery wastewater treatment. *International Journal of Environmental Science and Technology*, 2021 (2), 1-21. <https://doi.org/10.1007/s13762-021-03190-9>

(2) **Poster Presentation**