MICROWAVE SYNTHESIS OF SUPER-ABSORBENT HYDROGELS FROM RICE HUSKS CELLULOSE FOR SUSTAINABLE AGRICULTURE

ADAMU ABDULHAMEED (MSc.)
I84F/38510/2016

A Thesis Submitted in Fulfillment of the Requirements for the Award of the Degree of Doctor of Philosophy (Chemistry) in the School of Pure and Applied Sciences of Kenyatta University

OCTOBER, 2021

DECLARATION

I confirm that this thesis is my original work and has not been presented in any other university/institution for certification.

Adamu Abdulhameed
I84F/38510/2016

Signature .... Date.....................................

Department of Chemistry

SUPERVISORS

We confirm that the work reported in this thesis was carried out by the candidate under our supervision as university supervisors.

Signature................................Date.......................................

Dr. Harun Mbatha Mbuvi
Department of Chemistry
Kenyatta University

Signature................................Date.......................................

Dr. Evans Changamu Ogwagwa
Department of Chemistry
Kenyatta University

DEDICATION

I am proud to dedicate this work to my late grandparents, Alh. Sulaiman Muhammad and Hajiya Aishatu Muhammad, May Jannatul Firdausi be their final abode.

ACKNOWLEDGEMENTS

I thank Almighty Allah (SWT) for inspiring my life, giving me strength, good health and sound mind to accomplish my studies. I wish to express my sincere appreciation to my supervisors, Dr. Harun Mbatha Mbuvi and Dr. Evans Changamu Ogwagwa, who have the substance of a genius, they convincingly guided and encouraged me to be professional and do the right thing even when the road got tough. Without their persistent help, the goal of this project would not have been realized. I also take this opportunity to thank the Kenyatta University Department of Chemistry staff and laboratory technicians for their support during my research.

I am grateful to my parents, Barrister (Alkali) Danjuma Mustapha Ibrahim, Haj. Laraba, Haj. Binta and Haj. Bilkisu, for the immense love, prayers and support. May Allah bless you with Jannatul-Firdaus.

I want to express my sincere gratitude to my friends especially, Engr Auwal I. Haruna, Dr. Maingi, Dr. Katana, Dr. Irene Githinji, Hashim Ibrahim, Isah Mahmoud Mustapha, Umar Aliyu for their guidance, support and encouragement moral and invaluable support throughout this study. I thank my brothers and sisters, Bello, Dr. Ibrahim, Bilkisu, Hauwa, Taiba, Surayya, Shamsu, Kamalu, Mubarak, Abdulkadir, Khadija, Ummi, and Aisha, for their patience and support during the three years of distance learning. I am indebted to my fiancée Aisha Bello Kofar Na'isa, thanks for all her support, without which I would have stopped these studies a long time ago, May Allah (SWT) reward you abundantly. Lastly, I would like to thank BASUG for granting me study leave to complete my studies. Thank you all.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF PLATES

LIST OF SCHEMES

ABBREVIATIONS AND ACRONYMS

AGU	Anhydroglucose unit
ANOVA	Analysis of variance
CA	Cellulose acetate
CAB	Cellulose acetate butyrate
CAP	Cellulose acetate phthalate
CAT	Cellulose acetate trimelitate
CMC	Carboxymethylcellulose
CRDB	Complete random block design
DMF	Dimethylformamide
DS	Degree of substitution
EC	Ethylcellulose
EDX	Electron dispersive x-ray
FTIR	Fourier transform infrared
HEC	Hydroxyethylcellulose
HPC	Hydroxypropylcellulose
HPMC	Hydroxypropylmethylcellulose phthalate
LSD	Least significant difference
MC	Methylcellulose
MCA	Monochloroacetic acid
Na-CMC	Sodium carboxymethylcellulose
Na-MCA	Sodium monochloroacetic acid
RHA	Rice husks ash
SAH	Superabsorbent hydrogels
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
XRD	X-ray diffraction
XRF	X-ray fluorescence

ABSTRACT

The phenomenon of climate change coupled with increased demand for water all over the world calls for innovations in water conservation and use. Moreover, rainfall variability and the corresponding implications are expected to continue worsening owing to the anticipated effect of global warming. Currently, inadequate water is considered as the key factor affecting crop growth and productivity in arid and semi-arid regions of Africa. Hence, there is need to explore and develop innovative ways to reserve and conserve water and nutrients and reduce moisture stress in food crops during mid-season drought. The use of superabsorbent hydrogels in crop growing as a means of ensuring sustained water supply to growing of plants has shown promising results. The superabsorbent hydrogels are capable of absorbing and retaining high amounts of water and releasing it under appropriate conditions. However, majority of the superabsorbent hydrogels are known to be expensive, non-degradable and environmentally unfriendly and are therefore unsuitable for use in agriculture. Hence, there is need for the development and optimization of non-toxic and environmentally friendly alternatives for use in agriculture. The objective of this study was to synthesize and characterize cellulose-based superabsorbent hydrogels from rice husks (*Oryza sativa*) cellulose under microwave heating and to evaluate their efficacy in the growing of maize in a green house. The cellulose used in this study was extracted from rice husks using acetic acid-nitric acid mixture. Some of the extracted cellulose was modified to carboxymethylcellulose by alkalization followed by reaction with monochloroacetic acid (MCA) under microwave heating. One half of the carboxymethylcellulose obtained was cross-linked using ethane-1,2-diol and the other with ethane-1,2-diamine, under microwave heating to form two different hydrogels. The unmodified cellulose was converted to hydrogels by crosslinking with phosphoric and boric acid, respectively. Separately, optimum synthesis conditions, that is, microwave power out-put, time (minutes), and amount of cross-linkers required were determined by measuring the percentage swelling of the hydrogels produced under different synthesis conditions in water. All hydrogels produced were characterized by Fourier transform infrared (FTIR) spectroscopy, x-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). The ethane-1,2-diamine superabsorbent hydrogel from carboxymethylcellulose showed the highest percentage swelling of 1175 %. The efficacy of the hydrogels in maize growing was determined by planting maize in pots in a greenhouse under different hydrogels and varied hydrogel dose treatments and measuring growth parameters over a period of twelve weeks. Yield parameters were determined at harvesting after 12 weeks allowing for complete drying. The values of plant growth and yield parameters were found to increase with hydrogel dose with the best results being observed among maize plants grown under the hydrogel dose of 5 g per pot for all the superabsorbent hydrogels. It was observed that the maize plants in pots without any hydrogel dried off without any yield as expected when rains fail. These results are significant in that they demonstrate that rice husks cellulose-based hydrogels are efficacious in maize growing in a greenhouse. Furthermore, the use of the agricultural waste, rice husks as a source of the cellulose means the rice husks now becomes a resource rather than an agricultural waste.

CHAPTER ONE

INTRODUCTION

1.1 Background information

Sustainable agriculture has been described as one that seeks to meet society's present food and textile needs without compromising the ability of future generations to meet their own needs. This, therefore, means that all agricultural practices must be geared towards three key objectives namely, a healthy environment, economic profitability, as well as social and economic equity. In particular, farmers must use methods to promote soil health, minimize water use, and lower pollution levels on the farm (Brodt *et al.*, 2011).

In most African countries, however, sustainable agriculture is far from being realized given the wanton destruction of forest and pollution or exploitation of existing water sources. It is reported that food insecurity plagues one-third of the people across the continent while two-thirds of the population are trapped in a cycle of poverty, aggravated by climate change and rapid population growth (Abrams, 2018). Of particular interest to this study is the fact that 95% of food production in most African countries is rain fed and is done by small scale subsistence farmers who lack capacity to invest in irrigation or in effective use of "green" water. The study was inspired by the argument that the highest potential for improved food production and poverty reduction lies with improved rainfed farming, enabled through "green" water management (Abrams, 2018). This is more so because even if there were resources to invest in irrigation, only about 5.5% of cultivable land is irrigable because of limited water availability and unsuitable soil/topographical characteristics. “Green” water is water derived from rainfall that is available in the soil for plant growth through transpiration.

Generally in semi-arid regions crops use less than 30 percent of rainfall, while up to half the rain evaporates directly from the soil and the remainder runs off the surface or seeps into the groundwater. According to a World Bank report of 216, there is limited potential (less than 1.3 percent of cultivable area in dry land zones) for large-scale blue water investments in irrigation (Ward *et al*., 2016). Similarly, because of lack of adequate water in the dry lands small scale irrigation can only be done to a limited scale of about 7.2%. As such a whopping 92.5% of the dry land cultivable area depends solely on rainfed soil moisture. Technologies that can conserve moisture and release to the plant when required are necessary in order to maximize on the potential of arable lands in Africa for rain fed agriculture. One such technologies is th use of eco-friendly superabsorbent hydrogels. These ensure moisture availability to the individual plant for longer unlike the commonly used methods such zero tillage, using conservation tillage methods, and application of agro-ecology methods such as mulching, intercropping, windbreaks, using the right fertilizer, timely planting, weeding and pest control and so on.

Superabsorbent hydrogels are 3-dimensional hydrophilic polymers, which absorb and retain large volumes of water, and then release it under stress conditions (Li *et al*., 2004; Laftah *et al*., 2011; Chen *et al*., 2015). Their ability to absorb water is as a result of the hydrophilic functional groups (OH, $CONH_2$, COOH, and SO_3H) found on the polymer spine. The cross-linking between networks confers stability and insolubility to the hydrogels (Rowley *et al*., 1999; Raju *et al*., 2003). Because of the nature, the superabsorbent hydrogels have been used in a range of fields including as hygiene napkins, disposable diapers, soil conditioning for horticulture and agriculture, as well as water and food purification (Wang *et al*., 2008). Current research is focused on the development of hydrogels for tissue engineering (Khan *et al*., 2009), sensors (Sorber *et al*., 2008), as well as drug delivery and controlled release (Wu *et al*., 2008).

The search for hydrogels for use in sustainable agriculture from biodegradable materials is informed by the fact that most of the superabsorbent hydrogels (SAHs) in current use are obtained from nod-biodegradable petroleum-based products crosslinked with organic cross-linkers like poly-amido-amine (Ferruti *et al*., 2005), poly-vinyl alcohol (Martens *et al*., 2003), polyacrylamide (Gao *et al*., 2007), poly-N-isopropyl acrylamide (Nayak *et al*., 2004) and poly-ethylene glycol (Nagahama *et al*., 2008). These are environmentally unfriendly since they are bound to linger in the environment for long. For hydrogels to be acceptable for use in sustainable agriculture they must, of necessity, be biodegradable to non-toxic degradation products in addition to being able to support plants for complete season. This informs the the need to develop superabsorbent hydrogels that are eco-friendly, especially from natural materials such as chitosan, cellulose and starch. These have attracted much attention due to their cost-effectiveness, degradability and availability (Mahmoudian and Ganji, 2017).

Cellulose is the most abundant, biocompatible and degradable linear, long-chain, water-insoluble, natural polymer on earth (Klemm *et al*., 2011). It is found in plants such as grass (Sutiya *et al*., 2012), straw (Xu *et al*., 2013), wood (Sunardi *et al*., 2016) and cotton (Li *et al*., 2014). It has been isolated from several agricultural wastes including orange peels (Arslan, 2007), oil palms (Palamae *et al*., 2017), banana (Adinugraha *et al*., 2005), cotton (Haleem *et al*., 2014), durian (Rachtanapun *et al*., 2012), and sago (Pushpamalar *et al*., 2006). Cellulose is found in the plant cell wall with hemicellulose and lignin (Pushpamalar *et al*., 2006). Its isolation can be possible, utilizing accessible less expensive chemicals that produce physical and chemical properties better than cellulose obtained commercially. It serves as a basic item during the preparation of carboxymethylcellulose and its derivatives, including cellulose acetate, methylcellulose, cellulose nitrate, and ethylcellulose (Haleem *et al*., 2014).

Carboxymethylcellulose (CMC) is among the cellulose derivatives which are non-toxic to humans. Due to its availability as raw material (used in a diet pill, toothpaste, food additive) (Hussain *et al*., 2010) more attention has been given to its properties as anionic polymer (Chai and Mohamad, 2011), and aqueous solubility (Zhou and Zhang, 2000). The CMC is obtained when cellulose is reacted with monochloroacetic acid or sodium monochloroacetic acid sin the presence of an organic solvent under an alkaline condition (Putri and Kurniyata, 2016). This leads to different degrees of substitution of hydroxyl (OH) groups in cellulose at C2, C3 and C6 (Fig 1.1) by sodium carboxymethyl groups (Kayran and Aytekin, 2018).

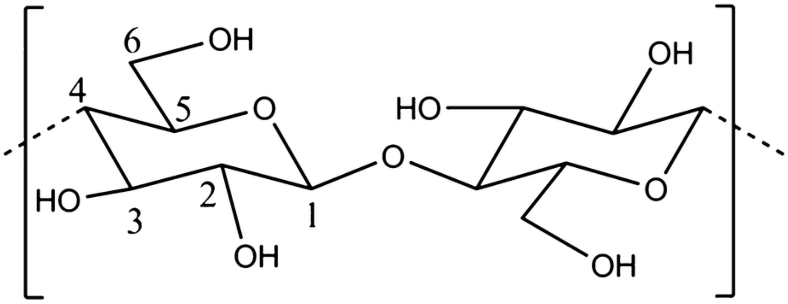


Figure 1.1: Hydroxyl groups of cellulose at C2, C3 and C6

Microwave heating has been used for various applications (Ekezie *et al.*, 2017). In comparison to other methods of heating, microwave heating allows instantaneously heating throughout and improves the heating efficiency. Moreover, in addition to being simple to use, microwave heating is environmentally friendly in that it, requires less energy, enhances yields and reduces the generation of byproducts. There is limited information on the use of microwave to synthesized superabsorbent hydrogels.

The present study reports optimized microwave synthesis of four superabsorbent hydrogels. The products were obtained after crosslinking modified cellulose and cellulose extract from rice husks with four different cross-linkers namely ethane-1,2-diol, ethane-1,2-diamine, boric acid and phosphoric acid. The report also includes an evaluation of the efficacy of the hydrogels in the growing of maize in a green house.

1.2 Problem statement and justification

Arid and semi-arid lands in Kenya make up more than 80 % of the country and are occupied by more than 16 million people who need food. However, such lands are regarded as unproductive especially with rainfed agriculture. Given that populations will continue growing and people in such areas will continue to need food, agricultural practices or food production methods must change with time and in tandem with prevailing climatic conditions if food security is to be realized and maintained. Rainfall variability and evapotranspiration are predicted to increase, while annual average rainfall is likely to decrease in much of Africa as a result of climate change, increasing the vulnerability of rainfed agriculture. The solution lies with technologies to retain green water in the soils for longer, reduce evapotranspiration in order to support crops during the dry and water-stressed seasons. Superabsorbent hydrogels (SAHs) are targeted for use in soil conditioning, controlled or sustained fertilizer release for agriculture especially in water-stressed regions because of their ability to absorb and retain enough water or aqueous solutions which they then release in a controlled manner in response to environmental stimuli.

Nearly all the hydrogels studied are made from synthetic polymers such as acrylic acid, methacrylic acid, polyethylene glycol, vinyl acetate, polyvinyl alcohol and various acrylates which tend to be environmentally undesirable upon disposal. A few hydrogels such as alginate, chitosan, collagen, dextran, cellulose and chitin, are based on more desirable natural polymers which are environmentally friendly and hence suitable for use in agriculture. The objective of this study was to synthesize cellulose-based hydrogels from rice husks cellulose with the help of microwave heating and to determine their efficacy in maize growing in a greenhouse. The cellulose was extracted from the rice husks and either converted to CMC under appropriate conditions before being exposed to selected cross-linkers under microwave heating or reacted directly with phosphate or borate cross-linker under microwave heating to produce the target superabsorbent hydrogels. Microwave assisted heating is attractive because of its uniform and rapid heating, energy and time saving and lower processing cost. The efficacy of the SAHs was evaluated by applying on maize growing in a green-house and measuring various growth and yield parameters. Maize planted without hydrogels was use as the negative control.

1.3 Hypothesis

Cellulose extracted from rice husks and cross-linked with appropriate ecofriendly linkers form cellulose-based superabsorbent hydrogels that can be used for maize growing.

1.4 Objectives

1.4.1 General objective

To synthesize cellulose-based superabsorbent hydrogels using cellulose extracted from rice husks and evaluate their efficacy by growing maize in a greenhouse.

1.4.2 Specific objectives

(i) To extract and characterize cellulose from rice husks

(ii) To synthesize and characterize carboxymethylcellulose from rice husks cellulose

(iii) To synthesize and characterize super-absorbent hydrogels from rice husks cellulose-based carboxymethylcellulose by crosslinking with ethane-1,2-diol and ethane-1,2-diamine

(iv) To synthesize and characterize super-absorbent hydrogels from rice husks cellulose, by crosslinking with boric acid and phosphoric acid

(v) To determine efficacy of the superabsorbent hydrogels in maize growing in a greenhouse.

1.5 Significance of the study

Positive results from this study are likely to change the way rice husks is viewed from a waste to a resource. The results are also likely to reduce the dependence of semi-arid farming on rainfall and improve crop productivity. The expected output is a series of superabsorbent cellulose-based hydrogels that can be used in farming.

CHAPTER TWO

LITERATURE REVIEW

2.1 Cellulose

Cellulose is the most abundant natural polymer on earth. The molecules are linear, long-chain, water-insoluble, inexhaustible, biocompatible, degradable and environmentally friendly. Being a polysaccharide, it is formed as a result of the repeating unit of D-glucose, linked by 1,4-β glycosidic linkages. The presence of three reactive hydroxyl groups (C2, C3 and C6) on each glucan unit of cellulose makes it relatively easy to modify (Singh and Singh, 2013). In the molecule, the OH group at C1 of one of the ends is an aldehyde group with reducing characteristic. Moreover, OH at C4 is an alcoholborne hydroxyl constituent usually referred to as a non-reducing end (Kayran and Aytekin, 2018). The OH group in cellulose plays a fundamental function in solubility and β-glycosidic linkages are prone to hydrolytic attack. Cellulose is insoluble in most organic solvents and in water because of intermolecular and intramolecular hydrogen bond formation (Bono *et al.*, 2009). Nuclear magnetic resonance spectroscopy (NMR), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) confirmed that the anhydroglucose (AGU) ring is in pyranose form and ${}^{4}{}_{1}C$ chair formation which constitute the lowest energy conformation for D-glucopyranose. Figure 2.1 shows the cellulose unit.

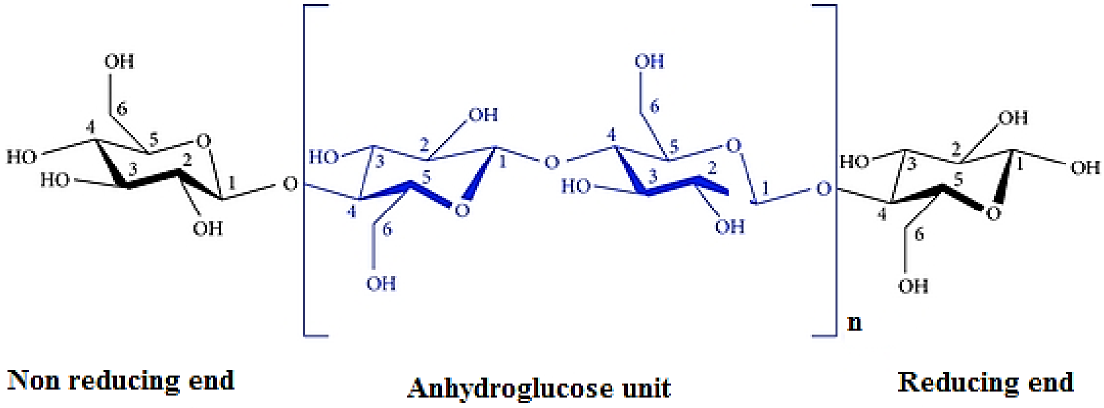


Figure 2.1: Cellulose unit

It is found in plants such as grass (Sutiya *et al*., 2012), straw (Xu *et al*., 2013), wood (Sunardi *et al*., 2016) and cotton (Li *et al*., 2014). Cellulose has been isolated from several agricultural wastes including, orange peels (Arslan, 2007) oil palms (Palamae *et al*., 2017), banana (Adinugraha *et al*., 2005), cotton (Haleem *et al*., 2014), durian (Rachtanapun *et al*., 2012), sago (Pushpamalar *et al*., 2006) and rice husks (Shulka *et al*., 2015; Abdulhameed *et al*., 2019). Cellulose consists of both amorphous and crystalline domains, depending on the source of cellulosic material (Diana *et al*., 2011). The physical an d chemical properties of cellulose are influenced by the arrangement of the cellulose molecule with respect to the fibre axis. The modification occurs in the amorphous region, the reactions take place by leaving the intracrystalline regions unaffected (Diana *et al*., 2011).

2.2 Rice husks (RH) and rice husks cellulose

Rice (*Oryza sativa*) is considered as the major food in most developing countries (Ajala and Gana, 2015). The rice husk is a protective cover of rice grain and a by-product in the rice milling industry, which is considered a waste material. Nowadays, it is being used in feeding of cattle and in the production of building materials in some regions. It has also been used as a soil additive, in agriculture or an additive in concrete and cement productions (Shafigh *et al*., 2014). Several researchers have reported that rice husks ash has high content of silica, therefore it can act as a good source of silica and serve as constituent when making ceramic materials such as silicon carbide (Baris, 2004) and silicon nitride (Abdulhameed *et al*., 2017). Rice husks contains about 70–85 % of natural matter, cellulose (35 %), lignin (20 %), hemicellulose (25 %), crude protein (3 %) and the rest is silica, which is available in the cell membrane (Vempati *et al*., 1995). Ugheoke and Mamat (2012), isolated cellulose from rice husks using acid hydrolysis and bleaching and obtained 13.54 %. Plate 2.1 shows a picture of rice husks samples.

Plate 2.1: Rice husks (Carolyn, 2013)

2.3 Other sources of cellulose

Agricultural waste materials are now fully used as fuel and source of cellulose due to their availability and degradability. Several agricultural waste materials are composed of cellulose, lignin and hemicellulose, depending on plants specie and the nature of the reagents used. Table 2.1 shows the percentage composition of hemicellulose, lignin and cellulose contents in some selected agricultural waste materials.

Table 2.1: Contents of hemicelluloses, lignin and cellulose in agricultural waste

Agricultural waste	Hemicellulose (%)	Lignin (%)	Cellulose (%)
Sugarcane bagasse	23 – 35	18 - 24	40 – 50
Corn cobs	35	15	45
Hardwood stems	24 – 40	18 - 25	45 – 50
Wheat straw	50	15	30
Softwood stems	23 – 35	18 - 24	45 – 50
Nut shell	25 – 30	30 - 40	25 – 30
Cotton seed hair	5 – 20	0	80 – 95
Leafs	80 – 85	0	15 – 20
Paper	0	0 - 15	85 – 99
Newspaper	25 – 40	18 - 30	40 – 55

Source: Mandal and Chakrabarty, 2011; Huntley *et al*., 2015.

2.4 Cellulose derivatives

2.4.1 Cellulose ether derivatives

Cellulose ether derivatives are formed by substituting the hydrogen atom of the hydroxyl (OH) group in the AGU with substituted alkyl groups (Haleem *et al*., 2014). Their importance is determined by molecular weight and degree of substitution. The viscosity is directly related to the molecular weight. They are highly chemical resistant, non-toxic in nature and have good solubility. They play a vital role in drilling innovation and building/constructing materials, as a supplement for boring fluids. They also act as stabilizers in pharmaceuticals, food and cosmetics (Colombo *et al*., 1999; Lowman and Peppas, 2000). The common cellulose ethers include methylcellulose (MC), ethylc ellulose (EC), carboxymethylcellulose (CMC), sodium carboxymethylcellulose (Na-CMC), hydroxyethylcellulose (HEC), hydroxypropylcellulose (HPC), hydroxypropyl methyl cellulose (HPMC) (Brandt, 2001; Poersch-Parcke and Kirchner, 2003) are soluble in common solvents. Cellulose ethers are hydrophilic (water loving), and when exposed to water, they absorb water to form hydrogels. Table 2.2 shows the commercially available cellulose ethers (Arthur, 1986).

Table 2.2: Commercially available cellulose ethers

Cellulose ethers	**Functional groups**	**Degree of Substitution**	**Solubility**
Carboxymethylcellulose	$-CH_2COONa$	0.5-2.9	Water
Methylcellulose	$-CH_3$	1.5-2.4	Hot water
Ethylcellulose	$-CH_2CH_3$	2.3-2.6	Organic solvents
Hydroxyethylcellulose	$-CH_2CH_2OH$	0.5-0.7	Water
Hydroxypropylcellulose	$-CH_2CH_2CH_2OH$	1.5-2.0	Water

2.4.2 Cellulose ester derivatives

Cellulose esters are divided into two groups, organic and inorganic cellulose esters. The organic cellulose esters find use in fillers, binders in composite and laminates (materials for photographic films), water purification, food and beverages, medicinal as well as pharmaceutical-bio-scientific investigations (Kusumocahyo *et al*., 2005; Malhotra *et al*., 2015). They include cellulose acetate pthalate (CAP), hydroxypropylmethylcellulose phthalate (HPMCP), cellulose acetate trimelitate (CAT), cellulose acetate butyrate (CAB), and cellulose acetate (CA). The inorganic cellulose esters are also important in pharmaceutical industries but less than the organic cellulose esters. The common inorganic cellulose includes cellulose nitrate, cellulose phosphate and cellulose sulfate.

2.5 Carboxymethylcellulose (CMC)

Carboxymethylcellulose is among the most paramount cellulose derivatives which play a vital role in the industry and our day-to-day activities. Due to its availability as a raw material (used in a diet pill, toothpaste, food additive) (Hussain *et al.*, 2010) more attention has been given to its properties as an anionic polymer (Chai and Mohamad, 2011), and aqueous solubility (Zhou and Zhang, 2000). Figure 2.2 shows the structure of CMC (Lin *et al.*, 2005).

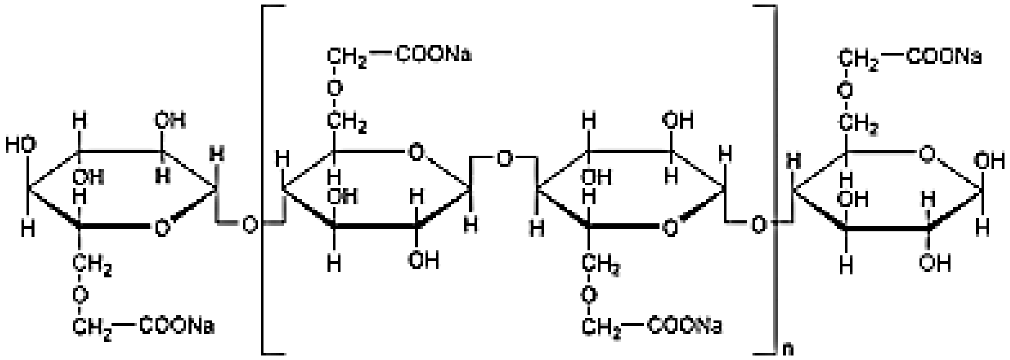


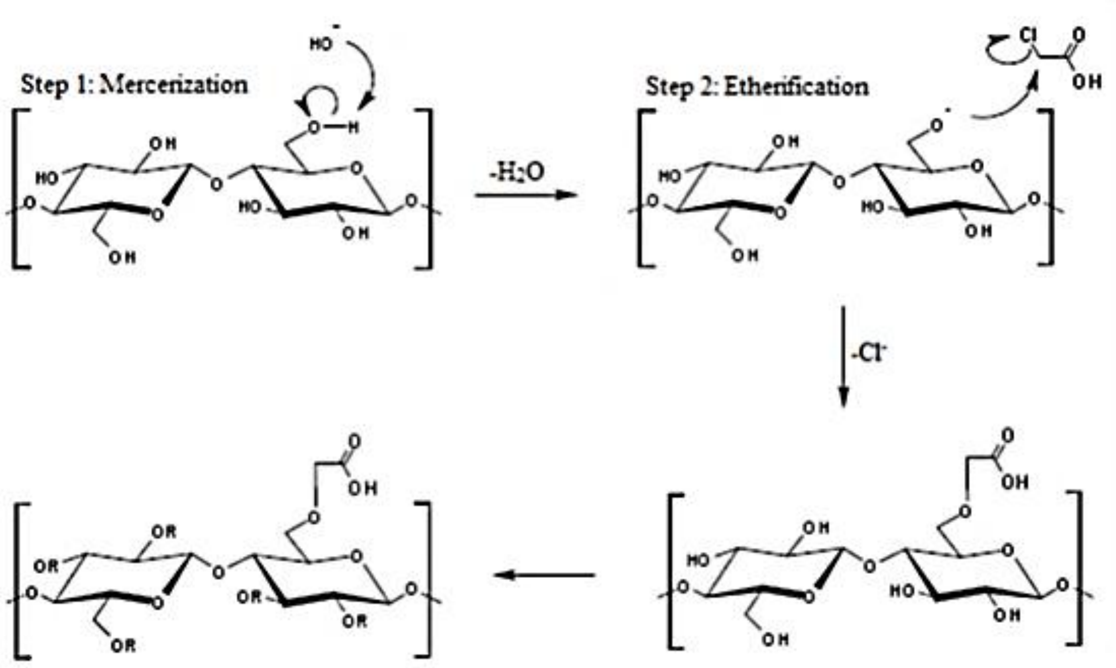
Figure 2.2: Carboxymethylcellulose

2.5.1 Preparation of carboxymethylcellulose

Sodium carboxymethylcellulose (Na-CMC) can be obtained when cellulose is reacted with monochloroacetic acid or Na-MCA in the presence of an organic solvent under alkaline conditions. The hydroxyl groups in cellulose are replaced by either carboxymethyl or sodium carboxymethyl group, depending on the DS, which is the average number of hydroxyl group in the cellulose structure which has been replaced by either carboxymethyl (CH_2COO) or sodium carboxymethyl group (CH_2COONa) at C2, C3, and C6 (Haleem *et al*., 2014).

Literature reports show that CMC has been prepared from cellulose obtained from agricultural waste biomass which include sugarcane bagasse (Alizadeh *et al*., 2017), palm carnel cake (Bono *et al*., 2009), cotton ginning (Haleem *et al*., 2014), sago waste (Pushpamalar *et al*., 2006), mulberry paper waste (Rachtanapun *et al*., 2015), papaya peel (Rachtanapun *et al*., 2010), and sugar beet pulp (Togrul and Arslan, 2003).

The mechanism of CMC synthesis involves the alkalization/mercerization of cellulose with NaOH, then followed by carboxymethylation/etherification using chloroacetic acid as shown in scheme 2.1.



Scheme 2.1: Reaction mechanism of the carboxymethylation reaction (Adeyanju *et al*., 2016)

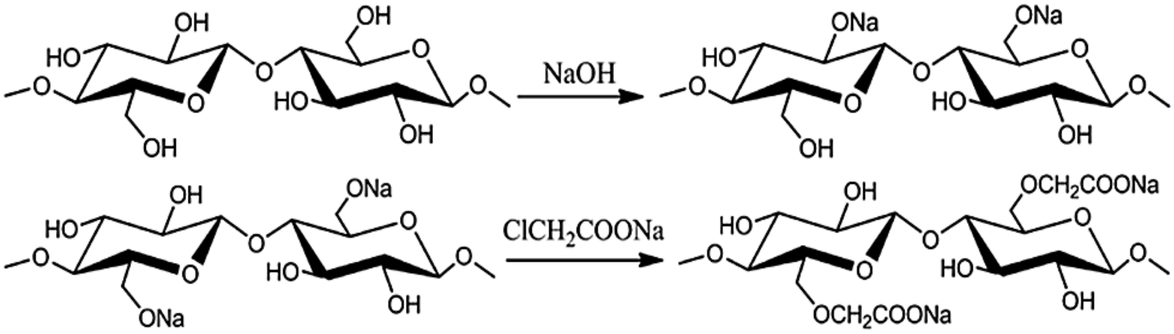
Studies according to Ladish *et al*. (1989), show that the enlargement of the indigenous cellulose fiber is brought about by the alkali, causing modification of the crystalline part of cellulose structure and increasing the it accessibility to chemicals. Hemicelluloses and lignin solubilized in a solution of 1.25 M NaOH between from 25 – 85 °C. A two-step reaction was used in the preparation of CMC. During preparation etherification was conducted by a slurry process where alkalization/mercerization were employed in the initial step (Heinze and Koschella, 2005). In the slurry technique, a good mixing efficiency is achieved by removing the cellulose in a mixture of water- alcohol-NaOH-systems with an alcohol (isopropanol or ethanol) at 20 – 30 ºC (Mann *et al*., 1998).

During mercerization on the other hand, the fluid stage goes about as a solvating specialist, breaks down the NaOH and circulates it equally to the cellulose hydroxyl bunches shaping salt cellulose. The fluid NaOH infiltrates the glasslike design of cellulose, at that point solvates its hydroxyl groups and in this way makes them accessible for etherification response by breaking the hydrogen securities (Sevege *et al.*, 1954; Yang and Zhu, 2007).

Apart from alkalized cellulose, the MCA or Na-MCA happens to be part of the second step, thereby forming CMC ethers. According to Krassig (1993), the responds NaOH with MCA or Na-MCA forms sodium chloride and sodium glycoate.). Williamson ether synthesis was used to obtain CMC based on the mechanisms shown in scheme 2.1 (Stigsson *et al.*, 2001).

2.5.2 Degree of substitution of carboxymethylcellulose

The degree of substitution (DS) of the carboxylic groups in CMC is the average number of the hydroxyl group (OH) in the cellulose structure which was substituted by either carboxymethyl or sodium carboxymethyl groups at C2, C3 and C6 of cellulose. As shown in scheme 2.2, cellulose unit has three hydroxyl (OH) group, namely C2, C3 and C6.



Scheme 2.2: Formation of carboxymethylcellulose (Lina *et al*., 2016)

The DS can be regarded as the number of the hydrogen in hydroxyl group (OH) of the cellulose unit replaced by carboxymethyl group. The DS is said to be 3, when all the hydroxyl groups are substituted by carboxymethyl groups (Salmi *et al*., 1994). To obtain a better DS, there is need for a proper selection of an etherifying agent, to fulfill the conditions for synthesis (Isogai, 2001). The majority of the DS obtained from the literature ranges between 0.5 – 2.0 (Zhao *et al*., 2003; He *et al*., 2009). The DS obtained from commercial CMC is usually between 0.4 – 1.4 (Sara and Lo, 2003; Silver *et al*., 2004). The DS plays a major role in thickening properties, water retention properties, viscosity modifier, emulsibility, solubility, acid resistance, salt tolerance and stability (Li *et al*., 2009). Carboxymethylcellulose has better emulsifying features when the DS is between 0.6 – 0.7, other properties can be enhanced when the DS is above 0.8. Table 2.3 shows the DS values of CMC from different source.

Table 2.3: The degree of substitution (DS) values of carboxymethylcellulose from different source

S/N	Cellulose source	Degree of Substitution	Reference
1.	Sago waste	0.33-0.82	Pushpamala *et al*., 2006
2.	Banana pseudo stem	0.26-0.75	Adinugraha *et al*., 2005
3.	Water hyacinth	0.24- 0.73	Barai *et al*., 1997
4.	Sugar beet pulp	0.11- 0.67	Togrul and Arslan, 2003
5.	Cotton fibre	0.15- 0.70	Heydarzadeh *et al*., 2009
6.	*Lantana camara*	0.21-1.22	Vershney *et al*., 2006
7.	Palm kernel cake	0.67	Bono *et al*., 2009
8.	Durian	1.632	Artanti and Kurniyati, 2016

2.5.3 Applications of carboxymethylcellulose

Carboxymethylcellulose is an important non-toxic material used as an emulsifier, a thickener, an adhesive, a coating (films) and protective colloid in food industries, pharmaceuticals, detergents, paper coating, medicine, agriculture and waste water treatment (Ahmad *et al*., 2014). Due to their low-cost and biodegradability, and ability to absorb high amounts of water, CMC hydrogels have attracted attention for numerous applications (Nie *et al*., 2004). Furthermore, because of its polymeric structure and high molecular weight, CMC can be used as a filler in biocomposite films (Almasi *et al*., 2010) and to improve the mechanical and barrier properties of pea starch-based films (Ma *et al*., 2008). Incorporation of CMC based hydrogel decreased water evaporation due to the high super absorbency feature of hydrogel (El-Salmawi, 2007). It enhanced water utilization, prolonged irrigation cycle and frequency (Zhan *et al*., 2004). During irrigation the amendment of soil using SAH composed of CMC and starch can serve another option of petroleum based SAH for water holding (Nnadi and Brave, 2011). Table 2.4 summarizes some of the applications of CMC.

Table 2.4: Examples of applications of CMC

Industry	Application	Function	Reference
Paper	Internal additive	Water binder	Seiichi and Shosuke (2000)
Detergents	Laundry	Soil anti-redisposition aid	Leupin and Gosselink (1999)
Cosmetics	Toothpaste	Thickener, suspension aid	Savage *et al*. (1954)
Textiles	Printing paste, dye	Water binder, thickener	Yang and Zhu (2007)
Foods	Frozen desserts	Inhibit ice crystal growth	Verraest *et al*. (1995)

2.6 Superabsorbent hydrogels (SAHs)

Superabsorbent hydrogels are 3-dimensional hydrophilic (water-loving) polymers. They have the ability of absorbing and retaining adequate water, and releasing it under stress conditions (Cheng *et al*., 2015). The physical entanglement (Jin *et al*., 2006), chemical crosslinking (Zhou *et al*., 2006), ionic bonding (Wong *et al*., 2009) and hydrogen bonds (Kang *et al*., 2007) are responsible for proper hydrogels network. Their water absorbency is as a result of the hydrophilic groups present on the polymer chain, such as OH, COOH, $CONH_2$ and SO_3H which forms hydrogen bonding with water molecules (Byrne *et al*., 2002). They are also sensitive to pH and ionic strength of the solution. Li *et al*. (2014) reported that superabsorbent hydrogels can be obtained from petroleum based and natural polymers, depending on the charge, mechanical and structural features. The petroleum based polymers (acrylates) were restricted from use due to being non-degradable, non- renewable and environmentally unfriendly. Native polymers like chitosan, cellulose and starch, are eco-friendly. Consequently, they have attracted much attention due to their cost-effectiveness, degradability and availability (Mahmoudian and Ganji, 2017).

Superabsorbent hydrogels are widely used in various fields such as hygiene napkins, disposable diapers, soil for horticulture and agriculture, water purification, food, construction and building, corneal, tendons, implant, substitute of skin, ligaments, cartilage, bones and biomedical applications such as controlled release of drugs (Wang *et al*., 2008; Chan *et al*., 2009; Chang *et al*., 2010). Other applications that have been researched on the include development of hydrogels for tissue engineering (Khan *et al*., 2009), sensors (Sorber *et al*., 2008) and drug delivery (Wu *et al*., 2008). Super-porous hydrogels (an exclusive class of hydrogels) have been used as pesticide release devices (Rudzinski *et al*., 2002), soil conditioner/improvers (Abd El-Rehim *et al*., 2004), slow-release fertilizers (Bowman *et al*., 1990; Teodorescu *et al*., 2009). They also have potential application in short and long term gastro-retentive drug delivery systems and super-disingrant and controlled release platforms (Sharma *et al*., 2016).

2.7 Crosslinking in cellulose based superabsorbent hydrogels

Cellulose-based hydrogels are obtained either by physical or chemical stabilization of cellulosic materials in aqueous solutions. In some instances the cellulose is combined with synthetic or natural polymers (Sannino *et al*., 2009). In chemical stabilization, polymer chemists use organic cross-linkers such as epichlorohydrin, carbodiimides, aldehydes, aldehyde-based reagents, urea and its derivatives and multifunctional carboxylic acids. However, these cross-linkers were proved to be toxic and expensive.

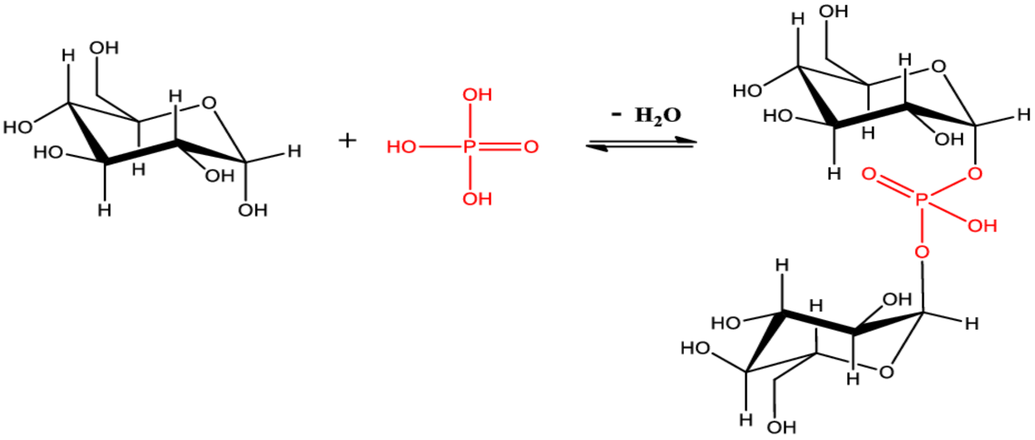
Alternatives include polycarboxylic acids such as citric acid, and other related chemicals like boric acid which are non-toxic, inexpensive and available, can at the same time offer the expected functional properties (Sawsan *et al*., 2018).

The process of crosslinking between the cellulose chains are activated by reagents which may occur either in dry state, or water solution, or organic solvents or even in the dry state (Wang and Chen, 2005; Dimitri *et al*., 2008). Cellulose-based hydrogels, have also been prepared through UV irradiation of the reactants (Chauhan *et al*., 2004; Ibrahim *et al*., 2007), and by absorption of a monomer solution into a dried porous cellulose network, followed by the crosslinking inside the network (Xie and Hsieh, 2003; Marsano *et al*., 2004). Cellulose nano-fibers or cellulosic fibers can provide water-retention ability and conveying of fluids over a wide dimensional range (Yoshimura *et al*., 2006). Other hydrogels, as superabsorbent materials, are used in a hygienic domain examples, female napkins, and disposable diapers. Moreover, in agricultural superabsorbent hydrogels are used as granules for holding soil moisture in arid areas.

2.7.1 Crosslinking of cellulose with phosphoric acid and its chemistry

The x-ray diffraction confirms that cellulose has a higher degree of crystallinity allying between 55 and 80 %, depending upon the source of the material (Wei *et al*., 1996). Cellulose with low crystallinity can be either prepared from the reaction of cellulose with concentrated mineral acid (sulfuric acid at 35 - 40 ^{o}C for 10 minutes, concentrated hydrochloric acid 37- 42 % at 30 - 50 ^{o}C). Phosphoric acid has been used for preparing amorphous cellulose and regeneration of cellulose (Jia *et al*., 2013). Literature has shown that at high concentrations of phosphoric acid, cellulose swells rapidly and the dissolution occurs with an increase in temperature (Hudson and Cucolo, 1980). The dissolution pattern of cellulose is accompanied by molecular packing density in a specific concentration of the aqueous phosphoric acid solution and the contact between cellulose and phosphoric acid thereby forming a C-O-P bridge. In comparison with other inorganic mineral acids (H_2SO_4, HCl, HNO_3), phosphoric acid is known to be safe, non-toxic, non-corrosive and low cost (Mosier *et al*., 2005). It represents other common mineral acids (Orthophosphoric acid, pyrophosphoric acid, tetraphosphoric acid among others).

The reaction of cellulose with phosphoric acid (heterogeneously) can be achieved by adding 85 % phosphoric acid to cellulose and increase the temperature to 100 ^{o}C for 30 minutes. In this reaction, phosphoric acid will attack the OH group of cellulose chain thereby forming a phosphorous acid group by ester linkage. The reaction of cellulose and phosphoric acid under molten urea (homogeneously) can be achieved by raising the temperature to 140 ^{o}C for 30 minutes. The reaction can also be achieved by using dimethylformamide (DMF) as a solvent, where cellulose is added to urea for 1 hour, followed by phosphoric acid, stirred for 4 hours at 130 ^{o}C. Scheme 2.3 shows the crosslinking of cellulose and phosphoric acid.

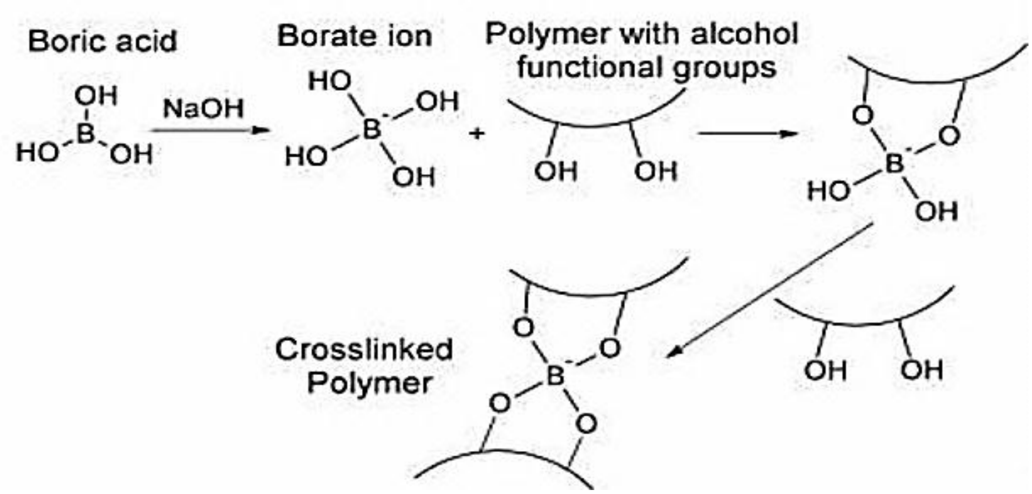


Scheme 2.3: Crosslinking of cellulose with phosphoric acid (González-Domínguez *et al*., 2018)

2.7.2 Crosslinking of cellulose with boric acid and its chemistry

Boric acid was tested and reported to be good and environmentally friendly (Erkmen and Yapici, 2015). Boron is one of the essential elements required for plant growth though toxic at high concentrations. Borax is a mineral of boron known to be environmentally friendly (Erkmen and Yapici, 2015). It is capable of crosslinking with molecules containing diol in aqueous solution under alkaline condition thereby forming borate complex.

Literature has shown that there is existence of strong bond between boric acid and hydroxyl groups in cellulose. The empty p orbital of boron, in boric acid is electrophilic in nature and as a result (it reacts rapidly with other nucleophiles) thereby forming a complex (Rietjen and Steenbergen, 2005). Cellulose on the other hand has several hydroxyl groups, and it is therefore expected that boric acid can crosslink them as shown in the scheme 2.4.



Scheme 2.4: Cross-linking of boric acid and available OH groups (Awada *et al*., 2014)

2.7.3 Crosslinking carboxymethylcellulose with ethane-1,2-diol

When in dry powder state, the CMC chains are twisted and lined with carboxyl groups, (-COOH). However, when placed into water, the carboxylic groups dissociate into charged carboxylate ions (COO^-) and the hydrogen ions, H^+. These ions repel each other on the polymer chain thereby widening the polymer coils permitting water to penetrate and come in to contact with many of carboxyl groups. Thus, treatment of sodium carboxylmethylcellulose (CMC) with 1,2-ethanediol, allows crosslinking through an ester linkages as shown in Figure 2.3.

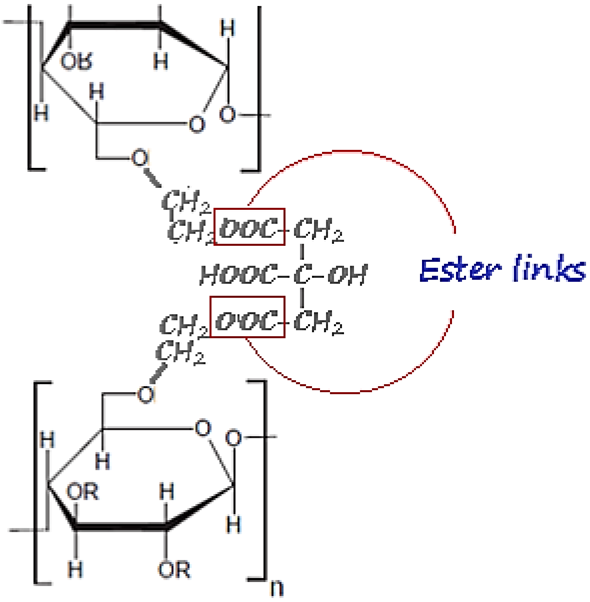


Figure 2.3: Formation of the ester linkage (Abdlhameed *et al*., 2020)

2.7.4 Crosslinking carboxymethylcellulose with ethane-1,2-diamine

Crosslinking is widely used as a method of modifying polymer properties (Thakur *et al*., 2018). It involves the formation of three dimensional structures causing substantial changes in material properties, thereby avoiding dissolution in the polymer network. Ethylenediamine has been used by several researchers as a cross-linker (Okamoto *et al*., 1999; Vanderck *et al*., 2010; Yan *et al*., 2010). Vanderck *et al*. (2010) used ethylenediamine to crosslink polyimide membrane in a methanol environment. The reaction can either be activated by a chemical reaction or UV irradiation. Bifunctional amines such as ethylenediamine and para-xylylethylenediamine have also been used as cross-linkers in gas separation membranes to avoid plasticization (Okamoto *et al*., 1999). Yan *et al*. (2010) observed that the solution of ethane-1,2-diamine was primarily used to crosslink the pore walls and active surfaces of the polymer membrane.

Using ethylenediamine as a cross-linker during the synthesis of few-layers reduced graphene oxide, was cost effective and that the product showed advantages as an electrolyte for a Li^+ ion battery with a charge density capacity of 346m Ah g^{-1} (Li *et al*., 2014). Luan *et al*. (2013) also used ethylenediamine as a cross-linker during the synthesis of a robust highly conductive 3D GO hydrogel, The product showed specific surface area of 745 m^2 g^{-1} and electrical conductivity of 1351 S m^{-1} with 10.3 MPa break strength. Electrostatic repulsions between the COO^- groups of CMC ions create more spaces within the hydrogel matrix, thereby absorbing a high amount of water.

2.8 Effect of superabsorbent hydrogels on soil

Studies have shown that water shortage and stress experienced by plants in arid areas, can be reduced by superabsorbent hydrogels (Bakass *et al*., 2002; Zohuriaan-Mehr and Kabiri, 2008; Han *et al*., 2010). The hydrogels improve soil physical properties such as water holding capacity and nutrient retention, thereby enhancing plant life cycle under difficult conditions (Huttermann *et al.*, 1999; Oscroft *et al.*, 2000; Viero *et al.*, 2002; Abedi Koupai and Asadkazemi, 2006; Orikiriza *et al.,* 2009). A lot of the literature report superabsorbent hydrogels that are derived synthetically from petroleum products and most of them are known to be toxic, non-degradable and non-biocompatible and therefore not suitable for use in agriculture (Shang *et al*., 2008). There is need therefore to develop SAHs that are eco-friendly, especially from natural materials such as cellulose, starch and chitosan. These have attracted much attention due to their cost-effectiveness, degradability and availability (Mahmoudian and Ganji, 2017). Mas'ud *et al*. (2013) conducted a research on improving benefit of cassava waste in preparing

SAHs. The synthesis was carried out by graft copolymerization, acrylamide, *N*,*N*-methylene bisacrylamide and ammonium persulphate as monomer and cross-linker. The findings showed that the waste (cassava) has great potentials in synthesis of SAHs. The SAHs improve texture and structure of soil, water penetration (Helalia and Latey, 1988; Helalia and Latey, 1989), soil crispiness (Azzam, 1980), water retention of soil (Tayel and El-hady, 1981), aeration and infiltration of soil, available water and water retension (Abedi-Koupia *et al*., 2008) and ease water maintenance in soil (Shooshtarian *et al*., 2011).

Sandy soils have low water retention capacity which means they allow irrigation or rain water and plant nutrients to leach below the root zone (Al-Omran and Al-Harbi, 1998). Because the superabsorbent hydrogels have the ability to absorb and retain water (Sannino *et al*., 2009), about 400 times of its original weight (Montesano *et al*., 2015), they are able to improve seedling survival and early growth of plants especially in arid areas if applied in correct amounts (Bakass *et al*., 2002).

It has been reported that the incorporation of superabsorbent hydrogels to sandy soil improves the accessibility of water to plants (Al-Harbi and Al-Omran, 1999; Konpai and Sohrab, 2004)). The hydrogels decrease saturated hydraulic conductivity, thereby, decreasing drainage pores and also increasing retention pores. It was exported in the study that water storage of sandy soil increased in the range of pF < 2 (Leciejewski, 2009) a result that agreed with the report of Paluszek and Zembrowski (2008).

Application of SAHs may conserve water and increase the soils capability for water retention, relative water content in leaf, ensuring accessible water, and plant growth increase under stress condition (Kramer, 1988).

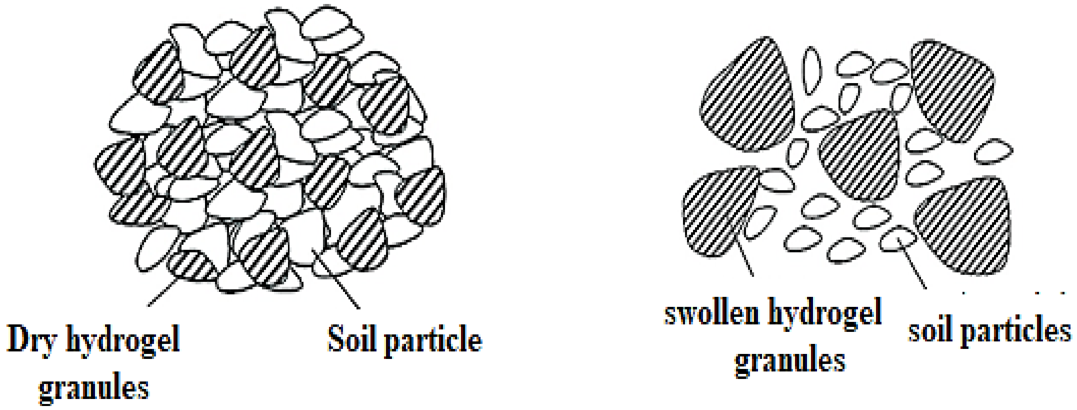


Figure 2.4: Effect of superabsorbent hydrogels on soil (Dimitri *et al*., 2013)

2.9 Effect of superabsorbent hydrogel on plants

Fanta *et al*. (1971) reported that SAH strengthens the growth of a plant and acts as a water reservoir. The application of SAHs in agriculture and horticulture is in the shape of seed coating, seed additives and root dips (Zohuriaan-Mehr and Kabiri, 2008). Several studies have shown that SAH increase in water holding ability and improves plant growth (Boatright *et al*., 1997; De Varennes and Queda, 2005) and decrease in drought stress (Gehring and Lewis, 1980). The water conserved by SAHs provide a better environment needed for plant growth, relieving drought stress and enhances the establishment phase (Johnson and Leah, 1990). Figure 2.5 shows the SAHs surrounding plant root (Khodadadi, 2016).

Figure 2.5: Superabsorbent hydrogels surrounding plants root

The impact of perlite on water use efficiency and grain yield in winter wheat (*Zarrin cultivar*) was investigated by Moghimi *et al*. (2011). The research was carried out in an open field using complete random block design (CRBD) with seven treatments (S_0, S_1, S_2, S_3, S_4, S_5 and S_6), 75, 150, 300, 600, 1200 and 2400 $kgha^{-1}$ with four replicates. The result from the statistical analysis shows that by the addition of perlite to the soil, there was an increase of about 39.9 and 31.5 % of biological yield and grain yield wheat, which is statistically significant at 1 % confidence level. The result from the study also revealed that in the treatment of applying 2400 $kgha^{-1}$ perlite, there was an increase up to 40.12 % of water use efficiency. Incorporation of K400 stockosorb hydrogels in 0.4 to 0.6 % weights showed a significant increase in buttonwood (*Conocarpus erectus*) seedlings in arid region of Saudi Arabia (Al Humaid and Moftah, 2007). Al Harbi *et al*.

(1999) reported that the addition of SAH up to 0.3 % had a positive effect on the plant, compared to 0.4 % concentration, however the effect was reversed.

The increase in hydrogel at high dose increased significantly the growth parameters (plant height, leaf area, stem diameter) of maize in the arid areas of China (Islam *et al*., 2011). The highest yield was obtained at 30 kgha^{-1} of the SAH. At 10 and 20 kgha^{-1}, the yield was lower, due to insufficient hydrogels. Maize yield increased following superabsorbent polymer application at 15 kgha^{-1} with half the amount (150 kgha^{-1}) of fertilizer by 11.2 % under low, 18.8 % under medium, and 29.2 % under high dose as compared to control receiving conventional fertilizer dose (300 kgha^{-1}). The use of SAH served as conveyor and regulator of nutrients release, which helped in limiting manure loss (Mikkelsen, 1994). The retained water and nutrients are released to the plants slowly to improve growth (Yazdani *et al*., 2007).

The leaf area and number of leafs of cucumber increased by incorporating SAH with soil (Mamun *et al*., 2017). The dry matter productions of tomatoes and cotton (Wallace and Wallace, 1986), maize (El Hady *et al*., 1981) significantly increased with an increase in SAH as compared to control.

2.10 Effect of superabsorbent hydrogel on root activities

Several researchers have reported the impacts of SAH on root activities (Taylor and Halfacre, 1986; Volkamar and Chang, 1995; Sendure *et al*., 2001; Shi *et al*., 2010). An increase in superabsorbent concentration significantly increases root parameters such as root volume and root length. The application of SAHs in known to increase root growth (Sendur *et al*., 2001; Yang *et al*., 2006; Shi *et al*., 2010).

Applying superabsorbent hydrogels at 1.87 g per pot improved root growth as related to the zero (control) (Volkamar and Chang, 1995). The SAHs significantly increased dry weight and root length as compared to the zero (control) (Taylor and Halfacre 1986; Sendur *et al*., 2001). Hutterman *et al*. (1999), synthesized a SAH from stockosorb K400, cross-linked with polyacrylamide and almost 40 % of the amide groups undergoes hydrolysed to form carboxylic groups. The findings from the study showed that SAH improved root and shoots performance of *Pinus halepensis* during dry season.

2.11 Effect of superabsorbent hydrogels on water use efficiency

The majority of farmers in the arid region solely depend on rainfall for agricultural practices. It will be of great important to increase the water holding capacity of soil, specifically in arid areas. This can be achieved by incorporation of soil with superabsorbent hydrogels. The SAHs were reported to retard the frequency of irrigation in semi-arid areas (Abedi-Koupai and Asadkazemi, 2006). Dorraji *et al*. (2010) reported that soil amendment with superabsorbent hydrogels increase plant growth, yield and water use efficiency. Superabsorbent hydrogels improves water release from soil as a result of decrease in soil water content (Narjary *et al*., 2012). The SAHs also improves water used efficiency in crops such as cucumber (El-Hady and Wanas, 2006), maize (Dorraji *et al*., 2010) and vegetables (Akhter *et al*., 2004; Huettermann *et al*., 2009).

2.12 Applications of superabsorbent hydrogels

Superabsorbent hydrogels are widely used in various fields such as hygiene napkins, disposal diapers, water and purification and agriculture (Wang *et al*., 2008). They are also important in oil drilling, production of paper, food packaging and pharmaceuticals (Li *et al*., 2004; Han *et al*., 2010). Table 2.5 shows the list of various SAHs and their applications.

Table 2.5: Listing of superabsorbent hydrogel and their applications

Applications	Superabsorbent hydrogels	References
Agriculture and waste treatment	Starch,	Trksak and Ford, 2008
	Poly(vinyl alcohol), poly(vinyl methyl ether), poly(*N*-isopropyl acrylamide,	Sen *et al*., 2007
Technical products (pharmaceuticals and cosmetics)	Starch	Trksak and Ford, 2008
	Chitosan and chitin, pectin, carrageenan, xanthan, bean gum, guar gum	Phillips *et al*., 2003
Tissue Engineering	Poly (acrylic acid), Poly (vinyl alcohol),	Rosiak *et al*., 1995
	Collagen	Drury and Mooney, 2003
Injectable polymeric system	Chitosan β-hairpin peptide, polypetides, polyphosphazenes and polyesters	Yan *et al*., 2010
Dental	Hydrocolloids	Al-assaf *et al*., 2009
Wound dressing	Carboxymethylcellulose, xanthan, algnite	Rosiak *et al*., 1995
	Agar, poly(ethylene glycol), poly(vinylpyrolidone)	Benamer *et al*., 2006
	Polyurethane, poly(ethylene glycol) and poly(propyleneglycol)	Rosiak and Yoshii, 1999

2.13 Chemical reactions under microwave heating

Conducting chemical reactions under microwave irradiation has been used in place of the usual heating by many researchers (Kumar *et al*., 2010; Danilo *et al*., 2015; Ekezie *et al*., 2017). It has been employed as the new system of heating polymers and organic compounds (Zhang *et al*., 2011). It improves heating efficiency and provides a volumetric heating process as compared to other conventional heating techniques. In comparison with other methods of heating, microwave irradiation speeds up the reaction rate within a few minutes. There is little information on the utilization of microwave heating, though some were performed under dissolvable free condition (Vladimíra *et al*., 2008). Mazzocchia *et al*. (2004) revealed that microwave irradiation speeds up conversion and chemical reaction rate.

2.14 Characterization of hydrogels

Hydrogels have been characterized by Fourier transform infrared (FTIR) spectroscopy, for functional group identification, x-ray fluorescence (XRF) utilized both quantitative investigations and subjective chemical elements (Mantler and Schreiner, 2000). The x-ray diffraction (XRD) is used to determine crystalline materials, scanning electron microscopy (SEM) used in studying the surface morphology), thermogravimetric analysis (TGA) is used to determine the material thermal stability (Ramaswamy *et al*., 2010).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Research design

This study utilized experimental design that involved:

1. Extraction of cellulose from rice husks, its conversion to carboxymethylcellulose and characterization of the CMC
2. Synthesis and characterization of superabsorbent hydrogels by crosslinking carboxymethylcellulose with ethane-1,2-diol and ethane-1,2-diamine, cellulose with boric acid and phosphoric acid; and
3. Application of the synthesized SAHs in the growing of maize (*Zea mays*) plants in a greenhouse and measuring growth and yield parameters

3.2 Collection and pre-treatment of raw materials

Rice husks were collected from Euro rice mills in Mwea, Kirinyaga County – Kenya and brought to Kenyatta University Department of Chemistry laboratories. The samples were rinsed with distilled water to remove soil and dust, filtered and dried at 100 ^{o}C for 1 hour in an electric oven and ground using a laboratory grinder.

3.3 Chemicals and reagents

All the chemicals used were of analytical grade and used as purchased. Hydrochloric acid HCl and phenolphthalein were bought from Sigma-Aldrich (Germany). Glacial acetic acid sodium hydroxide and were bought from Merck Chemical Co. (Darmstadt, Germany). Nitric acid, ethanol and methanol were purchased from Kobian Kenya Limited. Monochloroacetic acid was purchased from Daejung Co. (South Korea).

3.4 Instrumentations

The XRD- diffractograms were recorded on a D2 Phaser, Bruker AXS, Germany diffractometer. XRF spectra were recorded on XRF 200 (compact) spectrometer, while FTIR spectra were recorded using FTIR-8400 Spectrophotometer. Surface morphology of the hydrogels was determined by scanning electron microscopy at different magnifications. A regular kitchen Ramton microwave + grill (RM-240) was used in the synthesis, while oven WTC binder (W × D × H = 63.5 × 63 × 61.5 cm) was used to dry products.

3.5 Extraction of cellulose from rice husks

Cellulose was extracted from the rice husks following the cleaner method that uses eco-friendly solvent acetic acid solution (Xiudong *et al.*, 2016). The extraction was done from finely ground husks and from larger rice husks pieces. Five (5.00) g of rice husks (finely ground) was weighed and transferred into a 250 mL Erlenmeyer flask followed by 100 mL solution of 80 % acetic acid and 10 mL of 70 % nitric acid. The flask was then covered with aluminium foil and heated at 120 ^{o}C for 20 minutes in an oven (WTC binder). The mixture was allowed to cool to room temperature after which 60 mL of distilled water was added and mixed well. The mixture was filtered and the residue was washed with distilled water and 95 % ethanol. The residue was dried in an oven at 60 ^{o}C for 19 hours. This procedure was repeated for ground rice husks.

The yield of the cellulose extract was calculated using equation 3.1

$$\% \text{ Extraction yield} = \frac{Dry\ weight\ extract\ of\ RH}{Weight\ of\ RH} \times 100\ \% \qquad \text{.........3.1}$$

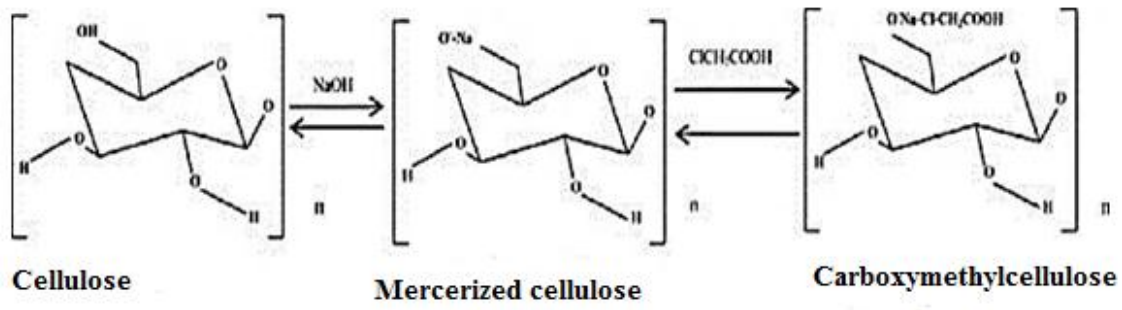
3.6 Synthesis of carboxymethylcellulose

The synthesis of CMC involved two stages: alkalization and carboxymethylation (etherification). About 6.00 g of the rice husks cellulose was added to 100 mL of distilled water in a 250 mL Erlenmeyer flask. Then 10 mL of 30 % of sodium hydroxide solution was added drop-wise. The alkalization process was carried out for 1 hour at 25 ^{o}C on a fitted shaker. After 1 hour, 5.00 g of MCA was added to the mixture and heated in a microwave oven at power output of 6 which correspond to 420 watts for 2 minutes (see appendices 1A – 1E for details of optimization of synthesis conditions). The resultant mixture was allowed to cool to room temperature and then filtered. The residue obtained was soaked in 100 mL of methanol for 24 hours, after which it was neutralized using glacial acetic acid. The mixture was filtered and the residue was dried in an oven at 60 ^{o}C. All conversions were done in triplicate.

The yield of CMC was calculated using equation 3.2,

$$\text{The yield of CMC (\%)} = \frac{Weight\ of\ CMC\ (g)}{Weight\ of\ Cellulose\ (g)} \times 100 \text{……………..3.2}$$

Scheme 3.1 shows the synthesis of CMC from cellulose (Park *et al.*, 2014).



Scheme 3.1: Synthesis of carboxymethylcellulose from cellulose

3.6.1 Determination of the degree of substitution (DS) in carboxymethylcellulose

One (1.00) g of CMC was added to 250 mL of Erlenmeyer flask, followed by 50 mL of 95 % ethanol. A solution of 2 M of nitric acid (5.00 mL) was added to the contents at room temperature, and then heated for 5 minutes on a hot plate after which the mixture was settle. The contents were filtered (using a filter paper) and the residue washed with 100 mL of 95 % ethanol to remove the salt. Five (5.00) g of CMC was added to 250 mL of Erlenmeyer's flask followed by 100 mL of distilled water, then 25 mL of 0.5 M NaOH solution after which the mixture was heated for 20 minutes. The resultant mixture was allowed to cool and then titrated against 0.3 mL HCl to a phenolphthalein indicator endpoint.

The DS of CMC was calculated using the equations below (Jiang *et al*., 2011).

$$A = \frac{BC-DE}{F}, \qquad \ldots\ldots\ldots\ldots 3.3$$

$$DS = \frac{0.162\times A}{1-(0.58\times A)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots 3.4$$

Where, A= Milli-equivalents of acid consumed per gram of CMC specimen

B= Volume of NaOH added

C= Concentration of NaOH

D= Volume of consumed HCl

E= Concentration of HCl used

F= Mass of CMC Specimen used

Plate 3.1 shows the extracted cellulose from rice before and after alkalization, before etherification.

(a) (b)

Plate 3.1: Cellulose (a) before alkalization, (b) after alkalization

3.7 Synthesis of cellulose-based hydrogels (SAHs)

Four different cellulose-based hydrogels were synthesized in this study by crosslinking CMC with ethane-1,2-diol, and ethane-1,2-diamine, respectively and cellulose with phosphoric acid and boric acid. The synthesis conditions that is, power output of the microwave oven, amount of cross-linkers required as well as time of heating during crosslinking were optimized as described in appendices 2 - 5.

3.7.1 Cross-linking of CMC with ethane-1, 2-diol

Three (3.00) g of CMC (DS = 0.79) was added to 30 mL of distilled water in a 200 mL beaker and stirred (by magnetic stirrer) at room temperature for 24 hours. The resulting solution was treated with 5 mL ethane-1,2-diol and heated in a microwave oven at a power output of 140 watts for 5 minutes. The mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled water and dried to a constant weight in an oven at 40 ^{o}C . The optimum synthesis conditions of the ethane-1,2-diol superabsorbent hydrogel were determined by synthesizing the SAH under different conditions of microwave power out-put, reaction time and amount of cross-linker and determining the percent swelling of the product. The conditions that gave hydrogel with the highest percentage swelling were taken as optimum working condition (See appendices 2A – 2C for details of optimization of synthesis conditions). The product was characterized by determining the percentage swelling, FTIR spectroscopy, XRD and SEM. Plate 3.2 shows SAH from CMC cross-linked with ethane-1,2-diol.

Plate 3.2: Superabsorbent hydrogel from carboxymethylcellulose crosslinked with ethane-1,2-diol seen stuck at the bottom of the beaker

3.7.2 Cross-linking of CMC with ethane-1,2-diamine

Three (3.00) g of CMC (DS = 0.79) was added to 30 mL of distilled water in a 200 mL beaker and stirred (by magnetic stirrer) at room temperature for 24 hours. The resulting solution was treated with 10 mL ethane-1,2-diamine and heated in a microwave oven at a power output of 420 watts for 5 minutes (See appendices 3A – 3C for optimization of reaction conditions). The mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled water and dried in an oven at 40 ^{o}C until it maintains a constant weight. The product was characterized by determining percentage swelling, FTIR spectroscopy, XRD.

3.7.3 Cross-linking of cellulose with phosphoric acid

Two (2.00) g of extracted cellulose was added to 30 mL of distilled water in a 200 mL beaker. The contents were dissolved by stirring at room temperature for 24 hours. The resulting solution was treated with 10 mL of 85 % phosphoric acid and heated in a microwave at a power output of 420 watts for 3 minutes. (See appendices 4A – 4C for optimization of reaction conditions). The mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled water and dried in an oven at 40 ^{o}C. The product was characterized by determining percentage swelling, FTIR spectroscopy, XRD. Plate 3.5 shows SAHs from cellulose crosslinked with phosphoric acid.

Plate 3.3: Superabsorbent hydrogel from cellulose crosslinked with phosphoric acid

3.7.4 Cross-linking of cellulose with boric acid under microwave heating

Pre-weighed rice husks cellulose (2.00 g) was added to 30 mL of distilled water in a 200 mL beaker stirred (by magnetic stirrer) at room temperature for 24 hours during which all the material dissolved. The resulting solution was treated with 1 g of boric acid and heated in a microwave oven at a power output of 280 watts for 5 minutes (See appendices 5A – 5C for optimization of reaction conditions). The mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled water and dried to constant weight in an oven at 40 ^{o}C. The product was characterized by determining percentage swelling, FTIR spectroscopy, XRD.

3.7.5 Crosslinking of cellulose with boric acid under reflux

Pre-weighed rice husks cellulose (2.00 g)was added to 30 mL of distilled water in a 200 mL beaker stirred (by a magnetic stirrer) at room temperature for 24 hours during which all the material dissolved. The solution was transferred into a round bottomed flask and refluxed with 1 g of boric acid was added and heated at 80 ^{o}C for 12 and 24 hours. The mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled water and dried in an oven at 40 ^{o}C. The product was subjected to FTIR spectroscopy.

3.8 Characterizations of cellulose, CMC and SAHs

3.8.1 Fourier Transform Infrared (FTIR) Spectroscopy

This was used to identify the functional groups in cellulose, CMC and the SAHs prepared. The FTIR spectra of cellulose and CMC and the SAH were taken in solid scale as KBr pellets. One (1) mg of dried sample was ground together with 25.00 mg of KBr and used to make a pellet. The Fourier transform infrared spectra were recorded on a Shimadzu IR Tracer -100 spectrophotometer in the mid-IR region of 3800 - 400 cm^{-1}.

3.8.2 X-ray Diffraction (XRD)

The x-ray diffraction patterns of the cellulose, CMC and SAHs were recorded on a D2 PHASER Bruker AXS X-ray diffractometer. The powder samples were dried in a hot air oven at 105 ^{o}C for 3 hours before analysis. The scattering angle (2θ) ranged from 10 to 60^{o} at a scan rate of 5^{o}/min.

3.8.3 Scanning electron microscopy (SEM)

The surface morphology of the cellulose, CMC, and the hydrogels was studied on a Jeol JSM-6490A scanning electron microscope at an accelerating voltage of 5.0 kV at the University of Cape Town, in South Africa. The samples were coated with a thin gold layer before conductivity. The images were captured at different magnifications (5.00 kx, 1.00 kx, 200 kx and so on).

3.8.4 Percentage swelling

To obtain the percentage swelling, the superabsorbent hydrogel sample was weighed and soaked in 30 mL of distilled water for 24 hours at room temperature. After the soaking time, the excess distilled water on the surface of the hydrogel was removed with filter paper (blotting), the hydrogel was weighed again. The percentage swelling of the SAH was determined using equation 3.5.

$$\text{Swelling percentage} = \frac{Wt - Wo}{Wo} \times 100\ \% \qquad \text{………3.5}$$

Where:

Wt – weight of the swollen hydrogel at a time, Wo – weight of the dry hydrogel.

3.9 Determination of the efficacy of the superabsorbent hydrogels

3.9.1 Planting conditions and application of superabsorbent hydrogels

The experiment was conducted in Darazo, Bauchi State, Nigeria in a greenhouse. The soils in the area are classified as sandy soils with, low fertility and productivity (Maduakor, 1999). The experiment was laid out in a randomized block design with three replications and six treatments. The treatments were 0 (control), 1.00, 2.00, 3.00, 4.00 and 5.00 g of four different SAHs (adding up to 72 pots). The soil samples were mixed with goat manure (2:1) and transferred into black polythene bags (pots).

The pots were saturated with borehole water for 2 days before planting. Two seeds of DMRESR-Y maize variety in each of the 72 pots, spreading them out across the soil, the seeds were pushed gently one inch into the soil. The pots were watered immediately after planting, and watered twice daily (morning and evening) until the seeds germinated (at 7 days). In order to improve the soil fertility, N. P. K. fertilizer with (20. 10. 10) formulation (Urea, diammonium phosphate, muriate of potash) was added after germination at 14 days. The watering was stopped after 21 days from planting. Variable amount of the SAHs (1.00, 2.00, 3.00, 4.00 and 5.00 g) was applied to the pots at depth of 5 - 8 cm mixed with soil closer to the plant roots, the doses were set in triplicate as shown in plates 3.5. The soil without amendment of the SAH was considered as a control.

Plate 3.4: Constructed local greenhouse

Plate 3.5: Inside the green house before planting

Plate 3.6: Maize plant after at 3 weeks

Parameters measured and recorded included plant height, the number of leaves, area of leafs, leaf length, leaf diameter after 3, 6, 9 and 12 weeks. Harvesting of maize was at week 12 (after matured), and maize stalk were cut using a machete. The maize cobs were dried by spreading on a mat. The yield parameters determined included number of cobs per pot, cob length , cob diameter, cob weight, grain weight and number of grains per cob. Cob weight and grain weight were determined using an electronic analytical balance.

3.10 Pre-harvest studies of maize grown in greenhouse

3.10.1 Plant height

The plant height of maize in each pot was determined using a meter ruler from ground level to the developing tip of the maize at 3, 6, 9 and 12 weeks and expressed in centimeters, and the mean values were worked out.

3.10.2 Number of leafs per plant

The numbers of leaves of each plant in the 72 pots were counted at weeks 3, 6, 9 and 12 after sowing; and the mean values were recorded

3.10.3 Leaf length and diameter

The leaf length and diameter were also measured using a meter rule, and used in determining the leaf area as shown in 3.10.4.

3.10.4 Leaf area

The leaf area was calculated from the leaf length and leaf diameter using equation 3.6.

$$\text{Leaf area} = \text{leaf length} \times \text{leaf diameter} \times k \qquad \ldots\ldots\ldots\ldots 3.6$$

where k is the coefficient for determination leaf area, typically taken as k = 0.75 (Yao *et al*., 2010; Musa and Usman, 2016; Liliane *et al*., 2019).

3.11 Post-harvest studies

3.11.1 Harvesting

The maize was harvested with the help of sickle and digger after it reached maturity that is 12 weeks, when the leaves and husks turn to yellow and dry. The maize was dried in the sun, then threshed, shelled and winnowed. The grains were packed and labeled properly and transported to the laboratory for further examination.

3.11.2 Yield attributes of maize

3.11.2.1 Number of cobs per plants

The number of cobs in each plant (maize) was counted at the harvesting stage; the mean value was calculated and recorded.

3.11.2.2 Length and diameter of cob (cm)

The biggest maize cob was taken out from each plant, the length and diameter were determined from the base to the tip of the cob using a metre rule, and the average mean was calculated and recorded in centimetres.

3.11.2.3 Cob weight (g)

The cob weight of the biggest maize cob was measured in g using an electronic weighing balance.

3.11.2.4 Number of grains per cob

The average number of grains per cob was counted manually and recorded.

3.11.2.5 Grain weight (g)

The grains from the biggest cobs obtained were also weighed in grams using an electronic weighing balance.

3.12 Statistical analysis

The optimizations results obtained from the studies were subjected to analysis of variance (ANOVA) using minitab software version 17, Fisher least significance difference (LSD) test to generate mean at 5 % confidence level of significance.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

The general objective of this study was to extract cellulose from rice husks and use it to synthesize cellulose-based superabsorbent hydrogels for soil conditioning in arid and semi-arid agricultural zones. This chapter therefore, reports the extraction of cellulose from rice husks, its characterization, its crosslinking with boric acid and phosphoric acid to form SAHs and its modification to carboxymethylcellulose which was then converted to SAHs by crosslinking with ethane-1,2-diol, ethane-1,2-diamine separately. This chapter also presents and discusses results from studies on the efficacy of the SAHs in the growing of maize in a greenhouse.

4.2 Extraction of cellulose from rice husks

The extraction was done from finely ground husks and from roughly rice husks. Treatment of the rice with (10:1 v/v) mixture of 80 % acetic acid and 70 % nitric acid resulted in the extraction of lignin and hemicellulose into the mixture leaving behind cellulose. Plate 4.1 and 4.2 shows rice husks after crushing and the extracted cellulose from rice husks.

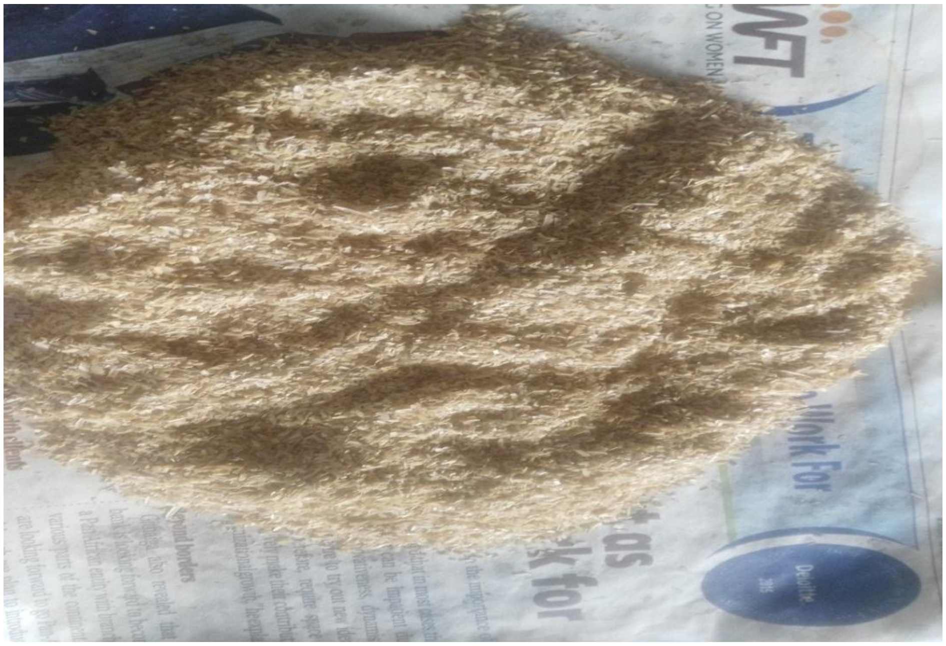


Plate 4.1: Rice husks after crushing

Plate 4.2: Cellulose extracted from rice husks

The Solid which was washed with distilled water followed by 95 % ethylalcohol and dried to a constant weight. Table 4.1 summarizes the results.

Table 4.1: Yield of extracted cellulose (%)

S/N	Type of rice husks	Dry weight of extracted RH (g)	Weight of RH (g)	% yield of extracted cellulose
1	Grounded RH	4.81±0.01	6.00	80.16±0.00
2	Finely RH	4.90±0.01	6.00	81.67±0.00

The cellulose extracted from rice husks was 81.67 ± 0.00 %. The value obtained from this study was higher than the cellulose obtained from rice husks reported by Ugheoke and Mamat (2020) to be 13.54 %, but lower than the amount of cellulose obtained from oil palm empty bunches which was revealed by Nazir *et al*. (2013) to be (93.7 %) and 97.1 % (Leh *et al*., 2008). Similarly, the value was higher than the 62.3 % reported by Wanrosli *et al*. (2011). The removal of lignin and hemicellulose using acid effectively produced cellulose content of 64 % (w/w) on dry weight. The value was higher than the cellulose yield revealed by Sun *et al*. (1999) and Wanrosli *et al*. (2004) to be 44.4 % and 60.6 % by using chlorite (ClO_2^-) and sodium hydroxide (NaOH), respectively. Cellulose extraction from rice husks (Bleaching and hydrolysis) yielded 13.45 % (w/w) (Rizki *et al*., 2020). This implies that the amount of cellulose solely depends on the plant and the nature of the reagents used in the process of extraction.

4.3 Characterization of cellulose extracted from rice husks

4.3.1 Fourier transform infrared (FTIR) of extracted cellulose

The FTIR spectra of both the rice husks and the extracted cellulose were recorded and compared (Figure 4.1 and 4.2, respectively).

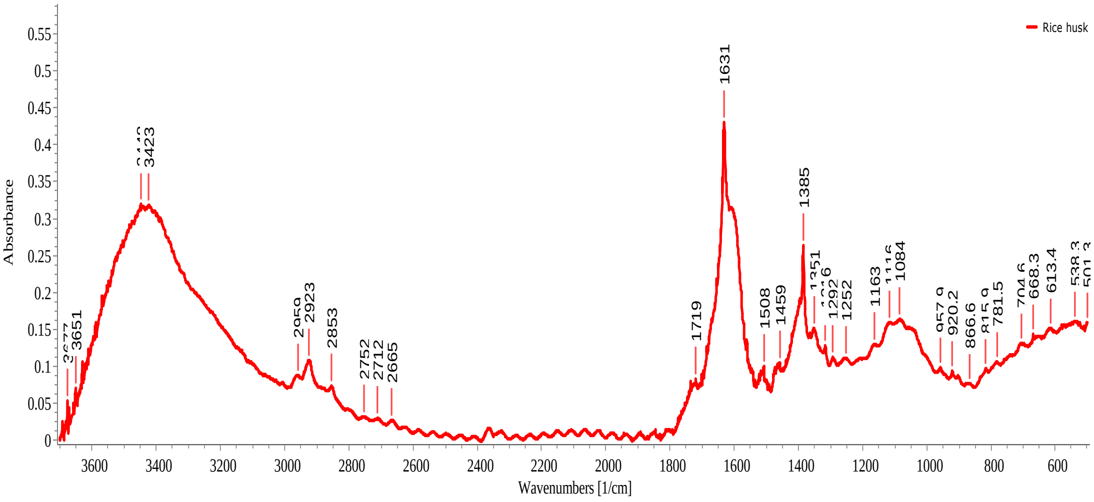


Figure 4.1: FTIR spectrum of rice husks before cellulose extraction

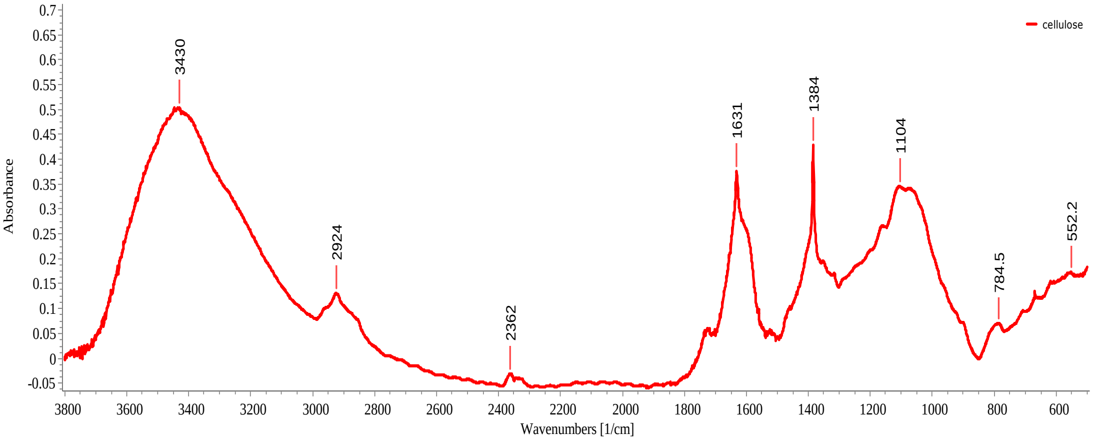


Figure 4.2: FTIR spectrum of cellulose extracted from rice husks

The spectrum of the cellulose extracted from rice husks showed characteristic absorption bands (see Figure 4.2). The broad absorption band at 3432.39 cm^{-1} was assigned to the OH-stretching vibration (Wingerson and Richard, 2002), while the band at 2924.13 cm^{-1} was assigned to the C–H stretching vibration. The absorption band at 1631.81 cm^{-1} was assigned to absorbed water and the absorption band at 1383 cm^{-1}, represents the symmetric CH_2 bending vibration. The hemicellulose and lignin peak at

1508 cm^{-1} and 1459 cm^{-1} (which were observed in Figure 4.1) fully disappeared after extraction (Figure 4.2) implying that cellulose has been successfully isolated. The absorption band at 1104.55 cm^{-1} represents the C–O–C stretching at β-(1-4)-glycosidic linkages (Kondo, 1997).

4.3.2 X-ray diffraction of extracted cellulose

Figure 4.3 shows the x-ray diffractogram of cellulose extracted from rice husks.

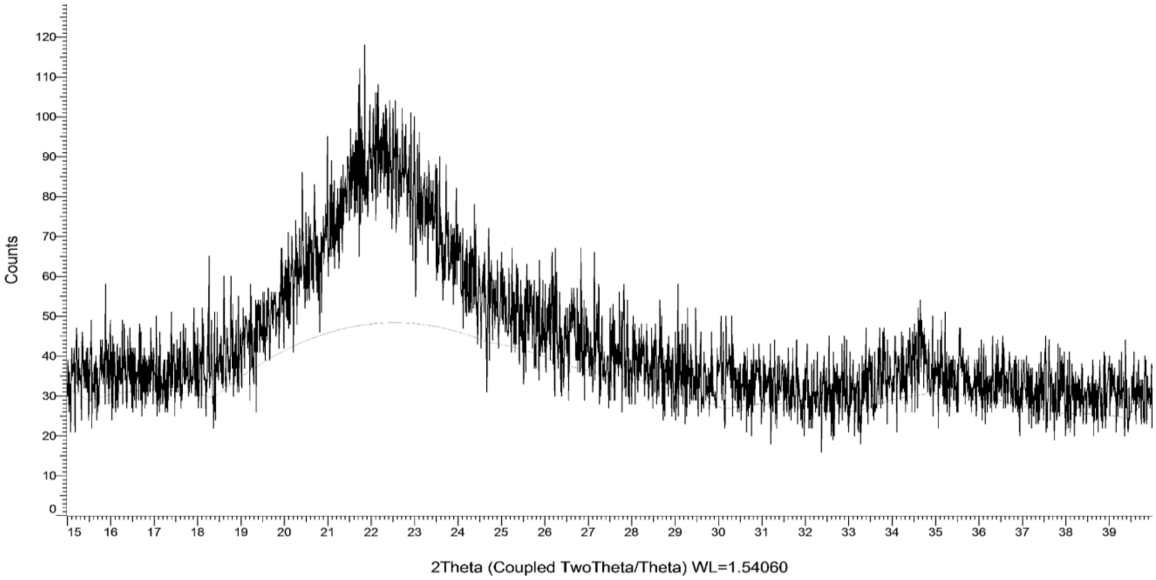


Figure 4.3: X-ray diffractogram of cellulose extracted from rice husks

The diffractogram shows a broad peak at 2θ = 22^{o}, indicating low crystallinity. Similar results have been reported for cellulose extracted from fibre (Loo *et al.*, 2012).

4.3.3 Scanning electron microscopy (SEM) and EDX of extracted cellulose

Figure 4.4 shows the scanning electron micrograph (SEM) of cellulose extracted from rice husks at 5.00 kx magnification.

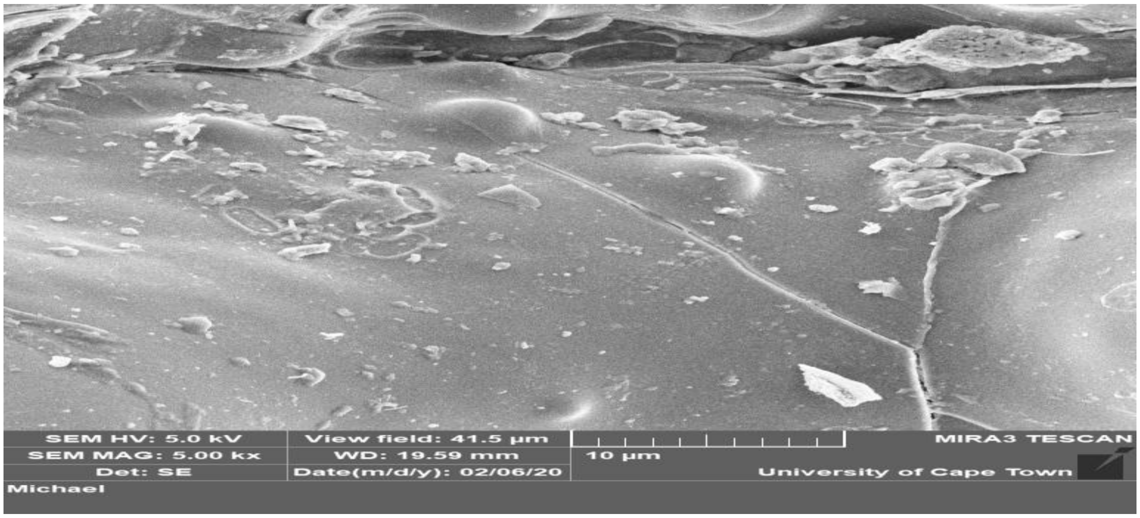


Figure 4.4: Scanning electron micrograph of extracted cellulose

The micrograph shows a rough and rigid surface which could be due to the processes involved in extraction. This could be attributed to the removal of hemicellulose, lignin and other impurities (metallic oxides) found in rice husks. As shown on the surface morphology, the white colour also confirms the removal of the non-cellulosic materials (Ang *et al*., 2012) which was also confirmed by the FTIR spectroscopy (Figure 4.2). Aydin *et al*. (2011) reported that, by removal of the non-cellulosic materials the fibrils structure was also deteriorated. The EDX analysis shows that SiO_2 was deposited on cellulose surface which is caused by coating of imperfection of cellulose and subsequent condensation of the OH groups on the surface.

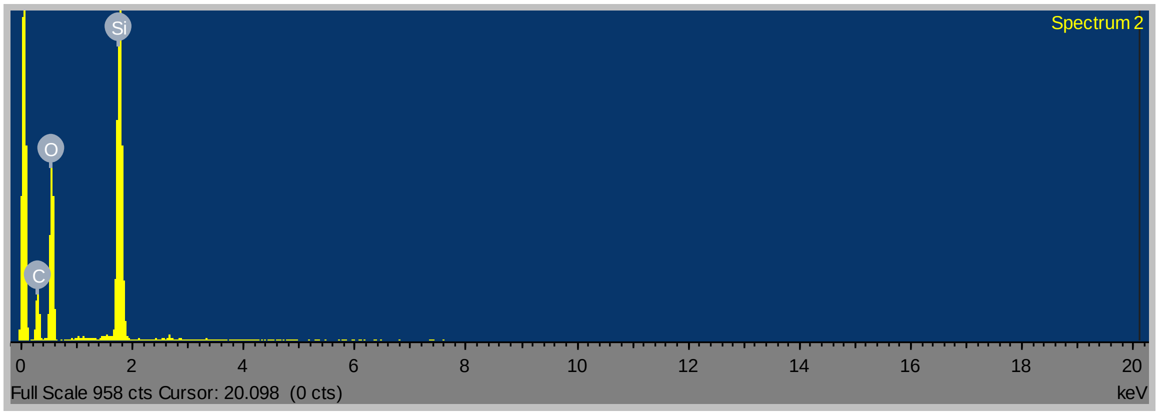


Figure 4.5: EDX spectrum of cellulose

The EDX result showed the formation of cellulose and SiO_2, Si peak was confirmed in relation to carbon and oxygen. A similar result was obtained by Jia *et al*. (2011). These characterizations confirm that cellulose was successfully isolated from rice husks.

4.4 Synthesis of carboxymethycellulose (CMC)

Carboxymethylcellulose was derived by etherification of cellulose under alkaline conditions. The yield of dry weighed CMC obtained was 81.25 %. The material was characterized by FTIR spectroscopy, XRD, SEM. This value is higher than value obtained from isolation Durian (*Durio zibethinus*) peel cellulose by Artanti Putri and Kurniyati (2016)

4.4.1 Degree of substitution (DS) of carboxymethylcellulose

The optimum DS obtained in this study was 0.79. The DS has direct influence in thickening property, emulsibility, salt tolerance, acid resistance and stability (Haleem *et al*., 2014). When the DS falls between 0.6 – 0.7, the CMC has better emulsifying features, while at DS above 0.8, its resistance to salt and acid increases. Table 4.2 shows the DS of CMC from various wastes biomass materials.

Table 4.2: Degree of Substitution values of carboxymethylcellulose from different source

S/N	**Cellulose source**	**Degree of Substitution (DS)**	**Reference**
1.	Banana pseudo stem	0.26-0.75	Adinugraha *et al*., 2005
2.	Cotton fibre	0.15- 0.70	Heydarzadeh *et al*., 2009
3.	Durian	1.632	Putri and Kurniyati, 2006
4.	*Lantana camera*	0.21-1.22	Vershney *et al*., 2006
5.	Palm kernel cake	0.67	Bono *et al*., 2009
6.	Sago waste	0.33-0.82	Pushpamala *et al*., 2006
7.	Sugar beet pulp	0.11- 0.67	Togrul and Arslan, 2003
8.	Water hyacinth	0.24- 0.73	Barai *et al*., 1997

4.4.2 Characterization of carboxymethylcellulose

4.4.2.1 Fourier transform infrared spectroscopy

The Figure 4.6 shows the Fourier transform infrared spectrum of Carboxymethylcellulose.

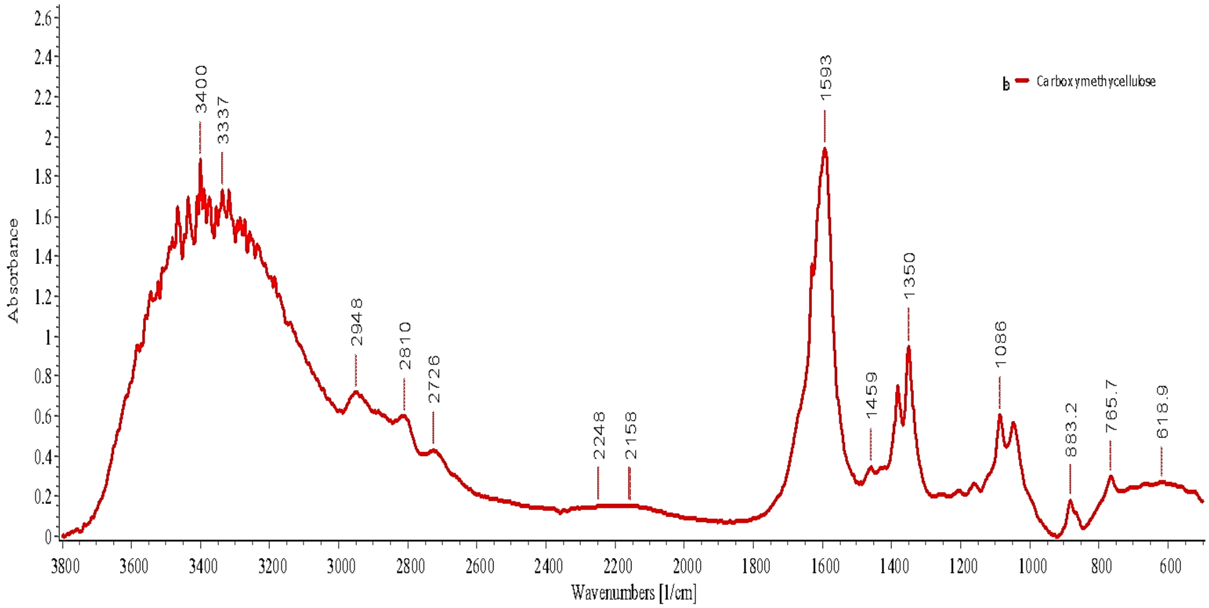


Figure 4.6: FTIR spectrum of carboxymethylcellulose

The Fourier transform infrared spectrum of CMC is similar to that of cellulose obtained from rice husks in that it shows the characteristic broad absorption band at 3337 cm^{-1} due to stretching vibration of the OH group. The peak at 2948 cm^{-1} is due to C-H stretching vibration (Viera *et al.*, 2007). The new absorption band at 1593 cm^{-1} is assigned to the COO^-group while the band at 1459 cm^{-1} is attributed to CH_2 scissoring (Yeasmin and Mondal, 2015). The band at 1086 cm^{-1} is due to CH–O–CH_2 stretching vibration. The bands at around 650-750 cm^{-1} are due to the deformation vibration of hydrogen bonds.

4.4.2.2 X-ray diffraction of carboxymethylcellulose

Figure 4.7 shows the x-ray diffractogram of carboxymethylcellulose.

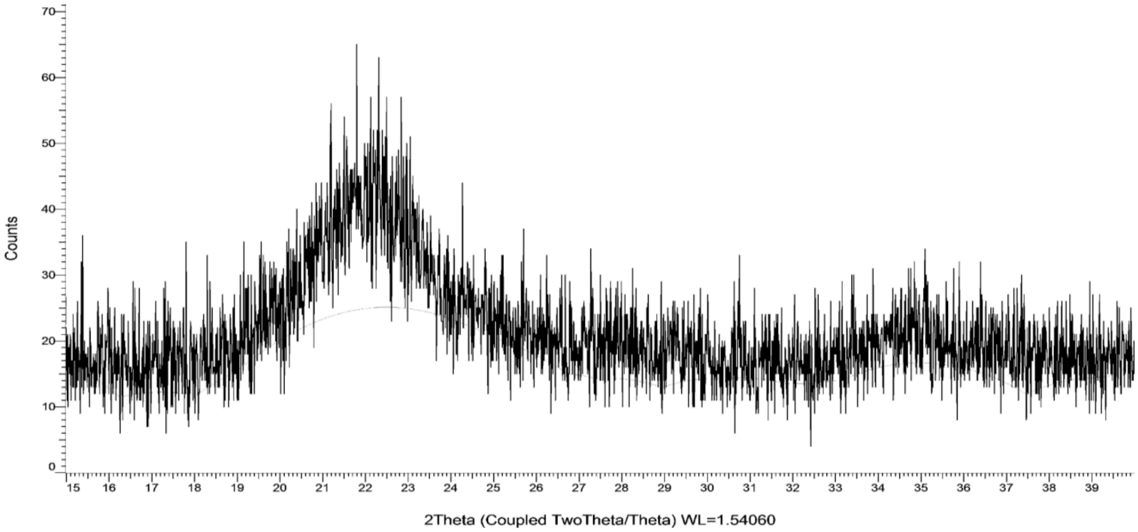


Figure 4.7: X-ray diffractogram of carboxymethylcellulose

The x-ray diffraction of CMC showed lower peak intensity than cellulose as seen in Figure 4.7 indicating that it was less crystalline. This can be due to cleavage of hydrogen bonding by sodium hydroxide being the activator of OH group in cellulose (Adinugraha *et al*., 2005). The substitution of MCA in the cellulose becomes easier as compared to non-alkalized cellulose. Thus, NaOH affects the crystallinity of CMC thereby reducing it, before undergoing etherification. Therefore, CMC becomes highly insoluble (Hebeish *et al*., 1992). Similar results have been reported for similarly treated Cavendish banana cellulose (Adinugraha *et al*., 2005; Rachtanapun *et al*., 2012). The degree of crystallinity is also known to decrease with increasing degree of substitution of the cellulose (Lin *et al*., 1990).

4.4.2.3 Scanning electron microscopy of carboxymethylcellulose

Figure 4.8 shows the scanning electron micrograph of carboxymethylcellulose of extracted cellulose from rice husks.

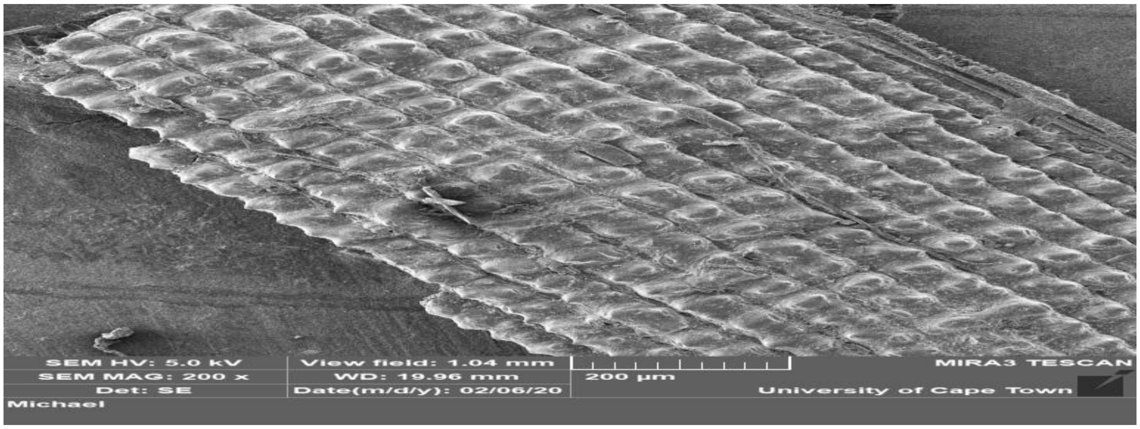


Figure 4.8: Scanning electron micrograph of carboxymethylcellulose

The surface morphology of CMC obtained from cellulose extracted from rice husks at 200 x magnification is presented in the scanning electron micrograph (SEM) shown in Figure 4.8. The SEM image shows that the surface of the CMC is uneven. This (SEM) image of CMC was different from the corresponding rice husks cellulose. The cellulose image had a rather smooth surface unlike the CMC surface. This implies that the cellulose surface was disrupted during the modification. This can be attributed to the solvating actions of ions, which lead to the swelling of the surface as observed in a similar study by Ang *et al*. (2012).

4.5 Crosslinking of carboxymethylcellulose with ethane-1,2-diol

The reaction of 3.00 g CMC with 5 mL of ethane-1,2-diol, at microwave power out-put of 2 (140 watts), for 5 minutes gave carboxymethylcellulose with highest percentage swelling of 1089 %. The final product was characterized by FTIR spectroscopy, XRD and SEM as well as determination of percent swelling.

4.5.1 FTIR spectroscopy

The Figure 4.9 shows the Fourier transform infrared spectrum ethane-1,2-diol of hydrogel.

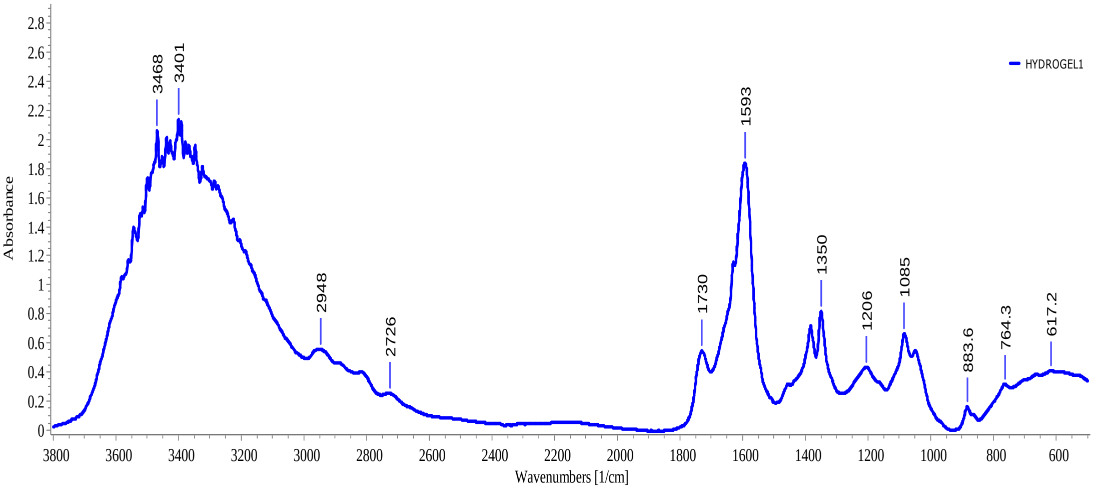


Figure 4.9: FTIR spectrum of cellulose-based superabsorbent hydrogels

The FTIR spectrum of the CMC hydrogel (Figure 4.9) shows the cellulose characteristic bands. The new absorption band at 1730 cm^{-1} was assigned to the formation of ester linkage between CMC and ethane-1,2-diol (Coma *et al.*, 2003). This is evidence that chemical crosslinking was successful.

4.5.2 X-ray Diffraction of the ethane-1, 2-diol superabsorbent hydrogel

Figure 4.10 shows the x-ray diffraction of ethane-1,2-diol superabsorbent hydrogels

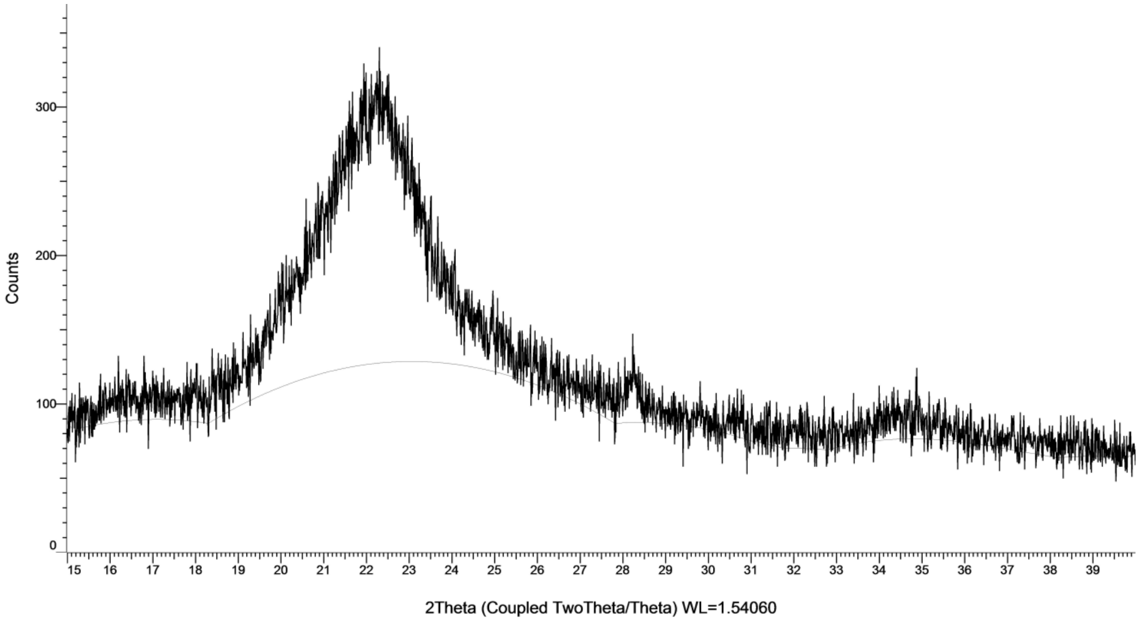


Figure 4.10: X-ray diffractogram of the ethane-1,2-diol superabsorbent hydrogel

The x-ray diffractogram of the ethane-1, 2-diol hydrogel shows a broad peak at 2θ=20º associated with the low crystallinity material. It is observed that the peak intensity of the SAH is higher than the peak of CMC at 2θ=20º. It is clear that CMC is not completely amorphous, but has a relatively higher degree of crystallinity. The decrease in crystallinity plays a vital role in hydrogel degradability, water uptake, and swelling ratio (Costa-Junior *et al*., 2009).

4.5.3 Scanning electron microscopy of the ethane-1,2-diol SAH

Figure 4.11 shows the scanning electron micrograph of ethane-1,2-diol hydrogel.

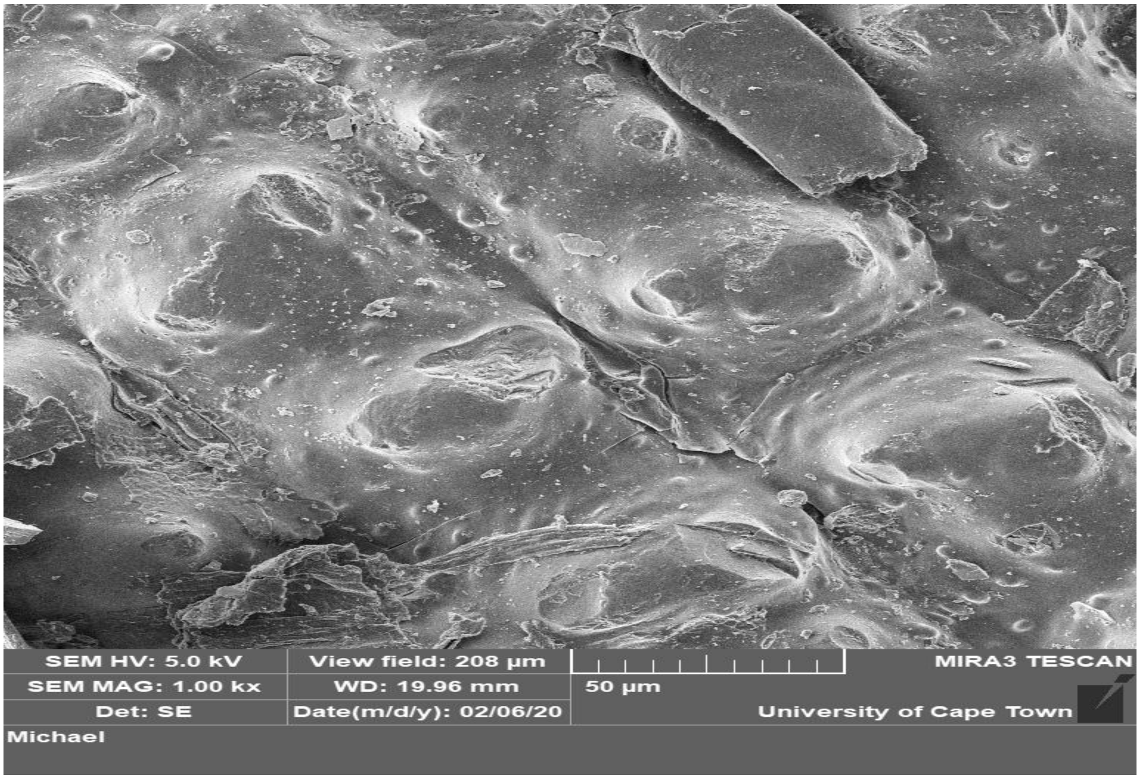


Figure 4.11: Scanning electron micrograph of the ethan-1,2-diol superabsorbent hydrogel

The surface morphology of SAH made from CMC crosslinked with ethane-1,2-diol at 1.00 kx magnification is shown in Figure 4.11. The SEM image shows that the surface of the SAH is uneven. This can be attributed to the crosslinking that occurred on the surface between CMC and ethan-1,2-diol. The CMC chains bound to ethane-1,2-diol from large number of point, which make granules appear on the surface. The surface of the SAH helps water penetrate into the polymeric network, which leads to high swelling capacity.

4.6 Crosslinking of carboxymethylcellulose with ethane-1,2-diamine

The reaction of 3.00 g CMC with 10 mL of ethane-1,2-diamine under microwave heating at power out-put of 6 (420 watts) for 5 minutes gave the superabsorbent hydrogel with highest percentage swelling of 1175 %. This was characterized by FTIR spectroscopy, and XRD as well as determination of percent swelling.

4.6.1 FTIR spectroscopy

Figure 4.12 shows the Fourier transform infrared of ethane-1,2-diamine hydrogel.

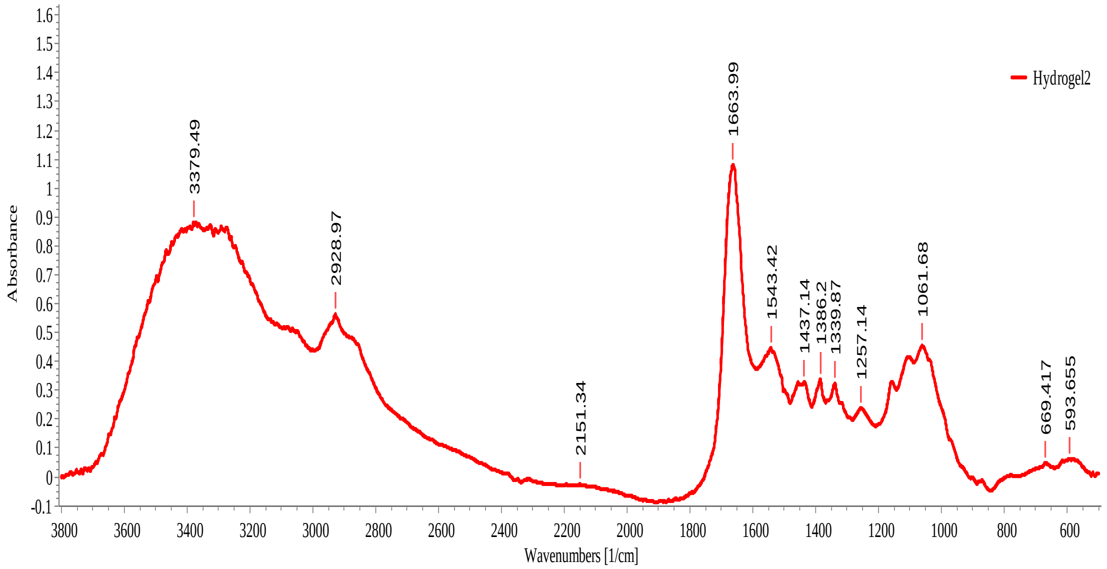


Figure 4.12: FTIR spectrum of hydrogel obtained by crosslinking cmc with ethane-1, 2-diamine

The FTIR spectrum of the hydrogel showed a peak at 3379 cm^{-1} assignable to the stretching vibration of hydroxyl (OH) groups. The peak at 2928 cm^{-1} is due to C-H stretching vibrations (Abdulhameed *et al*., 2019). The new sharp peak observed at 1663 cm^{-1} is assigned to the amide linkages (Mishra *et al*., 2008; Bakravi *et al*., 2017). The peaks at 1437 cm^{-1} and 1386 cm^{-1} could be a result of CH_2 and OH bending vibrations respectively. The peak at 1061 cm^{-1} was assigned to C-O-C stretching.

4.6.2 X-ray diffraction of the ethane-1, 2-diamine superabsorbent hydrogel

The Figure 4.13 shows the x-ray diffractogram of hydrogel by crosslinking CMC with ethane-1,2-diamine.

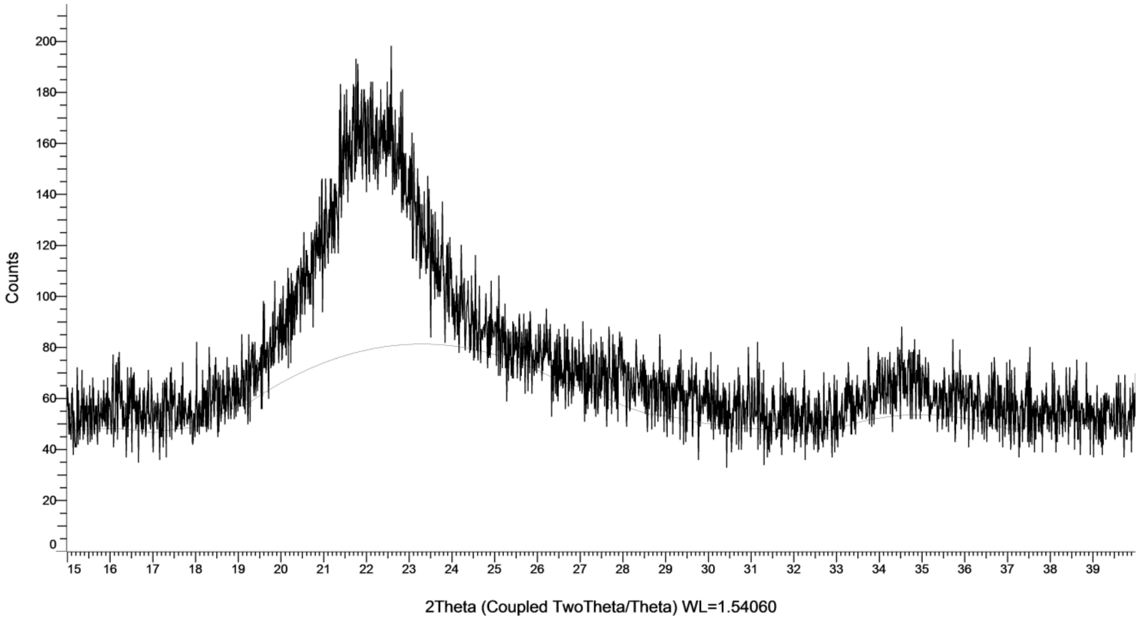


Figure 4.13: X-ray diffractogram of the ethane-1, 2-diamine superabsorbent hydrogel

The x-ray diffractogram shows a broad peak at $2\theta = 22^{o}$ implying that the hydrogel is more amorphous (Varapsad *et al.*, 2009). It is clear that CMC is not completely amorphous, but has a relatively higher degree of crystallinity. The decrease in crystallinity plays a vital role in hydrogel degradability, water uptake, and swelling ratio (Costa-Junior *et al*., 2009).

4.7 Synthesis of superabsorbent hydrogels by crosslinking cellulose with phosphoric acid

The reaction of 2.00 g cellulose with 10 mL of phosphoric acid under microwave heating at microwave power out-put of 6 (420 watts) for 3 minutes, gave the hydrogel with 860 % as highest percentage swelling. Phosphoric acid groups attack the OH groups of cellulose chain thereby forming phosphorous acid group by ester linkage. The product was characterized by FTIR spectroscopy, XRD as well as by determination of its percent swelling.

4.7.1 FTIR spectroscopy

Figure 4.14 shows the Fourier transform infrared spectrum of the hydrogel obtained by crosslinking cellulose extracted from rice with phosphoric acid.

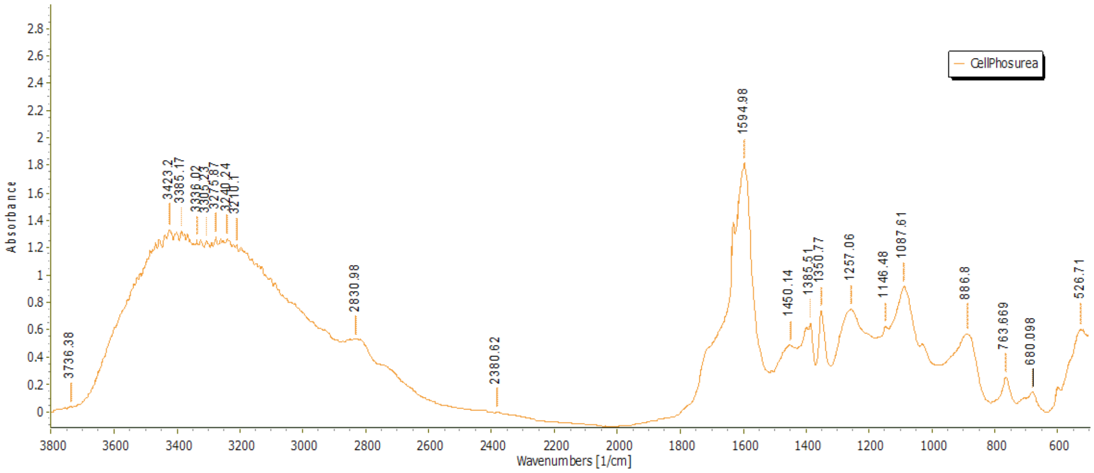


Figure 4.14: FTIR spectrum of cellulose cross-linked with phosphoric acid in the presence of urea

The FTIR spectrum shows a characteristic band at 2380.62 cm^{-1} attributed to the P-H stretching vibration (Suflet *et al*., 2006). The band at 1350.77 cm^{-1} is attributable to the P=O bond stretching (Jayakumar *et al*., 2009) while the peak at 886.80 cm^{-1} corresponds to the stretching in phosphate ester (Suflet *et al*., 2006). These clearly showed that there was a crosslinking between cellulose and phosphoric acid.

4.7.2 XRD of phosphoric acid superabsorbent hydrogels

Figure 4.15 shows the x-ray diffractogram of the hydrogel obtained by crosslinking cellulose extracted from rice with phosphoric acid.

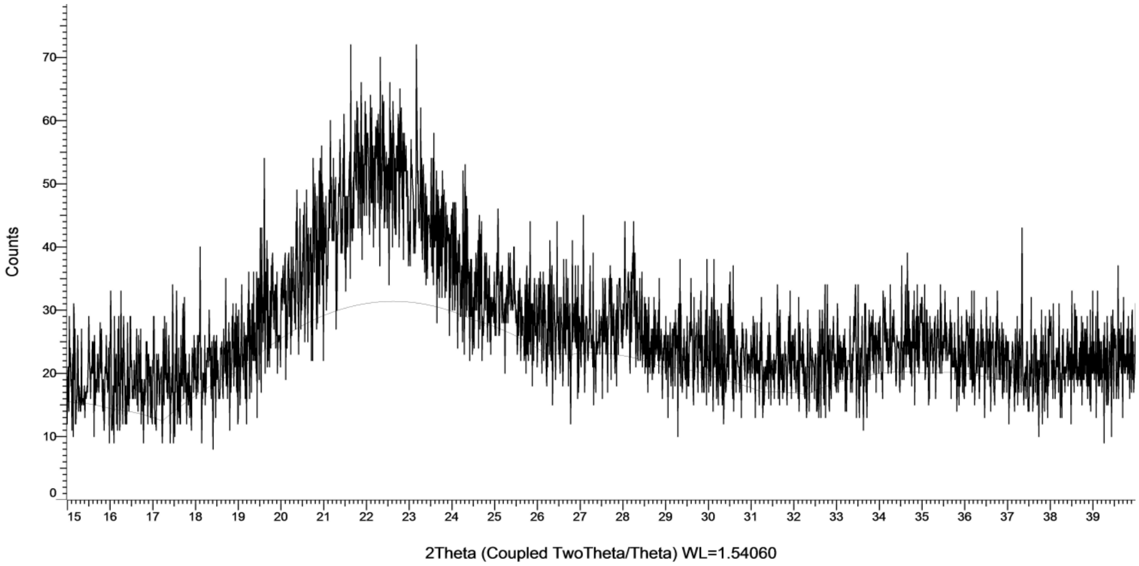


Figure 4.15: X-ray diffractogram of cellulose crosslinked with phosphoric acid.

The diffractogram shows a characteristic peak at 2θ between 20 - 24^o = 22^o. A remarkable change was observed after phosphorylation, in that there was a remarkable decrease in peak intensity when compared with that pattern observed for cellulose. This shows that the crystallinity of cellulose decreased. Wanrosli *et al*. (2011), have also reported the disruption of the cellulose backbone upon phosphorylation with subsequent loss or decline of cellulose crystallinity, as well as inter and intramolecular hydrogen bonding. Similarly, the functionalization of cellulose diminishes its crystallinity (Suflet *et al.*, 2006; Jayakumar *et al*., 2009).

4.7.3 Elemental analysis using X-ray fluorescence (XRF)

X-ray fluorescence (XRF) was used to determine the elemental composition of rice husks, cellulose, and cellulose crosslinked with phosphoric acid. The results in table 4.3

showed that after crosslinking cellulose with phosphoric acid, the percentage of P_2O_5 increases from 0.183 to 0.483 due to the crosslinking of cellulose with phosphoric acid.

Table 4.3: Elemental composition of rice husks, cellulose, and cellulose crosslinked with phosphoric acid by XRF analysis

Elemental component	**Rice husks (%)**	**Cellulose (%)**	**Cellulose crosslinked with H_3PO_4 (%)**
Al_2O_3	0.30	0.152	0.293
SiO_2	72.1	98.83	95.92
P_2O_5	0.06	0.183	0.483
S	-	0.133	0.244
Cl	-	0.203	0.167
K_2O	0.72	0.099	0.965
CaO	0.43	0.154	1.273
Ti	0.05	0.062	0.139
Cr	-	0.008	0.017
Mn	0.15	0.029	0.155
Fe	0.15	0.135	0.311

4.8 Synthesis of super-absorbent hydrogels by crosslinking cellulose with boric acid

The cellulose was crosslinked with boric acid under microwave oven heating for three minutes and under refluxing at 80 ^{o}C for twenty four hours, respectively. In both cases, there is a strong interaction between boric acid and hydroxyl groups of cellulose, leading to the formation of a borate complex. The FTIR spectra of the products from the two preparation methods were the same suggesting that the methods gave the product. Microwave irradiation was preferred to the conventional heating method because of the shorter time required to complete the reaction. The hydrogel obtained under microwave heating was characterized by FTIR spectroscopy, XRD as well as by determination of its percentage swelling under distilled water. The product from the reflux method was only subjected to FTIR spectroscopy.

4.8.1 FTIR spectroscopy

Figures 4.17 and 4.18 show the FTIR spectra of cellulose cross-linked with boric acid synthesized under microwave oven heating and under regular refluxing methods, respectively.

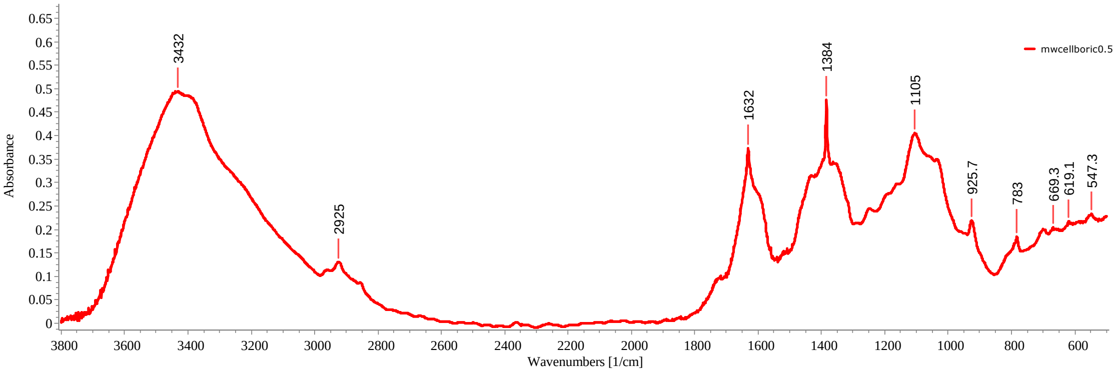


Figure 4.16: FTIR spectrum of cellulose cross-linked with 0.5 g of boric acid under microwave heating

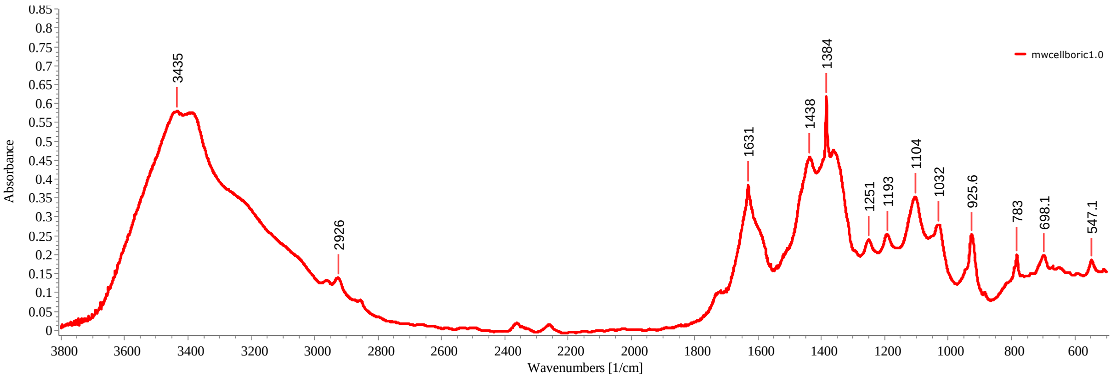


Figure 4.17: FTIR spectrum of cellulose cross-linked with 1.0 g of boric acid under microwave heating

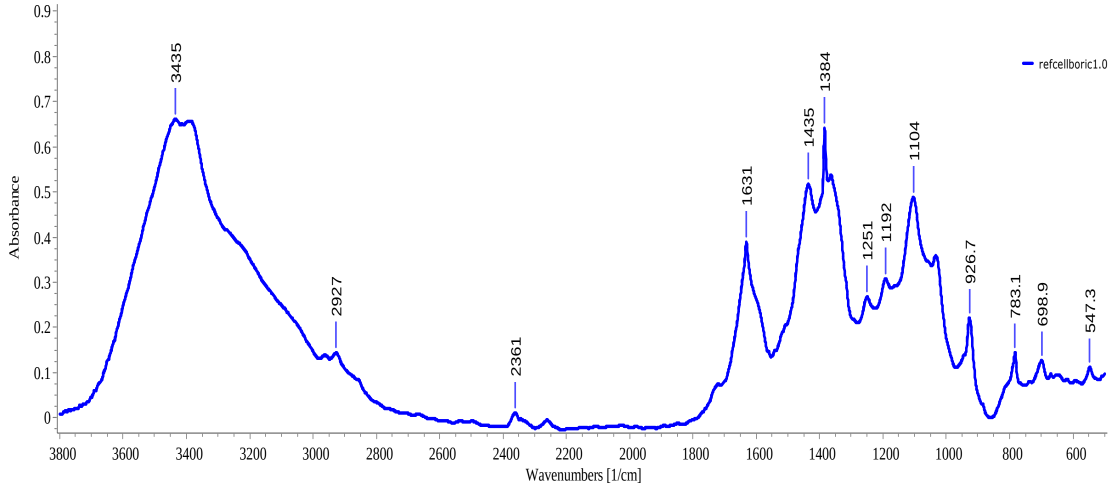


Figure 4.18: FTIR spectrum of cellulose cross-linked with 1.0 g of boric acid using reflux

Both spectra show characteristic absorption bands at 1438, 1251, 1193, 1032 and 925 cm^{-1} which were not observed in the spectrum of cross-linked with 0.50 g of boric acid under microwave heating as shown in Figure 4.16. The band assignment is summarized in Table 4.4. The reactions conducted under reflux (80 ^{o}C for 24 hours) and microwave irradiation (3 minutes), gave similar products.

Table 4.4: Absorption bands and their assignments for FTIR of boric acid SAH

Absorption bands (cm^{-1})	Assignment	Reference
685	B-O-B bending vibration	Rojas *et al*., 2006.
700	B-O-B bending vibration in borate ring	Ardelean and Toderas, 2006.
850 – 1100	B-O stretching of tetrahedral BO^{4-}	Kamitsos *et al*., 1987.
600 – 800	Bending vibration of various borate	Ardelean and Toderas, 2006.
907	B-O stretching vibration of BO^{4-} in tri, tetra, and pentaborate	Rojas *et al*., 2006.
1400	B-O stretching trigonal BO$_3$ unit	Kamitsos *et al*., 1987.

4.8.2 XRD of boric acid superabsorbent hydrogel

Figure 4.19 shows the x-ray diffractogram of the hydrogel obtained by crosslinking cellulose extracted from rice with boric acid.

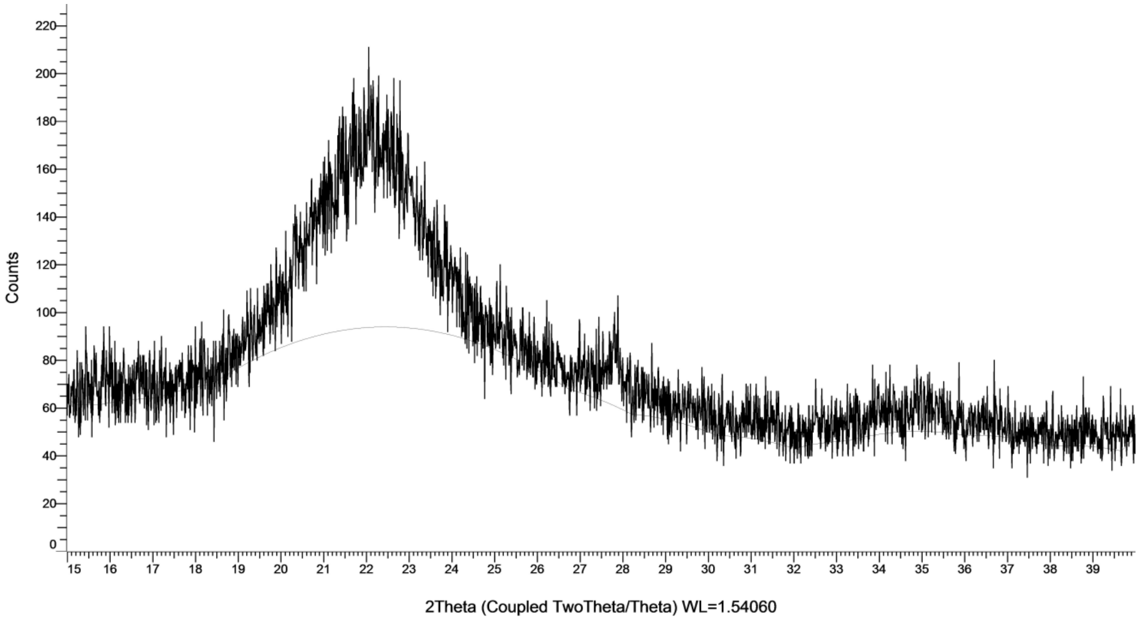


Figure 4.19: X-ray diffractogram of cellulose cross-linked with boric acid.

The diffractogram of cellulose cross-linked with boric acid showed a characteristic peak at 2θ = 22°. It is observed that the peak intensity of cellulose cross-linked with boric acid is higher than that of the cellulose, which indicated that the cellulose is not completely amorphous. A similar result was observed in our previous studies, when crosslinking CMC with ethane-1,2-diol. The decrease in crystallinity plays a vital role in hydrogel degradability, water uptake and swelling ratio (Costa-Junior *et al*., 2009). In a situation whereby the intensity of the hydrogel is lower than the cellulose, it indicates that there is a decrease in the crystallinity (material is more of amorphous). This was also observed by Manisha *et al*. (2013).

4.9 Efficacy of superabsorbent hydrogels in maize growing

The efficacy of the various SAHs prepared (i.e. ethane-1,2-diamine SAH, ethane-1,2-diol SAH, phosphoric acid SAH and boric acid SAH) in maize growing, was evaluated by measuring growth and yield parameters of maize plants grown under identical conditions but treated with varying amounts of SAHs. Growth parameters were monitored at regular intervals for a period of twelve weeks while yield parameters were measured at harvesting after 12 weeks. The results and discussions on the variations of the specific growth parameters of maize under different SAH treatments are presented in the subsections that follow. It is important to note that watering was done for the first 21 days after planting and discontinued to mirror the situation in arid and semi-arid regions where rains sometimes fail as soon as crops germinate.

4.9.1 Plant height (cm)

The heights of plants under different doses of each of the four types of Super-Absorbent Hydrogels studied were measured at weeks 3, 6, 9 and 12 after planting. The results are displayed in Figures 4.20 to 4.23, respectively.

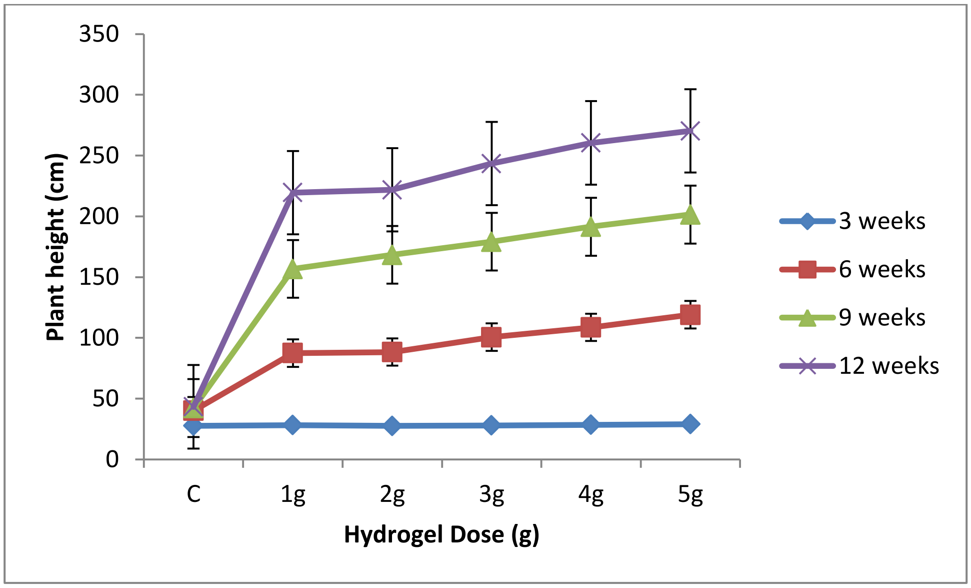


Figure 4.20: Variation of plant height in maize planted with ethane-1,2-diamine SAH

As can be seen in Figure 4.20, mean heights of maize plants grown under similar conditions but varying amounts of ethane-1,2-diamine SAH, that is , 0 (control), 1.00, 2.00, 3.00, 4.00 and to 5.00 g were found to be 27.69±1.60, 28.21±2.22, 27.52±1.83, 27.88±1.80, 28.97±2.49 and 28.97±2.49, respectively at week 3. The plant heights for all pots were not significantly different ($p > 0.05$) as would be expected. These mean heights increased to 43.24±0.56, 291.50±1.32, 221.74±1.99, 243.39±2.62, 260.41±1.02 and 270.23±2.28, respectively. At week 12, the plant heights in pots treated with 1.00 and 2.00 g, respectively, are not significantly different ($p > 0.05$) while those treated with 0.00, 3.00, 4.00 and 5.00 g of hydrogel are significantly different ($p < 0.05$). The increase in plants height can be attributed to continued availability of water to plants throughout the growth period due to the retention and slow release by the hydrogel even in the absence of regular watering. Sendure *et al*. (2011), reported similar results in tomatoes and Al-Harbi *et al*. (1999) in cucumber. The crops that were grown without the hydrogel died off. Similar results were observed by Yang *et al*. (2006) that drought stress significantly affected plant height. A similar plant height was observed by Hossain, (2009); Islam *et al.* (2011); and Niazuddin *et al*. (2002).

Similar trends were obtained for the other three hydrogels, ethane-1,2-diol SAH, phosphoric acid SAH, and boric acid SAH (see Figures 4.21 to 4.23).

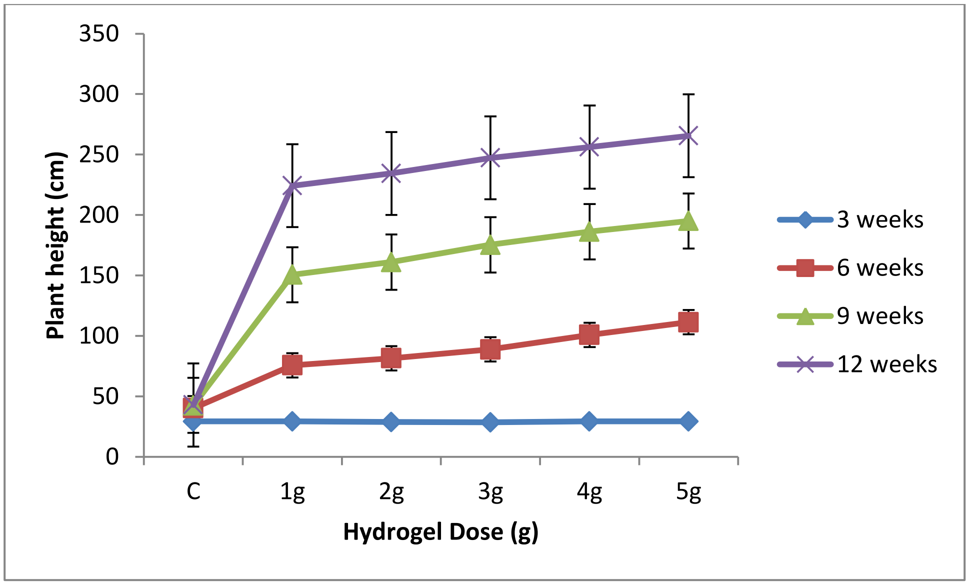


Figure 4.21: Variation of plant height in maize planted with ethane-1,2-diol SAH

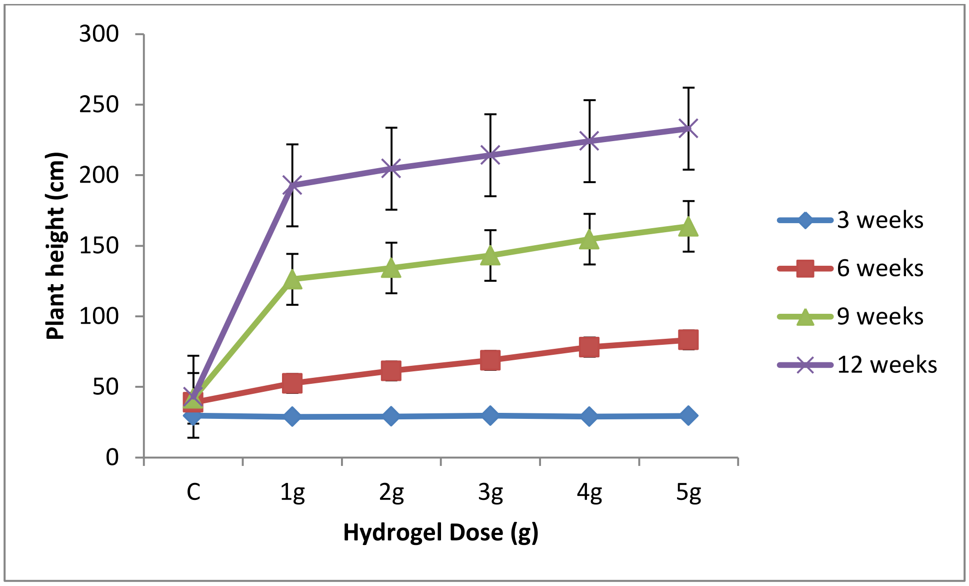


Figure 4.22: Variation of plant height in maize planted with phosphoric acid SAH

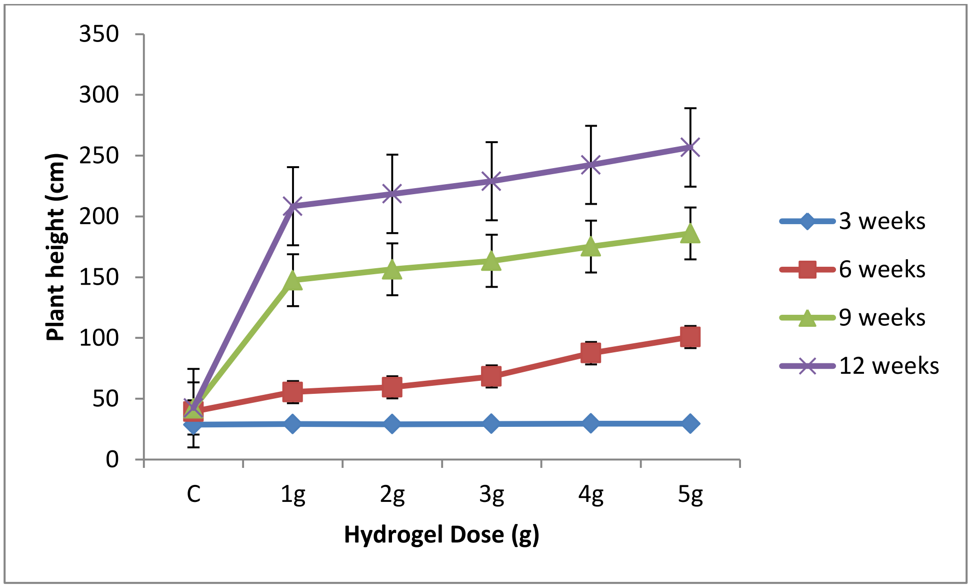


Figure 4.23: Variation of plant height in maize planted with boric acid SAH

In comparing the different hydrogels, it can be seen that the mean height for maize plants grown with 5 g of ethane-1,2-diamine SAH, ethane-1,2-diol SAH, phosphoric acid SAH, and boric acid SAH at week 12 were 270.23±2.28, 265.54±0.68, 256.77±1.45, and 232.96±1.85, respectively. They were significantly different ($p < 0.05$) with the ethane-1,2-diamine SAH performing better than all the other superabsorbent hydrogels doses (See appendix 9).

4.9.2 Number of leaves

The mean numbers of leaves were determined for plants under varying the hydrogel amounts that is. 0 (control), 1.00, 2.00, 3.00, 4.00 and 5.00 g at weeks 3, 6, 9 and 12 after planting. The results are summarized in Figures 4.24 to 4.27, respectively.

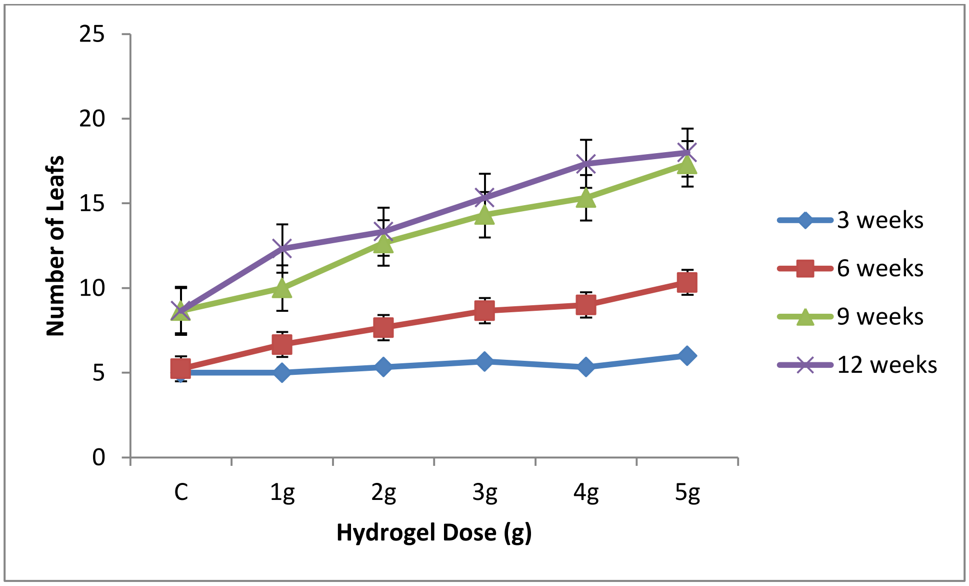


Figure 4.24: Variation of number of leafs in plants grown with the ethane-1,2-diamine SAH

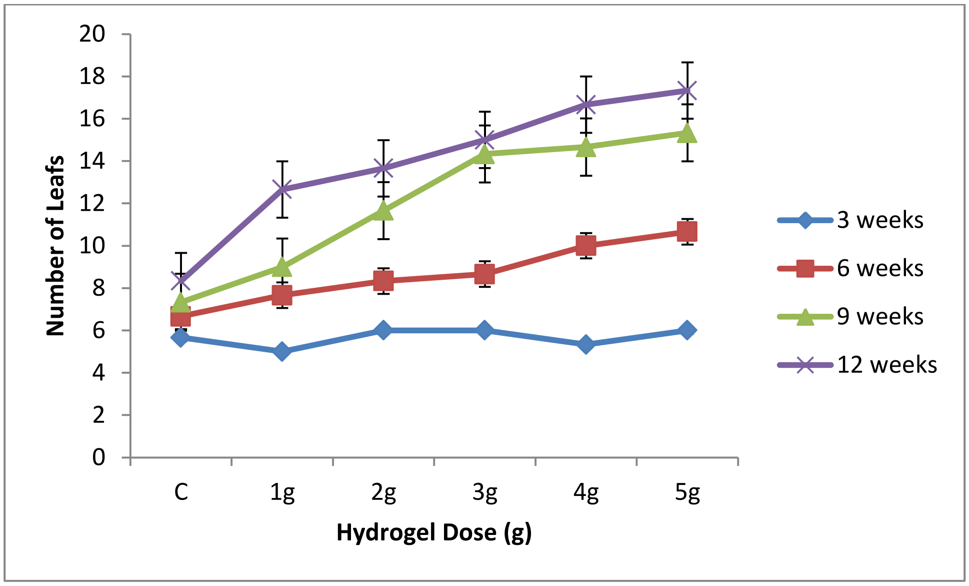


Figure 4.25: Variation of number of leafs in plants grown with ethane-1,2-diol SAH

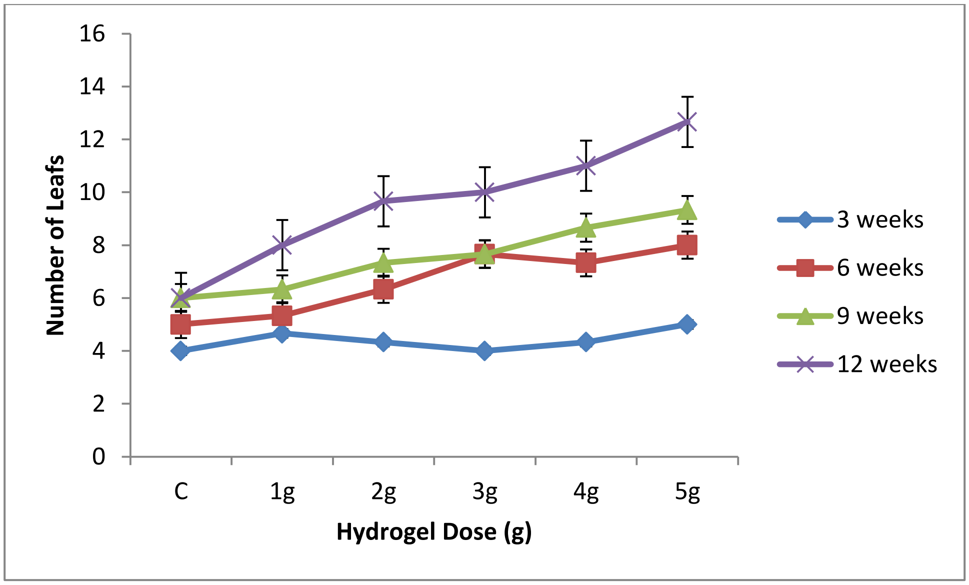


Figure 4.26: Variation of number of leafs in plants grown with phosphoric acid SAH

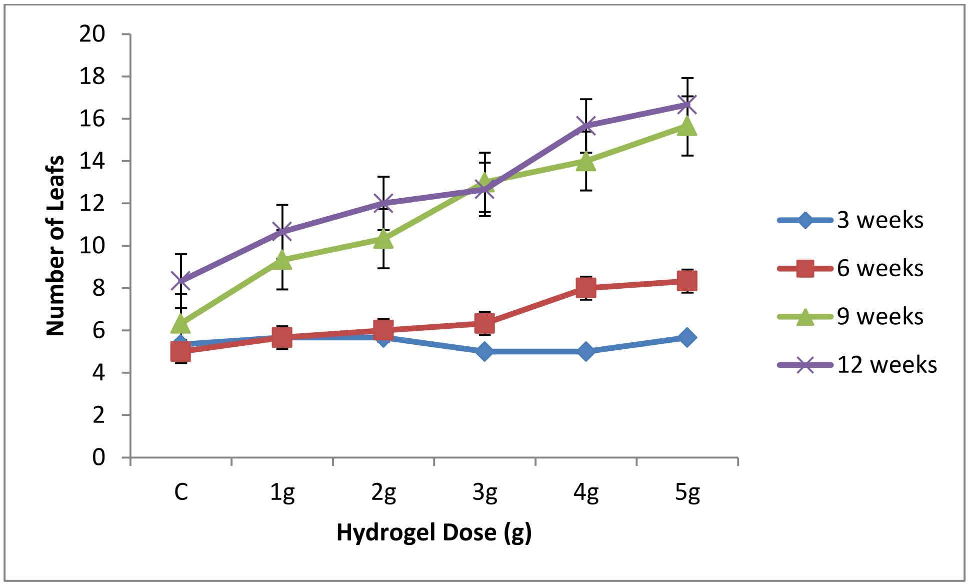


Figure 4.27: Variation of number of leafs in plants grown with boric acid SAH

It can be seen that the four hydrogels gave similar trends in number of leaves with time. From Figure 4.24, the mean number of leaves in maize plants grown under varying ethane-1,2-diamine SAH amounts, namely, 0 (control), 1.00, 2.00, 3.00, 4.00 and 5.00 g were found to be 5.66±1.52, 6.00±1.00, 6.00±1.00, 6.00±1.00, 5.33±0.57 and 6.00±1.00, respectively at week 3. The numbers of leaves for all plants at week 3 were not significantly different ($p > 0.05$). These leaf numbers increased to 8.33±0.57, 12.66±1.15, 13.66±1.52, 15.00±1.00, 16.66±1.15 and 17.33±0.57 in plants grown under treatments with 0 (control), 1.00, 2.00, 3.00, 4.00 and 5.00 g of hydrogels, respectively, at week 12. The number of Leafs in plants grown under treatments with 4.00 and 5.00 g of hydrogels were not significantly different ($p > 0.05$) while those with 0.00, 1.00, 2.00 and 3.00 g were significantly different ($p < 0.05$) at week 12.

Increase in water deficit and low amount of SAHs diminished the number of leafs which can led to dryness and leaf death of plants. Incorporation of SAH to soil around the root revealed that water stress significantly lowered the number of leafs. The increase in amount of SAH (hydrophillic) significantly increased the number of Leafs this implied that application of SAH mitigates the negative impact drought at high amount. Al-Harbi *et al*. (1999) and Sendur *et al*. (2001) observed similar results.

In comparing the different hydrogels, it can be seen that the mean number of leafs for maize plants grown with 5.00 g of ethane-1,2-diamine SAH, ethane-1,2-diol SAH, phosphoric acid SAH and boric acid SAH at week 12 were 18.33±0.57, 17.00±1.00, 16.66±1.52, and 12.66±1.52, respectively. Thus, ethane-1,2-diamine SAH performed better than all the other superabsorbent at different hydrogel dosage studies as shown in appendix 9.

4.9.3 Leaf length (cm)

The leaf lengths of maize plants treated with 0 (control), 1.00, 2.00, 3.00, 4.00 and 5.00 g of hydrogels, respectively, were measured at weeks 3, 6, 9 and 12 after planting. The results are summarized in Figures 4.28, 4.29, 4.30 and 4.31, respectively. It can be seen from the Figures that all the four hydrogels show similar trends in the variation of leaf length with maximum values attained at the 12th week.

It can be seen from Figure 4.28, that the mean Leaf length of maize plants grown under similar conditions but varying ethane-1,2-diamine SAH amounts of hydrogels namely, 0 (control), 1, 2, 3, 4 and 5 g were found to be 29.21±2.54, 27.09±0.73, 31.75±1.27, 34.71±0.73, 32.17±1.19 and 33.17±1.27, respectively at week 3 before hydrogel application. The leaf lengths of all plants in all pots were not significantly different ($p > 0.05$). The mean leaf lengths increased to 35.06±0.82, 81.70±0.73, 84.06±0.92, 86.36±0.00, 88.90±0.00 and 90.50±0.81, respectively by week 12. The leaf lengths of plants under the 4.00 and 5.00 g treatments were not significantly different ($p > 0.05$) while those with 0, 1.00, 2.00 and 3.00 g were significantly different ($p < 0.05$) at week 12.

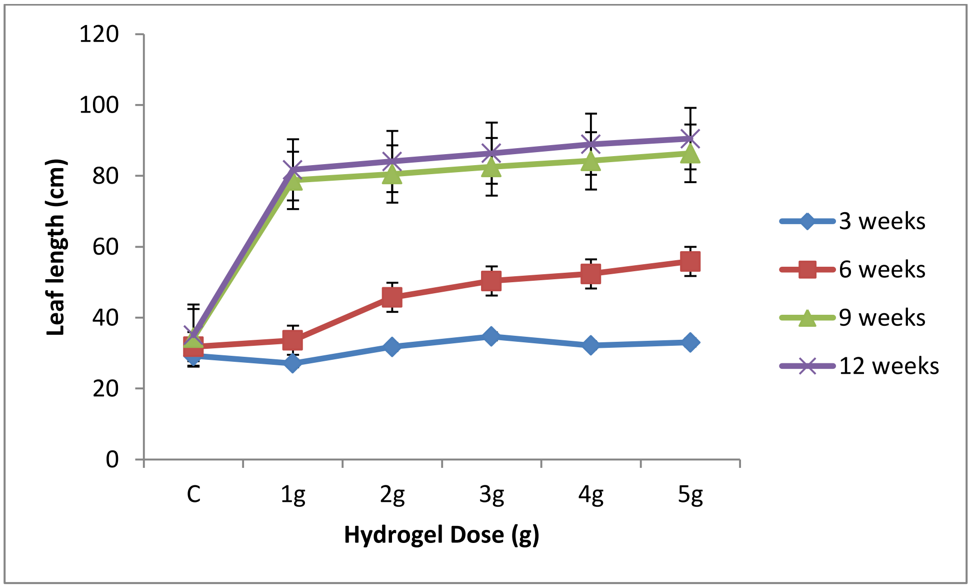


Figure 4.28: Variation of leaf length in maize plants treated with ethane-1,2-diamine SAH

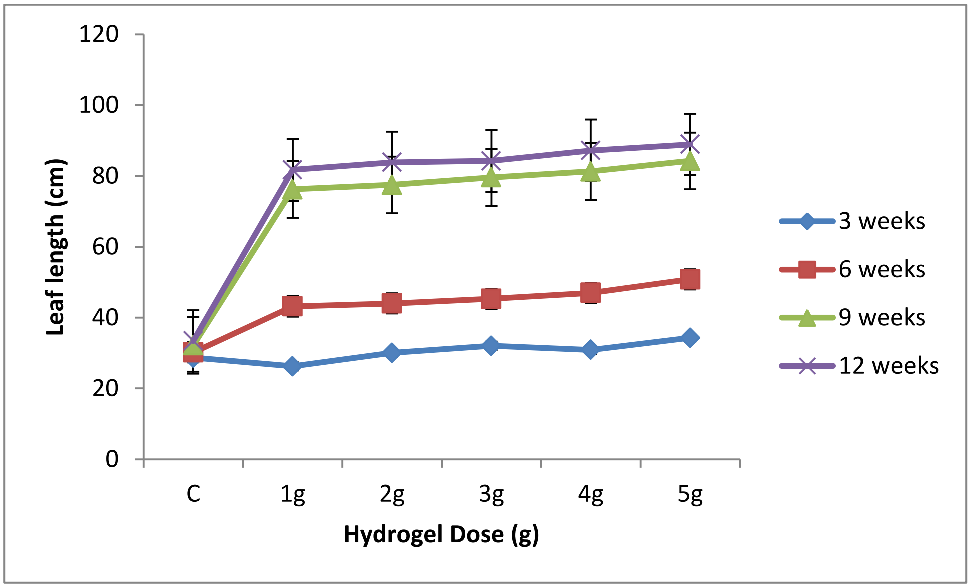


Figure 4.29: Variation of leaf length in maize plants treated with ethane-1,2-diol SAH

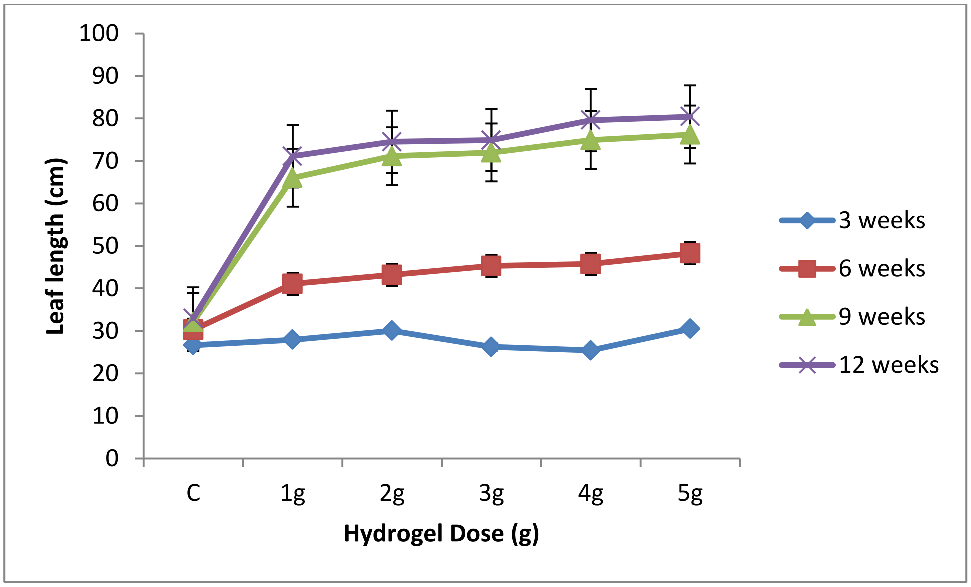


Figure 4.30: Variation of leaf length in maize plants treated with boric acid SAH

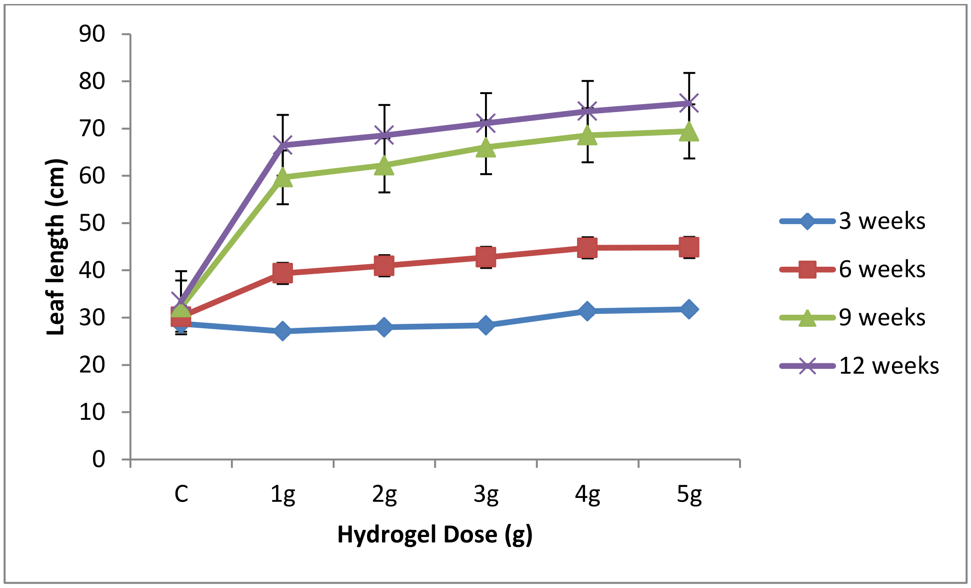


Figure 4.31: Variation of leaf length in maize plants treated with phosphoric acid SAH

At week 3, the leaf lengths of the maize in all experimental pots were not significantly different ($p > 0.05$), as would be expected because the hydrogel had not been applied. The leaf lengths increased with dosage of the SAH in the maize plants treated with different doses of hydrogels. The plants treated with 5g of hydrogel recorded the highest values of leaf lengths. Similar results were obtained for the other three superabsorbent hydrogels, that is, ethane-1,2-diol SAH, phosphoric acid SAH and boric acid SAH (see Figure 4.29 to 4.31).

In comparing the different hydrogels, it can be seen that the leafs lengths for maize plants grown with 5 g of ethane-1,2-diamine SAH, ethane-1,2-diol SAH, phosphoric acid SAH and boric acid SAH at week 12 were 90.50±0.81, 88.90±0.00, 80.42±1.45, and 75.35±1.46, respectively. This implies that ethane-1,2-diamine SAH performed better as than all the other superabsorbent hydrogels at different hydrogel dosages.

4.9.4 Leaf diameter (cm)

The variations of leaf diameter with hydrogel dose (0.00, 1.00, 2.00, 3.00, 4.00 and 5.00 g) in the experimental pots were determined by measuring the leaf diameters at weeks 3, 6, 9 and 12 after planting. The results for the four hydrogels applied are displayed in Figures 4.32, 4.33, 4.34 and 4.35, respectively. It can be seen from Figure 4.32, that the mean leaf diameter of maize plants at at week 3 were 2.36±0.15, 2.18±0.13, 3.63±0.15, 3.63±0.15, 3.63±0.15, 3.30±0.67 and 3.72±0.15 for the pots labelled 0 (control), 1, 2, 3, 4 and 5 g, respectively. The mean leaf diameters at week 3 were not significantly different as was expected ($p > 0.05$). After week 3, the mean leaf diameters increased to 2.72±0.01, 6.85±0.00, 7.06±0.07, 7.27±0.14, 7.44±0.15 and 7.78±0.14 for treatments with 0 (control), 1.00, 2.00, 3.00, 4.00 and 5.00 g, respectively at week 12. The leaf diameters in plants treated with 1.00 and 2.00 g of hydrogel, respectively, were not significantly different while those treated with 3.00, 4.00 and 5.00 g of hydrogel were significantly different ($p < 0.05$) at week 12. This suggests that at high dose even when the watering was discontinued, the plants did not experience drought stress because the amount of hydrogel was high and they continued supplying water to the plants allowing them to continue growing. These observations are replicated in the other hydrogels as seen in Figures 4.33 to 4.35.

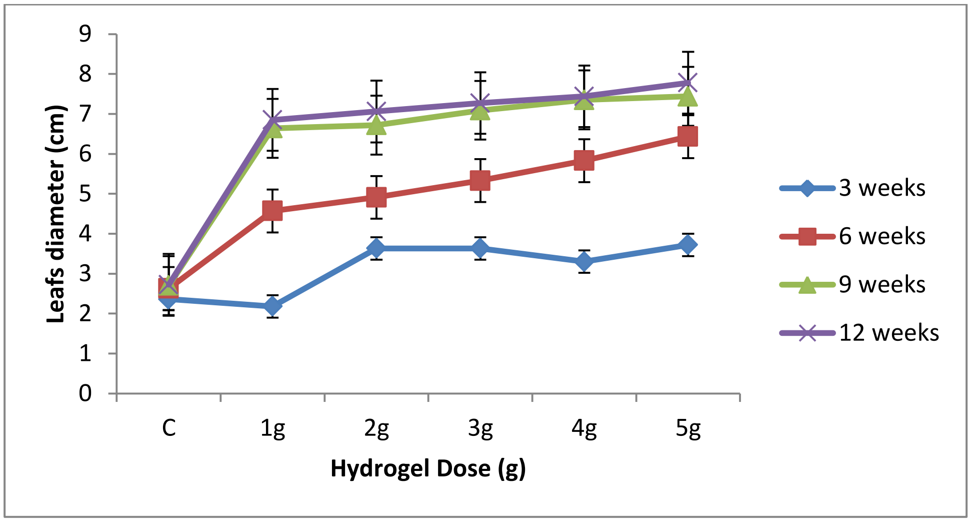


Figure 4.32: Variation of leaf diameter in plants treated with ethane-1,2-diamine SAH

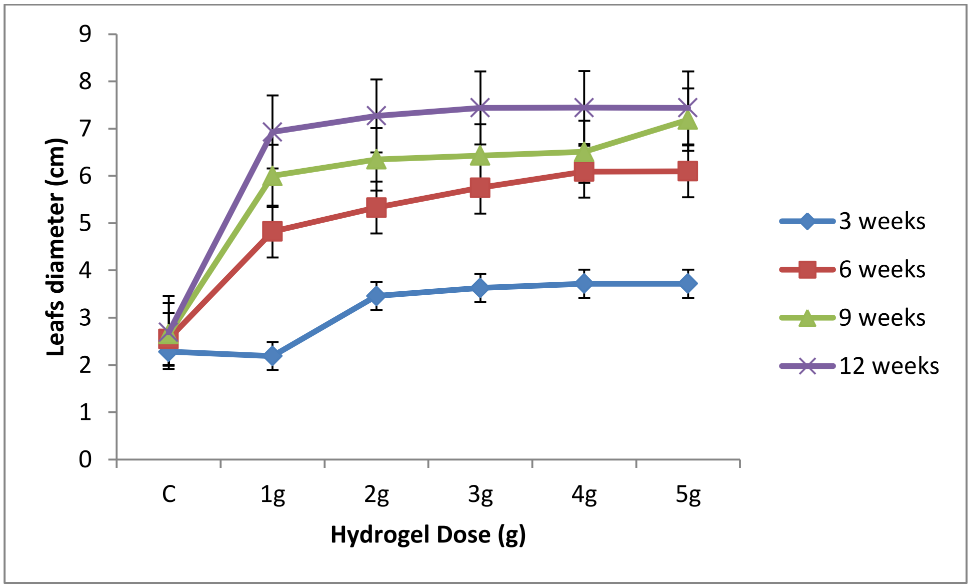


Figure 4.33: Variation of leaf diameter in plants treated with ethane-1,2-diol SAH

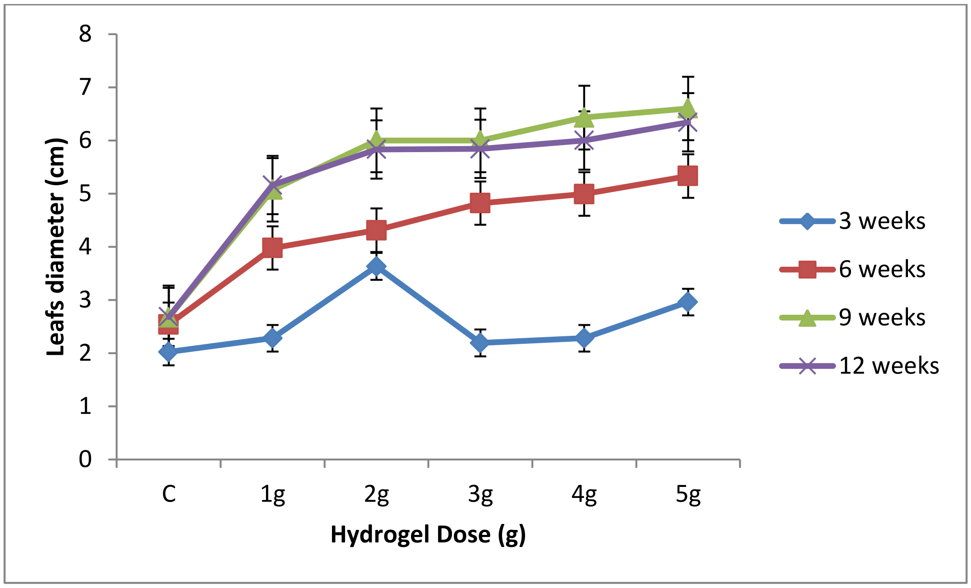


Figure 4.34: Variation of leaf diameter in plants treated with boric acid SAH

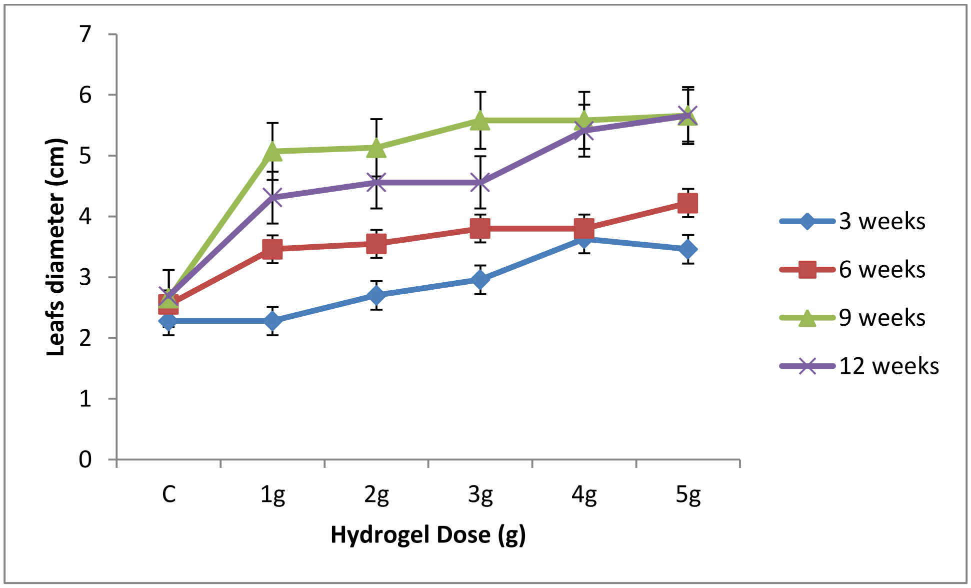


Figure 4.35: Variation of leaf diameter in plants treated with phosphoric acid SAH

In comparing the different hydrogels, it can be seen that the mean Leaf diameter for maize plants grown with 5.00 g of ethane-1,2-diamine SAH, ethane-1,2-diol SAH, phosphoric acid SAH and boric acid SAH at week 12 were 7.78±0.14, 7.44±0.15, 6.34±0.25, and 5.66±0.15, respectively. Thus, ethane-1,2-diamine SAH and ethane-1,2-diol SAH performed better than all the other superabsorbents at different hydrogel dosages studied.

4.9.5 Leaf area

The variation of leaf area in maize plants was investigated in maize planted with 0 (control), 1.00, 2.00, 3.00, 4.00 and 5.00 g of hydrogel while keeping the other parameters constant. The leaf area measurements were taken at weeks 3, 6, 9 and 12 after planting. The results are displayed in Figures 4.36, 4.37, 4.38 and 4.39, respectively.

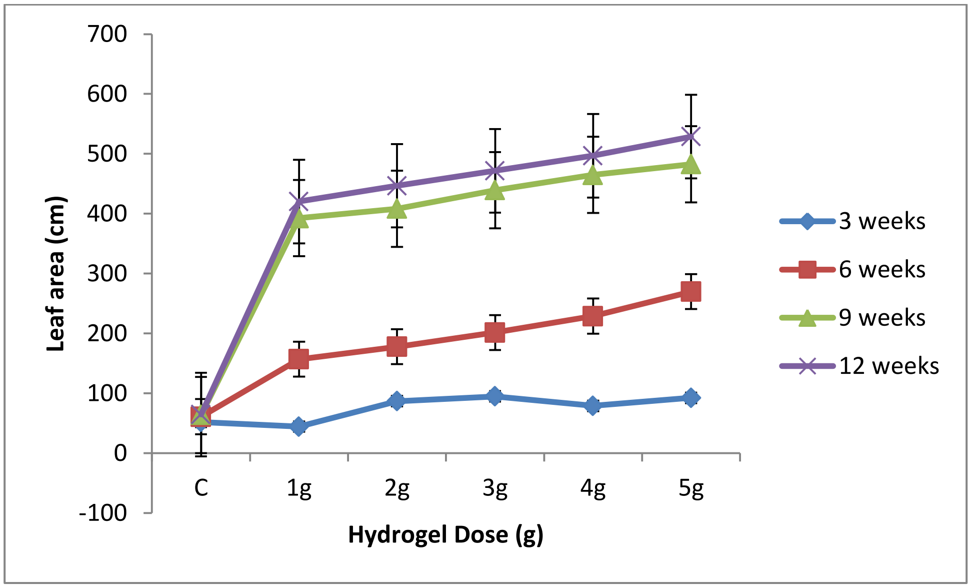


Figure 4.36: Variation of leaf area in maize plants grown with ethane-1,2-diamine SAH

As shown in Figure 4.36, leaf area of maize plants grown under similar conditions but varying ethane-1,2-diamine SAH amounts of 0 (control), 1, 2, 3, 4 and 5 g were found to be 52.10±1.60, 44.33.±1.60, 86.77±6.78, 94.75±3.27, 79.09±2.83 and 92.33±6.88 (cm), respectively at week 3. These leaf areas increased to 64.59±0.64, 420.24±3.77, 446.69±7.39, 471.61±9.50, 496.61±9.78 and 528.78±13.45 (cm) for plants treated with 0 (control), 1, 2, 3, 4 and 5 g of hydrogels, respectively at week 12. The leaf areas of plants treated with 4 and 5 g of hydrogels were not significantly different while those with 0.00, 1.00, 2.00 and 3.00 g were significantly different ($p < 0.05$) at week 12.

The highest leaf area was recorded at 5.00 g dose for all SAHs. The growth of crops, productivity and health are related to leaf area, being an aerial part of the plant playing vital role in photosynthesis through light absorbing pigments. Leaf area was seen to increase with the amount of SAH. This is probably related to increased availability of water to plants which in turn influences the amount of minerals available to the plants (Al-Harbi *et al.*, 1999; Yazdani *et al.*, 2007). In this way the water holding capacity of SAH influences the leaf area of maize. Similar results were obtained for the other three hydrogels, ethane-1,2-diol SAH, phosphoric acid SAH and boric acid SAH (see Figure 4.37 to 4.39).

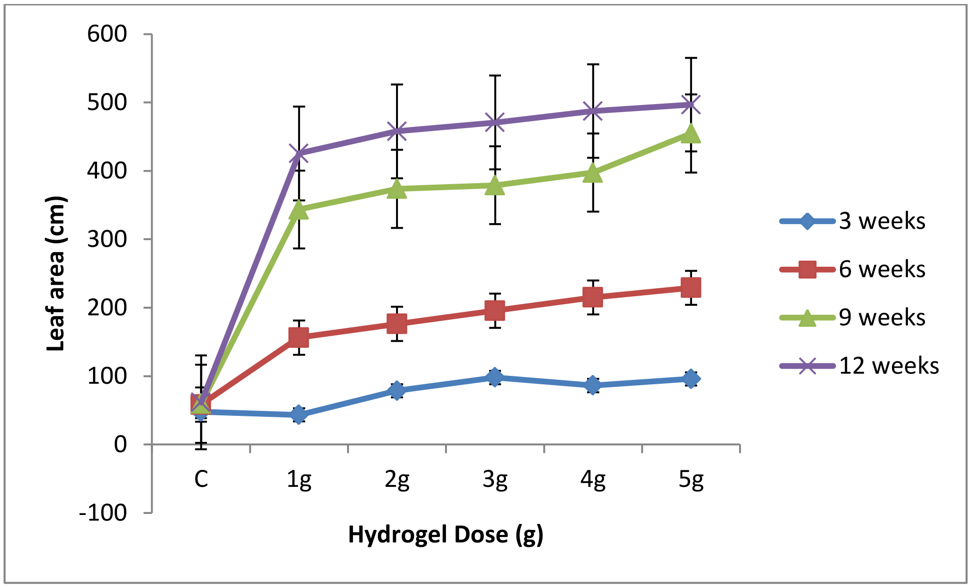


Figure 4.37: Variation of leaf area in maize plants grown with ethane-1,2-diol SAH

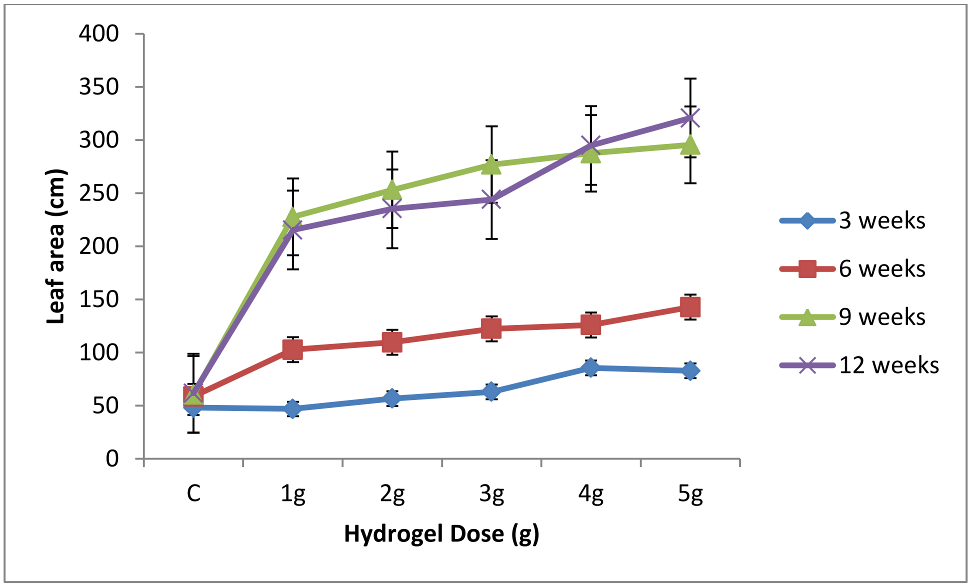


Figure 4.38: Variation of leaf area in maize plants grown with phosphoric acid SAH

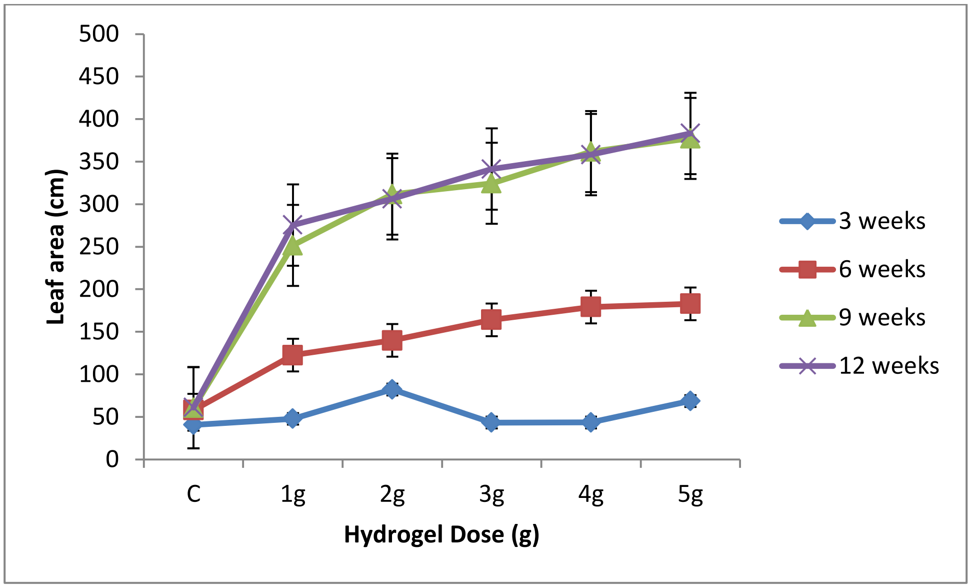


Figure 4.39: Variation of leaf area in maize plants grown with boric acid SAH

In comparing the different hydrogels, it can be seen that the mean leaf area for maize plants grown with 5.00 g of ethane-1,2-diamine SAH, ethane-1,2-diol SAH, phosphoric acid SAH and boric acid SAH at week 12 were 528.78±13.45, 946.77±9.78, 383.20±21.60 and 320.64±12.63, respectively. The leaf areas for treatments with ethane-1,2-diamine SAH, ethane-1,2-diol SAH, phosphoric acid SAH and boric acid SAH were significantly different ($p < 0.05$). This implies that ethane-1,2-diamine SAH performed better than the other superabsorbent hydrogels at different hydrogel doses.

4.10 Evaluation of post-harvest parameters

The yield parameters measured included the number of cobs per plant, length of cob, cob diameter, weight of cob, grain weight and number of grains. The results are presented and discussed below.

4.10.1 Number of cobs per plant

The variation of the number of cobs per plant with hydrogel and hydrogel dose was investigated for the four hydrogels at varied doses, namely, 0 (control), 1.00, 2.00, 3.00, 4.00 and 5.00 g. The results are presented in Figure 4.40.

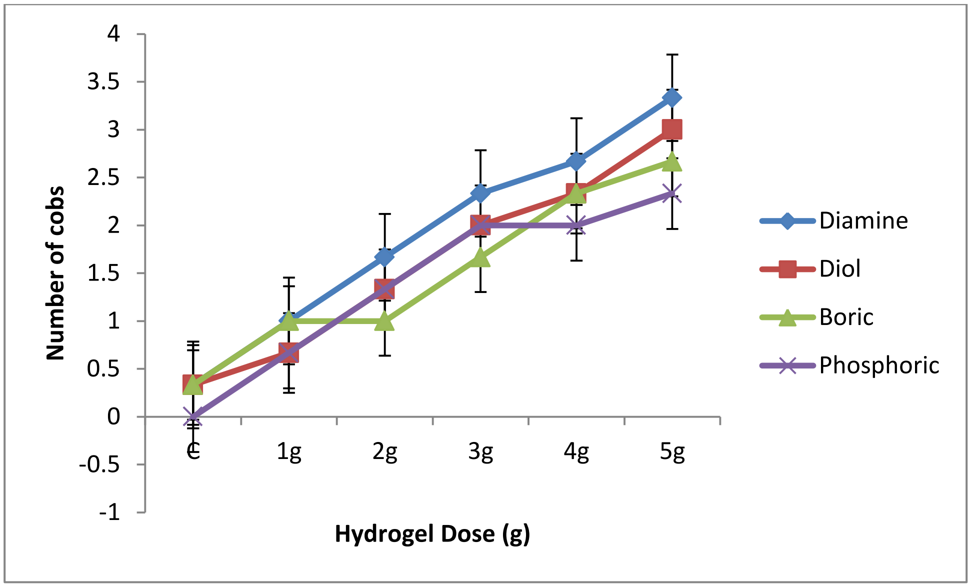


Figure 4.40: Variation of number of cobs with type of hydrogels and hydrogel dosage

The mean number of cobs increased from 0.33 to 3.33 in the plants treated with the ethane-1,2-diamine SAH; 0.33 to 3.00 for plants treated ethane-1,2-diol SAH; 0.33 to 2.66 for plants treated with the boric acid SAH; and 0.00 to 2.33 for plants treated with the phosphoric acid SAH; respectively. The increase in hydrogel dose increased the number of cobs. Similarly, Kumar (2015) observed that the number of cob was influenced the SAHs.

4.10.2 Maize cob length (cm)

The variation of maize cob length with type of hydrogel and hydrogel dose was investigated for the four hydrogels synthesized. The results are displayed in Figure 4.41.

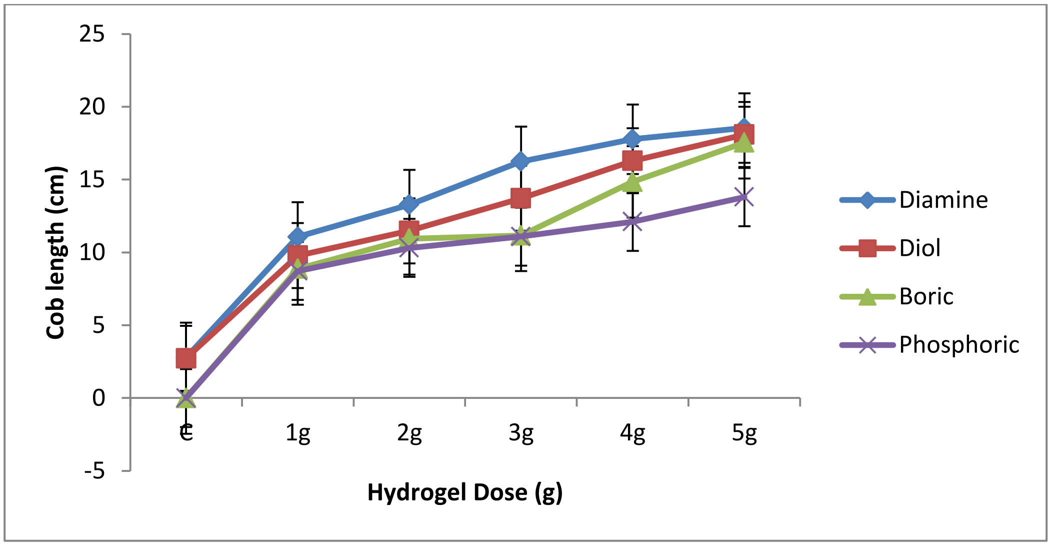


Figure 4.41: Variation of maize cob length with type of hydrogel and hydrogel dose

Figure 4.41 shows that the mean cob length increased from 2.77 to 18.53 cm in the plants treated with the ethane-1,2-diamine SAH; 2.73 to 18.09 cm for plants treated with the ethane-1,2-diol SAH; 0.00 to 17.54 cm, in the plants treated with the boric acid SAH; and 0.00 to 13.79 cm in the plants treated with the phosphoric acid SAH, respectively. The length of the cob was significantly affected in the plants in pots treated with high doses and produced larger cobs compared to those with 1, 2, or 3 of SAH. Kumar (2015) observed that application of 150 % SAH to soil had a significant effect on cob length. The highest value of the cob length was observed in plants grown under the ethane-1,2-diamine SAH. This was, however, not significantly different from results obtained with the other SAHs. Similar cob lengths were also reported by Hossain (2009) and (Niazuddin *et al*. (2002).

4.10.3 Cob diameter (cm)

The effect of superabsorbent hydrogels ethane-1,2-diamine SAH, ethane-1,2-diol SAH, phosphoric acid SAH and boric acid SAH on cob diameter was investigated at varied dose ranging from 0 (control) to 5.00 g. The results are presented in Figure 4.42.

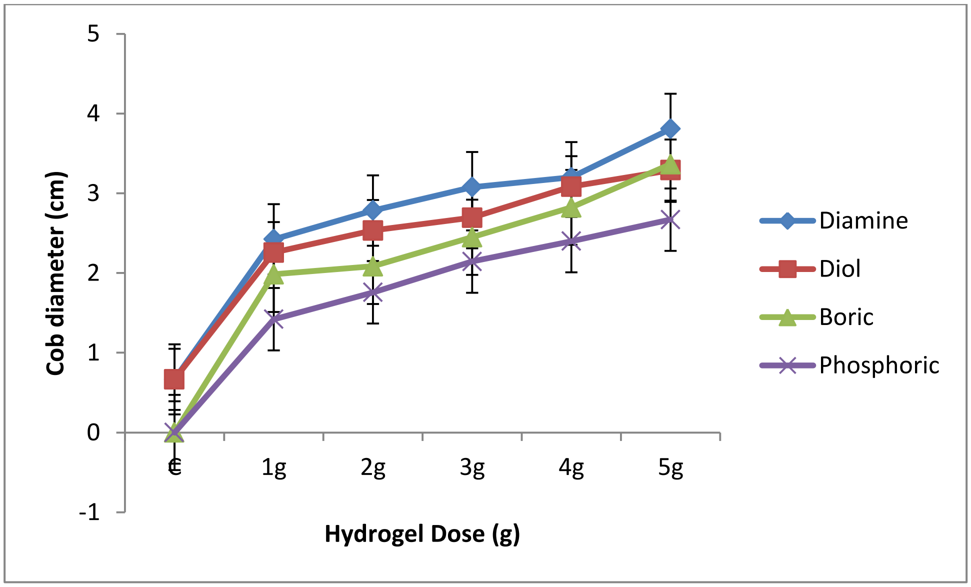


Figure 4.42: Variation of maize cob diameter with superabsorbent hydrogels

The mean cob diameter increased from 0.66 to 3.80 cm plants treated with ethane-1,2-diamine SAH, 0.66 to 3.29 cm for those treated with ethane-1,2-diol SAH, 0.00 to 3.36 cm in plants treated with phosphoric acid SAH and 0.00 to 2.67 cm in plants treated with boric acid SAH, respectively. The results obtained show that the cob diameter increased with increase in hydrogel dose. The highest value of the cob diameter was observed in plants grown under ethane-1,2-diamine SAH.

4.10.4 Cob weight (g)

The variation of cob weight with type and dose of superabsorbent hydrogels ethane-1,2-diamine SAH, ethane-1,2-diol SAH, phosphoric acid SAH and boric acid SAH was investigated at varied doses ranging from control to 5.00 g. The results are displayed in Figure 4.43.

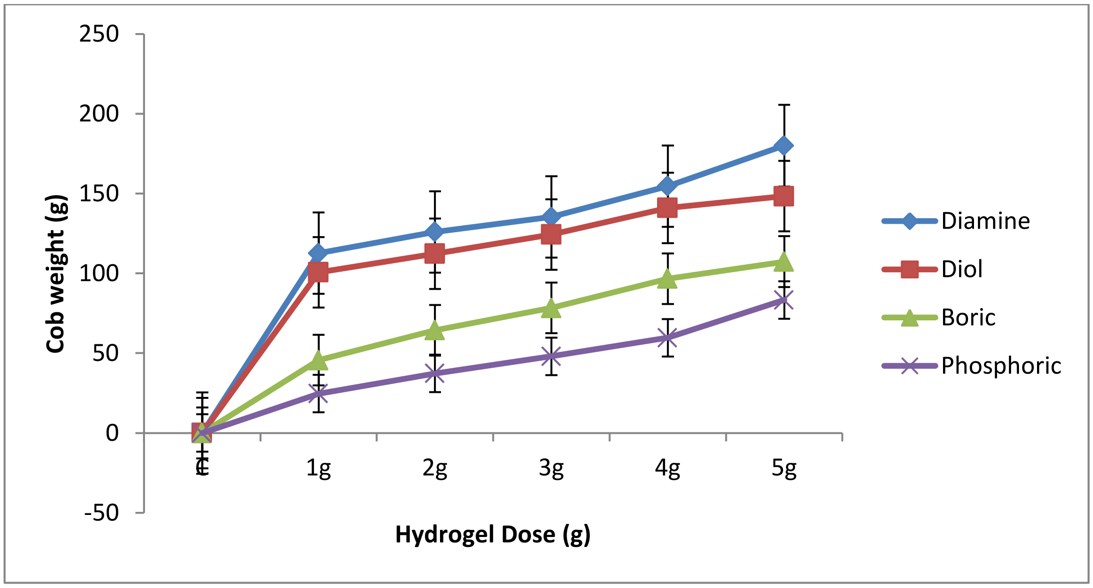


Figure 4.43: Variation of cob weight with superabsorbent hydrogels

The mean cob weight increased from 0.00 to 180.00 g in plants grown under ethane-1,2-diamine SAH, 0.00 to 148.33 g for plants under ethane-1,2-diol SAH, 0.00 to 107.33 g for those under phosphoric acid SAH, and 0.00 to 83.33 g for those under boric acid SAH, respectively. A similar result was observed by Sendure *et al.* (2001), which found that increase in fruit weight of tomatoes in soils incorporated with superabsorbent hydrogels. The highest value of the cob weight was observed under ethane-1,2-diamine SAH.

4.10.5 Number of grains

The variation of the number of grains with the type and dosage of SAHs was investigated for SAH doses ranging from 0 (control) to 5.00 g. The results are displayed in Figure 4.44 below.

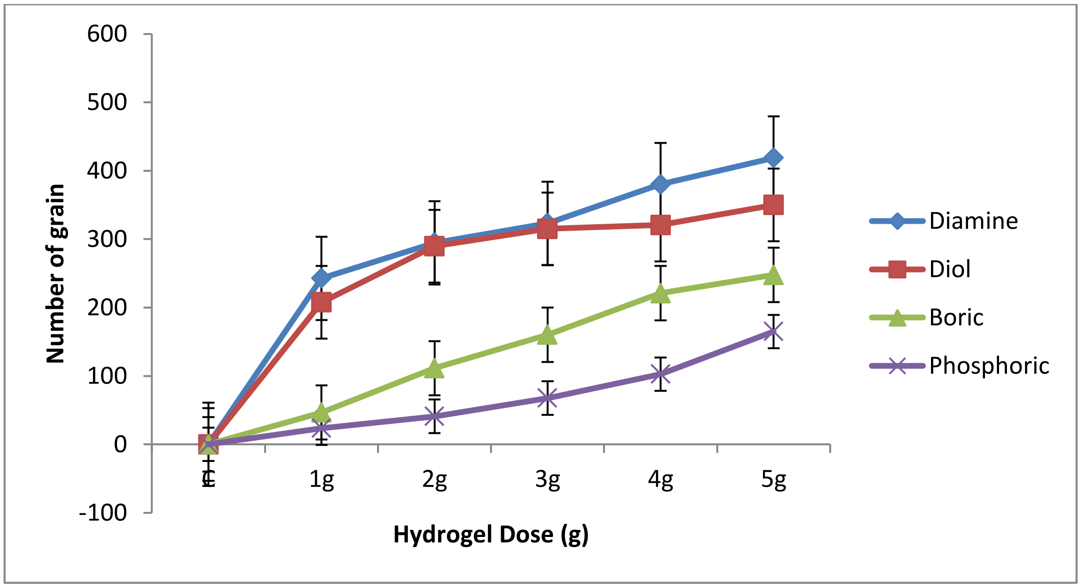


Figure 4.44: Variation of number of grains per cob with the type and dosage of superabsorbent hydrogels

The mean number of grains increased from 0.00 to 418.67 for ethane-1,2-diamine SAH, 0.00 to 350.00 in the maize plants treated with the ethane-1,2-diol SAH; 0.00 to 247.67, in the maize plants treated with the boric acid SAH; and 0.00 to 165.00 for the maize plants treated with the phosphoric acid SAH, respectively. The results revealed that the number of grains was significantly influenced by the SAHs. The increase in dose significantly affects the number of grain obtained in the maize. In a similar kind of study, Khadem *et al*. (2010) observed that application of superabsorbent hydrogels to soil increased the number of grains by 16.2 % as compared to zero (control). In this study, the highest number of grains was observed in maize plants grown under the ethane-1,2-diamine SAH at 5 g.

4.10.6 Grain weight (g)

The effect of superabsorbent hydrogels on grain weight was investigated by varying the superabsorbent doses ranging from 0 (control) to 5.00 g. The results are displayed in Figure 4.45.

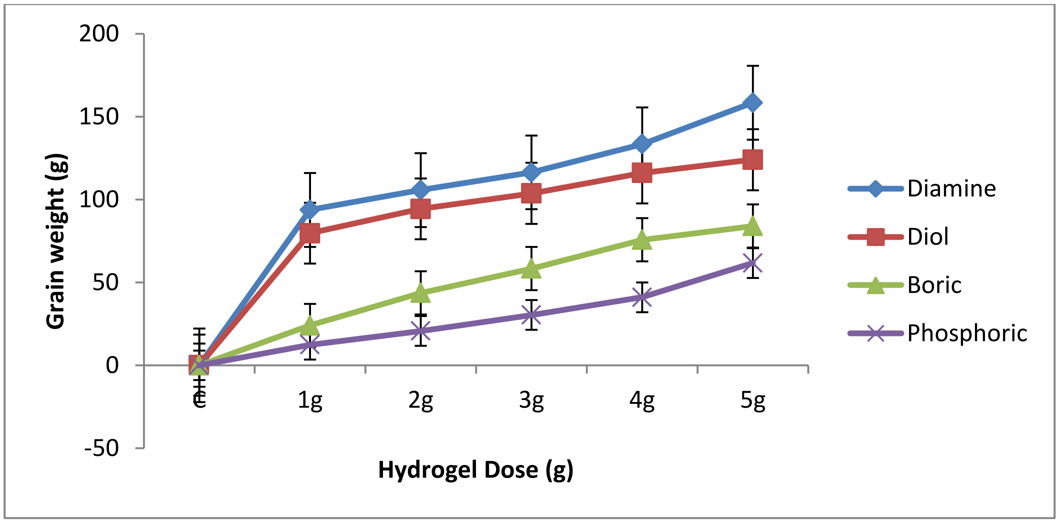


Figure 4.45: Variation of grain weight with superabsorbent hydrogels

The mean grain weight increased from 0.00 to 158.33 g for plants grown under ethane-1,2-diamine SAH, 0.00 to 124.00 g for plants under ethane-1,2-diol SAH, 0.00 to 84.00

g for plants under phosphoric acid SAH and 0.00 to 61.67 g for plants grown under boric acid SAH, respectively. The results show that grain weight per pot increased significantly with increase in SAH dose. It has been reported that application of superabsorbent hydrogel enhanced the 100 seed weigh of sunflower as compared to the zero (control) (Nazarli, 2010). The grain weight of plants grown under ethane-1,2-diamine SAH was higher than all the other treatments.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Based on the results obtained in this study and discussed in the previous chapter it can be concluded that cellulose was successfully extracted from rice husks using acetic and nitric acids in 81.67 % yield and characterized by FTIR spectroscopy, x-ray diffraction, scanning electron microscopy and energy dispersive x-ray spectroscopy. The cellulose was successfully converted to carboxymethylcellulose (CMC) by alkalization with NaOH and etherification with MCA under microwave heating. It was also characterized by FTIR spectroscopy, x-ray diffraction, and scanning electron microscopy as well as determination of degree of substitution.

Cellulose was successfully converted to the superabsorbent hydrogels (SAHs) by crosslinking it with boric and phosphoric acids. Carboxymethylcellulose on the other hand was converted to the SAHs by crosslinking with ethane-1,2-diol and ethane-1,2-diamine. The hydrogels were characterized by FTIR spectroscopy, x-ray diffraction, scanning electron microscopy and by determination of percentage swelling in water.

All the superabsorbent hydrogels prepared were found to be efficacious in maize growing in a greenhouse as determined from plant growth and yield parameters measured. They were able to support plant growth for nine weeks with watering which was only done during the first three wees of planting. The growth and yield were found to be significantly influenced by type and dose of SAHs. The highest parameters were recorded at 5.00 g SAHs dose.

5.2 Recommendations

5.2.1 Recommendations from this work

Cellulose can be extracted from the agricultural waste, rice husks, modified to CMC, and crosslinked to obtain superabsorbent hydrogels for use in agriculture. This has the potential to reduce the disposal problem posed by the waste rice husks in the rice milling industry. The use of microwave heating during the synthesis is more efficient than using the reflux method as it consumes less energy, time and is likely less costly. Piloting scale rice husks cellulose-based hydrogels production for use to improve maize grown production in arid and semi-arid areas is also recommended.

5.2.2 Recommendations for further studies

The following are recommended for further studies.

(i) Feasibility of pilot scale production of the rice husks cellulose and conversion to superabsorbent hydrogels.

(ii) Investigation of the efficacy of the SAHs obtained from this study, in an open field farm on pilot scale to determine possibility of up scaling.

(iii) Investigation of the efficacy of SAHs on other crops and vegetables in an open field farm and green house.

(iv) Investigation of the potential of other waste materials such as coffee husks, banana peels for synthesis of SAHs with other cross-linkers to improve absorption capacity.

(v) Determination of the degradation pathways for the hydrogel products obtained in this study.

(vi) Investigate the efficacy of ethane-1,2-diamine SAH, ethane-1,2-diol SAH, phosphoric acid SAH and boric acid SAH dose above 5 g, but it looks like the more SAH, the better the yield.

REFERENCES

Abd El-Rehim H. A., Hegazy E. S. A., and Abd El-Mohdy H. L. (2004). Radiation synthesis of hydrogels to enhance sandy soils water retention and increase plant performance. *Journal of Applied Polymer Science*, **93(1)**:1360-1371.

Abdulhameed A., Mbuvi H. M., and Changamu E. O. (2020). Synthesis of cellulose-based superabsorbent hydrogel from rice husks using a microwave. *American Journal of Materials Science*, **(10)1**: 1-8.

Abdulhameed A., Mbuvi H. M., and Changamu E. O. (2017). Removal of fluoride ion by silicon nitride powder. *International Journal Water and Wastewater Treatment*, **3(1)**: 1-7

Abdulhameed A., Mbuvi H. M., Changamu E. O., and Maingi F. M. (2019). Microwave synthesis of carboxymethylcellulose (CMC) from rice husks. *IOSR Journal of Applied Chemistry*, **12(12)**: 33-42.

Abedi-Koupai J., and Sohrab F. (2004). Effect evaluation of superabsorbent application on water retention capacity and water potential in three soil textures. *Journal of Science and Technology Polymer*, **17(3)**: 163-173.

Abedi-Koupai J., Eslamian S. S., and Asadkazemi J. (2008). Enhancing the available water content in unsaturated soil zone using hydrogel, to improve plant growth indices. *Ecohydrology and Hydrology*, **8(1)**: 67-75.

Abedi-Koupai J., and Asadkazemi J. (2006). Effects of a hydrophilic polymer on the field performance of an ornamental plant (*Cupressus arizonica*) under reduced irrigation regimes. *Iranian Polymer Journal*, **15(9)**: 715-720.

Abedi-Koupai J., Mesforoush M., and Sohrab F. (2004). Effect of superabsorbent polymers on soil hydraulic properties. proceedings of 8th national conference on hydraulic engineering. Gold coast, Australia, 1-12.

Abrams L. (2018), Unlocking the potential of enhanced rainfed agriculture. Report no. 39. SIWI, Stockholm.

Adeyanju O., Olademehin O. P., Hussaini Y., Nwanta U. C., Adejoh A. I., and Plavec J. (2016). Synthesis and characterization of carboxymethyl *Plectranthus esculentus* starch. a potential disintegrant. *Journal of Pharmaceutical and Applied Chemistry*, **2(3)**: 189-195.

Adinugraha M. P., Marseno D. W., and Hayadi A. (2005). Synthesis and characterization of sodium carboxymethylcellulose from cavendish banana pseudo stem (*Musa cavendishii* Lambert). *Carbohydrate Polymers*, **62(1)**: 164-169.

Aflakpui G. K. S., Gregory P. J., and Froud-williams R. J. (2002). Growth and biomass partitioning of maize during vegetative growth in response to *Striga hermonthica* infection and nitrogen supply. *Experimental Agriculture*, **38(1)**: 265-276.

Ahmad N., Wahab R., and Sulaiman S. Y. A. (2014). Thermal decomposition kinetics of sodium carboxymethylcellulose: Model-free methods. *European Journal of Chemistry*, **5(1)**: 247–251.

Ajala A S., and Gana A. (2015). Analysis of challenges facing rice processing in Nigeria. *Journal of Food Processing,* **2(2)**: 1-6.

Akhter J., Mahmood K., Malik K., Mardan A., Ahmad M., and Iqbal M. (2004). Effects of hydrogel amendment on water storage of sandy loam and loam soils and seedling growth of barley, wheat and chickpea. *Plant Soil Environment*, **50(10)**: 463--469.

Al-Harbi A. R., Al-Omran A. M., Shalaby A. A., and Choudhary M. I. (1999). Efficacy of a hydrophilic polymer declines with time in greenhouse experiments. *Horticulture Science*, **34(2)**: 223–224.

Al-Humaid A., and Moftah A. E. (2007). Effects of hydrophilic polymer on the survival of Buttonwood seedlings grown under drought stress. *Journal of Plant Nutrition,* **30(1)**: 53-66.

Al-Assaf S., Dickson P., Phillips G. O., Thompson C., and Torres J. C. (2009). Compositions comprising polysaccharide gums, in: World Intellectual Property Organization. Phillips Hydrocolloid Research Limited (UK).

Alizadeh-Asl S., Mousavi M., and Labbafi M. (2017). Synthesis and characterization of carboxymethylcellulose from sugarcane bagasse. *Journal of Food Process Technology*, **8(1)**: 687-694.

Almasi H., Ghanbarzadeh B., and Entezami A. A. (2010). Physicochemical properties of starch-CMC-nanoclay biodegradable films. *Biological Macromolecules,* **46(1)**:1-5.

Ang T. N., Ngoh G. C., Chua1 A. S. M., and Lee M. G. (2012). Elucidation of the effect of ionic liquid pretreatment on rice husks via structural analyses. *Biotechnology for Biofuels*, **5(67)**: 1-10.

Anupama M. C., Singh R. K., and Parmar B. S. (2007). Performance of a new superabsorbent polymer on seedling and post planting growth and water use pattern of chrysanthemum grown under controlled environment. *Acta Horticulturae,* **742(1)**:43-49.

Ardelean I., and Toderaş M. (2006). FTIR structural investigation of $3B_2O_3{\cdot}BaO$ glass matrix containing manganese ions. *Journal of Optoelectronics and Advanced Materials,* **8(3)**: 1118 – 1120.

Arslan N. (2007). Flow properties of cellulose and carboxymethylcellulose from orange peel. *Journal Food Engineering,* **81(1)**: 187–199.

Artanti P. W., and Kurniyati Z. (2016). Effect of sodium chloroacetate towards the synthesis of cmc (carboxymethyl cellulose) from durian (*Durio zibethinus*) peel cellulose. *International Journal of Innovative Research in Advanced Engineering (IJIRAE),* **3(3)**: 28-32.

Arthur Jr J. C. (1986). In: G. Allen and J. C. Bevington, eds. Comprehensive polymer science. Vol. 6. Pergamon: Oxford.

Arun-Kumar R., Subramani K., and Ravichandran S. (2010). Montmorillonite K-10 clay– catalyzed microwave synthesis of some mannich bases and their characterization. *International Journal of Chemistry Technology Research*, **2(1)**: 278–281.

Awada H., Montplaisir D., and Daneault C. (2014). The development of a composite based on cellulose fibres and polyvinyl alcohol in the presence of boric acid**.** *BioResources,* **9(2)**: 3439-3448.

Aydin M., Tozlu H., Kemaloglu S., Aytac A., and Ozkoc G. (2011). Effects of alkali treatment on the properties of short flax fiber-poly(lactic acid) eco-composites. *Journal of Polymers and the Environment,* **19(1)**: 11–17.

Azzam Rai. (1980). Agricultural polymers, polyacrylamide preparation, application and prospects in soil conditioning. *Communications in Soil Science and Plant Analysis,* **11(8)**: 767- 834.

Bakass M., Mokhlisse A., and Lallemant M. (2002). Absorption and desorption of liquid water by a superabsorbent polymer: Effect of polymer in the drying of the soil and the quality of certain plants. *Journal of Applied Polymer Science,* **83(2)**: 234-243.

Bakravi A., Ahamadian Y., Hashemi H., and Namazi H. (2017). Synthesis of gelatin-based biodegradable hydrogel nanocomposite and their application as drug delivery agent. *Advanced Polymer Technology,* **2(2)**: 1-11.

Barai B. K., Singhal R. S., and Kulkarni, P. R. (1997). Optimization of a process for preparing carboxymethylcellulose from water hyacinth (*Eichornia crassipes*). *Carbohydrates Polymer,* **32(1)**: 229–231.

Baris Y. A. (2014). Investigations of the productions of silicon nitride from Turkish rice husks. Thesis. The graduate school of natural and applied science, Middle East University.

Begna S. H., Hamilton R. I., Dwyer L. M., Stewart D. W., Cloutier D., Assemat L., Foroutan-pour K., and Smith D. L. (2001). Morphology and yield response to weed pressure by corn hybrids differing in canopy architecture. *European Journal of Agronomy*, **14(4)**: 293-302.

Benamer S., Mahlous M., Boukrif A., Mansouri B., and Youcef S. L. (2006). Synthesis and characterization of hydrogels based on poly(vinyl pyrrolidone). *Nuclear Instrumental Methods Physical Research*, **248(1)**: 284–290.

Bennour S., and Louzri F. (2014). Study of Swelling Properties and Thermal Behavior of Poly (N, N-Dimethylacrylamide-co-maleic acid) based hydrogels. *Advances in Chemistry*, **1(2)**: 1-10.

Boatright J. L., Balint D. E., Mackay W. A., and Zajicek J. M. (1997). Incorporation of a hydrophilic polymer into annual landscape beds. *Journal of Environmental Horticulture*, **15(1)**: 37-40.

Bono A., Ying P. H., Yan F. Y., Muei C. L., Sarbatly R., and Krishnaiah D. (2009). Synthesis and characterization of carboxymethylcellulose from palm kernel cake. *Advances in Natural and Applied Sciences*, **3(1)**: 5-11.

Bowman D. C., Evans R. Y., and Paul J. L. (1990). Fertilizer salts reduce hydration of polyacryamide gels and affect physical properties of gel-amended container media. *Journal of American Society for Horticultural Science*, **115(1)**: 382-386.

Brandt L. (2001). Cellulose ethers. In: Wilks ES, editor. Industrial Polymers Handbook. Weinheim: Wiley-VCH. **3**: 1569-1613

Brodt S., Six J., Feenstra G., Ingels C., and Campbell D. (2011). Sustainable Agriculture. *Nature Education Knowledge*, **3(10)**: 1-7.

Byrne M., Parka K., and Pepas N. A. (2002). Molecular imprinting within hydrogels. *Advanced Drug Delivery Reviews*, **54(1)**: 149–161.

Carolyn M. (2013). Rice husks electrode. The brief. https://www.stylus.com/ccfflh.

Chai M., and Mohamad Isa M. I. N. (2011). Carboxylmethylcellulose solid polymer electrolytes: ionic conductivity and dielectric study. *Journal of Current Engineering Research*, **1(1)**: 23–27.

Chan A. W., Whitney P. A., and Neufeld R. J. (2009). Semi-synthesis of a controlled stimuli-responsive alginate hydrogel. *Biomacromolecules*, **10(1)**: 609-616.

Chang C., Duan B., Cai J., and Zhang L. (2010). Superabsorbent hydrogels based on cellulose for smart swelling and controllable delivery. *European Polymer Journal*, **46(2)**: 92-100.

Chauhan G. S., Lal H., and Mahajan S. (2004). Synthesis, characterization, and swelling responses of poly (*N*-isopropylacrylamide) and hydroxypropylcellulose-based environmentally sensitive biphasic hydrogels. *Journal of Applied Polymer Science*, **91(2)**: 479–488.

Chemar J. H., Kristy D. C., and Michael L. C. (2015). Chemical functionalization and characterization of cellulose extracted from wheat straw using acid hydrolysis methodologies. *International Journal of Polymer Science*, **1(1)**: 1-9

Cheng W. M., Hu X. M., Wang D. M., and Liu G. H. (2015). Preparation and characteristics of corn straw-co-amps-co-aa superabsorbent hydrogel. *Polymers*, **7(2)**: 2431-2445.

Colombo P., Bettini R., and Peppas N. A. (1999). Observation of swelling process and diffusion front position during swelling in hydroxypropylmethylcellulose (HPMC) matrices containing a soluble drug. *Journal of Controlled Release*, **61(2)**: 83-91.

Coma V., Sebti J., Pardon P. Pichavant F. H., and Descahmps A. (2003). Film properties from crosslinking of cellulosic derivatives with a polyfunctional carboxylic acid. *Carbohydrate Polymers*, **51(3)**: 265-271.

Costa-Ju´nior E. S., Barbosa-Stancioli E. F., Mansur A. A., Vasconcelos W. L., and Mansur H. S. (2009). Preparation and characterization of chitosan/poly (vinyl alcohol) chemically crosslinked blends for biomedical applications. *Carbohydrate Polymers*, **76(3)**: 472–481.

Danilo M. D. S., Andreade L. B., Diego P. R. A., Roberta S., and Gilberto L. B. D. (2015). Microwave-assisted carboxymethylation of cellulose extracted from brewer’s spent grain. *Carbohydrate Polymers*, **131(1)**: 125–133.

De Varennes A. D., and Queda C. (2005). Application of an insoluble polyacrylate polymer to copper-contaminated soil enhances plant growth and soil quality. *Soil Use and Management*, **21(4)**: 410-414.

Dimitri C., Scalera F., Madaghiele M., Sannino A., and Maffezzoli A. (2013). Potential of cellulose-based superabsorbent hydrogels as water reservoir in agriculture. *International Journal of Polymer Science*, **1(2)**: 1-7.

Demitri C., Del Sole R., Scalera F., Sannino A., Vasapollo G., Maffezzoli A., Ambrosio L., and Nicolais L. (2008). Novel superabsorbent cellulose-based hydrogels crosslinked with citric acid. *Journal of Applied Polymer Science*, **110(1)**: 2453-2460.

Diana C., Florin C., and Valentin I. P. (2011). Amorphous cellulose – Structure and characterization. *Cellulose Chemistry and Technology*, **45(1-2)**: 13-21.

Dorraji S. S., Golchin A., and Ahmadi S. (2010). The effects of hydrophilic polymer and soil salinity on corn growth in sandy and loamy soils, *Clean – Soil Air Water*, **38(7)**: 584--591.

Drury J. L., and Mooney D. J. (2003). Hydrogels for tissue engineering: scaffold design variables and applications, *Biomaterials*, **24(1)**: 4337–4351.

Efrani M., Elias S., Nayereh S., Mansor H., Wan Saffiey B., Wan Abdullah A., and Manizheh N. (2012). Facile synthesis of calcium borate nanoparticles and the annealing effect on their structure and size. *International Journal Molecular Science*, **13(2)**: 14434-14445.

Ekezie F. C., Sun D., Han Z., and Chang J. (2017). Microwave-assited food processing technologies for enhancing product quality and process efficiency: A review of recent development. *Trend in Food Science and Techonology*, **67(1)**: 58-69.

El-Hady O. A., and Abo-Sedera S. A. (2006). Conditioning effect of composts and acrylamide hydrogels on a sandy calcareous soil. II - Physico-bio-chemical properties of the soil. *International Journal of Agriculture and Biology*, **8(1)**: 876-884.

El-Hady O. A., Tayel M. Y., and Lofty A. A. (1981). Super gel as a soil conditioner: its effect on plant growth, enzymes activity, water use efficiency and nutrient uptake. *Acta Horticulturae*, **119(2)**: 257–265.

El-Hady O., and Wanas S. A. (2006). Water and fertilizer use efficiency by cucumber grown under stress on sandy soil treated with acryl amide hydrogels. *Journal of Applied Science Research*, **2(12)**: 1293—1297

El-Salmawi K. M. (2007). Application of polyvinyl alcohol (PVA)/carboxymethyl cellulose (CMC) hydrogel produced by conventional crosslinking or by freezing and thawing. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, **44(1)**: 619–624.

Erkmen J., and Yapici S. (2015). A environmentally friendly process for boric acid and sodium hydroxide production from borax; bipolar membrane electrodialysis. *Desalination and Water Treatments*, **57(43)**: 20261-20269.

Fanta G. F., Burr R. C., and Doane W. M. (1971). Influence of starch-granule swelling on graft-copolymer composition. A comparison of monomers. *Journal of Applied Polymer Science*, **15(11)**: 2651-2660.

Fatah I. Y. A., Khalil H. P. S. A., and Aziz A. A. (2014). Exploration of a chemo-mechanical technique for the isolation of nanofibrillated cellulosic fiber from oil palm empty fruit bunch as a reinforcing agent in composites materials. *Polymers (Basel),* **6(4)**: 2611–2624.

Ferruti P., Bianchi S., Ranucci E., Chiellini F., and Piras A. M. (2005). Novel agmatine-containing poly (amidoamine) hydrogels as scaffolds for tissue engineering. *Biomacromolecules,* **6(3)**: 2229–2235.

Gao D., Xu H., Philbert M. A., and Kopelman R. (2007). Ultrafine hydrogel nanoparticles: synthetic approach and therapeutic application in living cells. *Angewwandte Chemie International Edition England,* **46(2)**: 2224–2227.

Gehring J. M., and Lewis A. J. (1980). Effect of hydrogel on wilting and moisture stress of bedding plants. *Journal of American Society for Horticultural Science,* **105(5)**: 511-513.

Gupta V. N., and Shivakumar H. G. (2012). Investigation of swelling behavior and mechanical properties of a pH-sensitive superporous hydrogel composite. *Journal of Pharmacutical Resources,* **11(2)**: 481–493.

González-Domínguez J. M., Fernández-González M. C., Alexandre-Franco M., and Gómez-Serrano V. (2018). How does phosphoric acid interact with cherry stones? A discussion on overlooked aspects of chemical activation. *Wood Science and Technology*, **52**: 1645-1669.

Haleem N., Arshad M., Shahid M., and Tahir M. A. (2014). Synthesis of carboxymethylcellulose from waste of cotton ginning industry. *Carbohydrate Polymer,* **113(2)**: 249–255.

Han B., Benner S. G., and Flores A. N. (2018). Evaluating impacts of climate change on future water scarcity in an intensively managed semi-arid region using a coupled model of biophysical processes and water rights. Hydrology and Earth System Sciences Discussions, 153-165.

Han Y. G., Yang P. L., Luo Y. P., Ren S. M., Zhang L. X., and Xu L. (2010). Porosity change model for watered super absorbent polymer-treated soil. *Environmental Earth Sciences,* **61(6)**: 1197-1205.

Harsh D. C., and Gebrke S. H. (1991). Controlling the swelling characteristics of temperature sensitive cellulose ether hydrogels. *Journal of Controlled Release,* **17(2)**: 175-186.

He X. J., Wu S. Z., Fu D. K., and Ni J. R. (2009). Preparation of sodium carboxymethylcellulose from paper sludge. *Journal of Chemical Technology and Biotechnology*, **84(2)**: 427-434.

Hebeish A., Higazy A., El-Shafei A., and Sharaf S. (2010). Synthesis of carboxymethyl cellulose (CMC) and starch-based hybrids and their applications in flocculation and sizing. *Carbohyrates Polymers*, **70(3)**: 60-69.

Heinze T., and Koschella A. (2005). Carboxymethylethers of cellulose and starch. *Macromolecular Symposium*, **223(4)**: 13–39.

Heinze T., and Pfeiffer K. (1999). Studies on the synthesis and charcterization of carboxymethylcellulose. *Angewandte Makromolekulare Chemie*, **266**: 37–45.

Helalia A. M., and Letey J. (1989). Effects of different polymer on seedling emergence, aggregate stability and crust hardiness. *Soil Science*, **148(2)**: 199-203.

Helalia A., and Letey J. (1988). Cationic polymer effects on infiltration rates with a rainfall simulator. *Soil Science Society of America Journal*, **52(1)**: 247-250.

Heydarzadeh H. D., Najafpour G. D. and Nazari-Moghadam A. A. (2009). Catalsy-free conversion of alkali cellulose to fine carboxymethylcellulose at mild conditions. *Journal of Water and Applied Sciences*, **6(4)**: 564-569.

Hossain M. S. (2009). Effect of deficit irrigation on yield and water productivity of maize. M. S Thesis (Agriculture Enginnering), Department of Irrigation and Water Management. pp. 26-38.

Hudson S. M., and Cuculo A. J. (1980). The solubility of unmodified cellulose: A critique of the literature. *Journal of Macromole Science—Review Macromolecule Chemistry*, **18(1)**:1–82.

Huettermann A., Orikiriza L. J., and Agaba H. (2009). Application of superabsorbent polymers for improving the ecological chemistry of degraded or polluted lands. *Clean – Soil Air Water*, **37(7)**: 517--526.

Huntley C. J., Crews K. D., and Curry M. L. (2015). Chemical functionalization and characterization of cellulose extracted from wheat straw using acid hydrolysis methodologies. *International Journal of Polymer Science*, **3(1)**: 1-9.

Hussain P. R., Meena R. S., Dar M. A., and Wani A. M. (2010). Carboxymethyl cellulose coating and low-dose gamma irradiation improves storage quality and shelf life of pear (*Pyrus communis L.*, cv. Bartlett/ William). *Journal of Food Science*, **75(3)**: 586–596.

Huttermann A., Zommorodi M., and Reise K. (1999). Addition of hydrogels to soil for prolonging the survival of *Pinus halepensis* seedlings subjected to drought. *Soil and Tillage Research*, **50(3)**: 295-304.

Ibrahim S. M., El Salmawi K. M., and Zahran A. H. (2007). Synthesis of crosslinked superabsorbent carboxymethylcellulose/acrylamide hydrogels through electron-beam irradiation. *Journal of Applied Polymer Science*, **104(3)**: 2003-2008.

Isogai A. (2001). Wood and cellulosic chemistry- chemical modification of cellulose, 2nd edition, Marcel Dekker, New York.

Islam M. R., Hu Y., Mao S., Jia P., Eneji A. E., and Xue X. (2011). Effects of watersaving superabsorbent polymer on antioxidant enzyme activities and lipid peroxidation in corn (*Zea mays L.*) under drought stress. *Journal of the Science of Food and Agriculture*, **91(4)**: 813–819.

Jayakumar R., Egawa T., Furuike T., Nair S. V., and Tamura H. (2009). Synthesis, characterization, and thermal properties of phosphorylated chitin for biomedical applications, *Polymer Engineering Science,* **49(2)**: 844-849.

Jia N., Li S., Ma M., Zhu J., and Sun R. (2011). Synthesis and characterization of cellulose-silica composite fiber in ethanol/water mixed solvents. *BioResources*, **6(2)**: 1186-1195.

Jia X., Chen Y., Shi C., Ye Y., Wang P., Zeng X., and Wu T. (2013). Preparation and characterization of cellulose regenerated from phosphoric acid. *Journal of Agriculture and Food Chemistry*, **61(1)**: 12405-12414.

Jiang M., Zhao M. M., Zhou Z. W., Huang T., Chen X. L., and Wang Y. (2011). Isolation of cellulose with ionic liquid from steam exploded rice straw. *Industrial Crops and Products,* **33(3)**: 734–738.

Jin S., Liu M., Zhang F., Chen S., and Niu A. (2006). Synthesis and characterization of pH-sensitivity semi-IPN hydrogel based on hydrogen bond between poly(N-vinylpyrrolidone) and poly(acrylic acid). *Polymer,* **47(1)**: 1526-1532.

Johnson D., Hooper P., and Conrey R. (1999). XRF analysis of rocks and minerals for major and trace elements on a single low dilutions tetraborate fused bead. *Advances in X-ray Analysis,* **41(1)**: 843-867.

Johnson M. S., and Leah A. (1990). Effects of superabsorbent polyacrylamides on efficiency of water use by crop seedlings. *Journal of the Science of Food and Agriculture,* **52(3)**: 431-434.

Kamitsos E. I., Karakassides M. A., and Chryssikos G. D. (1987). Vibrational spectra of magnesium-sodium-borate glasses. 2. Raman and mid-infrared investigation of the network structure. *Journal Physical Chemistry*, **91(3)**: 1073-1079.

Kang H. S., Park S. H., Lee Y. G., and Son T. I. (2007). Polyelectrolyte complex hydrogel composed of chitosan and poly(-glutamic acid) for biological application: Preparation, physical properties, and cytocompatibility. *Journal of Applied Polymer Science*, **103(2)**: 386–394.

Kayra N., and Aytekin A. O. (2018). Synthesis of Cellulose-Based Hydrogels: Preparation, Formation, Mixture, and Modification. Cellulose-Based Superabsorbent Hydrogels: Polymers and Polymeric Composites: A Reference Series book series (POPOC), 1-28.

Khadem S.A., Galavi M., Ramrodi M., Mousavi S. R., Rousta M. J., and Rezvani-Moghadam P. (2010). Effect of animal manure and superabsorbent polymer on corn leaf relative water content, cell membrane stability and leaf chlorophyll content under drycondition. *Australian Journal of Crop Science,* **4(1)**: 642-647.

Khan F., Tare R., Richard O., Oreffo R., and Bradley M. (2009). Versatile biocompatible polymer hydrogel: scaffolds for cell growth. *Angewandte Chemie International Edition*, **48(5)**: 978-982.

Khodadadi D. D. (2016). The effects of superabsorbent polymers on soils and plants. *Pertanika Journal of Tropical Agricultural Science*, **39(3)**: 267–298.

Klemm D., Kramer F., Moritz S., Lindström T., Ankerfors M., Gray D., and Dorris A. (2011). Nanocelluloses: A New Family of Nature-Based Materials. *Angewandte Chemie (International Edition in English)*, **50(1)**: 5438–5466.

Kondo T. (1997). The assignment of IR absorption bands due to free hydroxyl groups in cellulose. *Cellulose,* **4(4)**: 281–292.

Kramer P. J. (1988). Measurement of plant water status: Historical perspectives and current concerns. *Irrigation Science,* **9(1)**: 275–287.

Krassig H. A. (1993). Cellulose: Structure, Accessibility and Reactivity. *Switzerland: Gordon and Brech Science Publishers,* **1(1)**: 307-313.

Kusumocahyo S. P., Ichikawa T., Shindo T., Iwatsubo T., Kameda M., Ohi K. J., Yoshimi Y., and Kanamori T. (2005). Pervaporative separation of organic mixtures using dinitrophenyl group-containing cellulose acetate membrane. *Journal of Membrane Science*, **253(9)**: 43-48.

Kumar R. (2015). Evaluation of hydrogel on the performance of Rabi maize (*Zea mays L*). Bihar Agricultural College, Sabour, Bhagalpur Bihar Agricultural University, Sabour Bhagalpur-813 210 (Bihar) India.

Ladish M. R. (1989). *Biomass Handbook. In*: Kitani, O. and Hall, C.W., editions. New York: Gordon and Breach Science Publisher, 435.

Laftah W. A., Hashim S., and Ibrahim A. N. (2011). Polymer hydrogels: A review. *Polymer Plastic Technology,* **50(2)**: 1475–1486.

Leciejewski P. (2009). The effect of hydrogel additives on the water retention curve of sandy soil from forest nursery in Julinek. *Journal of Water and Land Development*, **13(2)**: 239-247.

Leh, C. P., Wan Rosli, W. D., Zainuddin, Z., and Tanaka, R. (2008). Optimization of oxygen delignification in production of totally chlorine-free cellulose pulps from oil palm empty fruit bunch fibre. *Industrial Crops and Products,* **28(2)**: 260-267.

Leupin J. A., and Gosselink E. P. (1999). Laundry detergent compositions with cellulosic polymers as additives for improving appearance and integrity of laundered fabrics. W.O. Patent 9914295.

Li D. J., Yang P. L., and Han Y. G. (2004). Application effects of super absorbent polymers on grape cultivation. In G. H. Huang and S. P. Luis (Eds.), *Land and Water Management Decision Tools and Practices* (pg. 798–803). Beijing, China: Agricultural Science and Technology Publishing House.

Li W., Sun B., and Wu P. (2009). Study on hydrogen bond of carboxymethylcellulose sodium film with two-dimensional correlation infrared spectroscopy. *Carbohydrate Polymer,* **78(3)**: 454–461.

Li Y., Li G., Zou Y., Zhou Q., and Lian X. (2014). Preparation and characterization of cellulose nanofibers from partly mercerized cotton by mixed acid hydrolysis. *Cellulose*, **21(2)**: 301-309.

Li Y., Liu C., Tan Y., Xu K., Lu C., and Wang P. (2014). In situ hydrogel constructed by starch-based nanoparticles via a Schiff base reaction. *Carbohydrate Polymers*, **110(2)**: 87-94.

Liliana N. T., Bradley G., and Mutengwa C. (2019). Morphological response of maize to drought, heat and combined stresses at seedling stage. *Journal of Biological Sciences*, **19(3)**: 7-16.

Lin O. H., Kumar R. N., Rozman H. D and Noor M. A. M. (2005). Grafting of sodium carboxymethylcellulose (CMC) with glycidyl methacrylate and development of UV curable coatings from CMC-g-GMA induced by cationic photoinitiators. *Carbohydrate Polymers,* **59(1)**: 57-69.

Lin X., Qu T., and Qi S. (1990). Kinetics of the carboxymethylation of cellulose in the isopropyl alcohol system. *Acta Polymerica*, **41**: 220-222.

Lina Y., Yudong Z., Yajie X., Shumin L., Shaolin G., Bowen Y., and Tianzhu T. (2016). Preparation of a carboxymethylated bacterial cellulose/polyaniline composite gel membrane and its characterization. *RSC Advanc*es, **6(1)**: 68599-68605.

Loo M. M. L., Hashim R., and Leh P. C. (2012). Recycling of a valueless paper dust to a low grade cellulose acetate: effects of pretreatment on acetylation. *Bioresources,* **7(1)**, 1068-1083.

Lowman A. M., and Peppas N. A. (2000). Hydrogels. In Mathiowitz E, editor. Encyclopedia of controlled drug delivery. New York: Wiley, 397-417.

Luan V. H., Tien H. N., Hoa L. T., Hien N. T. M., Oh E. S., Chung J. S., Kim E. J., and Choi W. M. (2013). Synthesis of a highly conductive and large surface area graphene oxide hydrogel and its use in a supercapacitor. *Journal of Materials Chemistry,* **1(2)**: 208-211.

Ma X., Chang P. R., and Yu J. (2008). Properties of biodegradable thermoplastic pea starch/carboxymethyl cellulose and pea starch/microcrystalline cellulose composites. *Carbohydrates Polymer*, **72(2)**: 369-375.

Mahmoudian M., and Ganji F. (2017). Vancomycin-loaded HPMC micro-particles embedded within injectable thermosensitive chitosan hydrogels. *Progamme Biomaterials,* **6(1)**: 49–56.

Malhotra B., Keshwani A., and Kharkwal H. (2015). Natural polymer based cling films for food packaging. Review Article. *International Journal of Pharmacy and Pharmaceutical Sciences,* **7(1)**: 10-18.

Mamun Hossain S. A. A., Wang L. X., Chen T. T., and Li Z. H. (2017). Leaf area index assessment for tomato and cucumber growing period under different water treatments. *Plant Soil Environment*, **63(1)**: 461–467.

Manisha P., Mohd C. I., Mohd A., Naveed A., and Muhammad M. A. (2013). Rapid synthesis of superabsorbent smart-swelling bacterial cellulose/acrylamide-based hydrogels for drug delivery. *International Journal of Polymer Science*, **1(2)**: 1-10.

Mann G., Kunze J., Loth F., and Fink H. P. (1998). Cellulose ethers with a blocklike distribution of the substituents by the structure-selective derivatization of cellulose. *Polymer,* **39(2)**: 3155–3165.

Marsano E., Bianchi E., and Viscardi A. (2004). Stimuli responsive gels based on interpenetrating network of hydroxypropylcellulose and poly(*N*-isopropylacrylamide). *Polymer,* **45(2)**:157-163.

Martens P. J., Bryant S. J., and Anseth K. S. (2003). Tailoring the degradation of hydrogels formed from multivinyl poly (ethylene glycol) and poly (vinyl alcohol) macromers for cartilage tissue engineering. *Biomacromolecules*, **4(1)**: 283–292.

Marzialetti T., Miller S. J., Jones C. W., and Agrawal P. K. (2011). Switch grass pretreatment and hydrolysis using low concentrations of formic acid. *Journal of Chemical Technology and Biotechnology,* **86(5)**: 706-713.

Mas'ud Z. A., Khotib M., Farid M., Nur A., and Amroni M. (2013). Superabsorbent derived from cassava waste pulp. *International Journal of Recycling of Organic Waste in Agriculture*, **2(1)**: 1-8.

Mazzocchia C., Modica G., Kaddouri A., and Nannicini R. (2004). Fatty acid methylesters synthesis from triglycerides over hetrogenous catalyst in the presence of microwave. *Comptes Rendus Chimie,* **7(1)**: 601-605.

Mikkelsen, R. L. (1994). Using hydrophilic polymers to control nutrient release. *Fertilizer Research*, **38(2)**: 53-59.

Mishra R. K., Datt M., Pal K., and Banthia A. K. (2008). Preparation and characterization of amidated pectin based. Hydrogels for drug delivery system. *Journal Material Science: Materials in Medicine*, **19(1)**: 2275–2280.

Moghimi E., Fathi P., Toashih V., and Moez Ardalan M. (2011). Impact of perlite on water use efficiency and some growth components in wheat (cultivar of zarrin). *Journal of Water and Irrigation Management,* **1(2)**: 31-42.

Mandal A., and Chakrabarty D. (2011). Isolation of nanocellulose from waste sugarcane bagasse (SCB) and its characterization. *Carbohydrate Polymer*, **86(2)**: 1291-1299.

Montesano F. F., Serio F., Mininni C., Signore A., Parente A., and Santamaria P. (2015). Tensiometer-based irrigation management of subirrigated soiless tomato: Effects of substrate matric potential control on crop performance. *Frontiers in Plants Science*, **6(1)**: 1150-1155.

Mosier N., Wyman C., and Dalem B. (2005) Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource Technology,* **96(3)**: 673–686.

Musa U. T., and Usman T. H. (2016). Leaf area determination for maize (*Zea mays L*), okra (*Abelmoschus esculentus L*) and cowpea (*Vigna unguiculata L*) crops using linear measurements. *Journal of Biology, Agriculture and Healthcare,* **6(4)**: 103-111.

Nagahama K., Ouchi T., and Ohya Y. (2008). Temperature-induced hydrogels through self-assembly of cholesterol-substituted star PEG-b-PLLA copolymers: an injectable scaffold for tissue engineering. *Advanced Function Materials*, **18(2)**: 1220–1231.

Narjary B., Aggarwal P., Singh A., Chakraborty D., and Singh R. (2012). Water availability in different soils in relation to hydrogel application, *Geoderma*, **187(1)**: 94--101.

Nayak S., Lee H., Chmielewski J., and Lyon L. A. (2004). Folate-mediated cell targeting and cytotoxicity using thermoresponsive microgels. *Journal of American Chemical Society,* **126(4)**: 10258–10259.

Nazir M. S., Wahjoedi B. A., Yussof A. W., and Abdullah M. A. (2013). Eco-friendly extraction and characterization of cellulose from oil palm empty fruit bunches. *BioResources,* **8(2)**: 2161-2172.

Nazarli H., Zardashti M. R., Darvishzadeh R., and Najafi S. (2010). The effect of water stress and polymer on water use efficiency, yield and several morphological traits of sunflower under greenhouse condition. *Notulae Scientia Biologicae,* **2(1)**: 53-58.

Niazuddin M., Talukder M. S. U., Shirazi S. M., and Hye M. A. (2002). Response of maize to irrigation and nitrogenous fertilizer. *Bangladesh Journal of Agricultural Science*, **29(2)**: 283-289.

Nie H., Liu M., Zhan F., and Guo M. (2004). Factors on the preparation of carboxymethycellulose hydrogel and its degradation behaviour in soil. *Carbohydrates Polymer*, **58(3)**: 185-189.

Nnadi F., and Brave C. (2011). Environmentally friendly superabsorbent polymers for water conservation in agricultural lands. *Journal of Soil Science and Environmental Management*, **2(7)**: 206-211.

Okamoto K., Wang H. Y., Ijyuin T., Fujiwara S., Tanaka K., and Kita H. (1999). Pervaporation of aromatic/non-aromatic hydrocarbon mixtures through crosslinked membranes of polyimide with pendant phosphate ester groups. *Journal of Membrane Science,* **157(4)**: 97–105.

Orikiriza L. J. B., Agaba H., Tweheyo M., Eilu G., Kabasa J. D., and Huttermann A. (2009). Amending soils with hydrogels increases the biomass of nine tree species under non-water stress conditions. *Clean-Soil, Air, Water,* **37(8)**: 615-619.

Oscroft D. G., Little K. M., and Vireo P. W. M. (2000).The Effect of a Soil-Amended Hydrogel on the Establishment of *Pinus elliottii* caribaea Rooted Cuttings on the Zululand Coastal Sands. *ICFR Bulletin Series,* **19(3)**: 1-8.

Palamae S., Dechatiwongse P., Choorit W., Chisti Y., and Prasertsan P. (2017). Cellulose and hemicellulose recovery from oil palm empty fruit bunch (EFB) fibers and production of sugars from the fibers. *Carbohydrate Polymer*, **155(6)**: 491–497.

Paluszek J., and Zembrowski, M. (2008). Improvement of water-air properties of eroded soils in a loss landscape after the application of agrohydrogel. *Land Reclamation,* **39(4)**: 85-93.

Park J., Gulati I., Sanjeev M., and Min-Gu L. (2014). Production of carboxymethylcellulose fibers from waste lignocellulosic sawdust using NaOH/$NaClO_2$ pretreatment. *Fibers and Polymers,* **15(4)**: 680-686.

Penjumras P., Rahman R. A., Talib R. A., and Abdan K. (2015). Response surface methodology for the optimization of preparation of biocomposites based on poly (lactic acid) and durian peel cellulose. *The Scientific World Journal*, **1(2)**: 1-13.

Phillips G. O., Plessis T. A. D., Saphwan Al-Assaf., and Williams, P. A. (2003). Biopolymers obtained by solid state irradiation in an unsaturated gaseous atmosphere, U. S. Patent 6,610,810, Phillips Hydrocolloid Research Limited, New York,

Poersch-Parcke H. G., and Kirchner R. (2003). Solutions. 2nd edition. Wolff Cellulosics GmbH: Walsrode.

Pushpamalar V., Langford S. J., Ahmad M., and Lim Y. Y. (2006). Optimization of reaction conditions for preparing carboxymethylcellulose from sago waste. *Carbohydrate Polymers*, **64(2)**: 312–318.

Putri D. A., and Kurniyati Z. (2016). Effect of Sodium Chloroacetate towards the Synthesis of CMC (Carboxymethylcellulose) from Durian (*Durio zibethinus*) peel Cellulose. *International Journal of Innovative Research in Advanced Engineering (IJIRAE)*, **3(3)**: 28-32.

Rachtanapun P., Eitssayeam S., and Pengpat K. (2010). Study of carboxymethylcellulose from papaya peels binder in ceramics. *Advanced Materials Research*, **93(94)**: 17-21.

Rachtanapun P., Kumthai S., Mulkarat N., Pintajam N., and Suriyatem R. (2015). Value added of mulberry paper waste by carboxymethylation for preparation a packaging film. *Materials Science and Engineering*, **87(2)**: 1-7.

Rachtanapun P., Luangkamin S., Tanprasert K., and Suriyatem R. (2012). Carboxymethylcellulose film from durian rind. *LWT - Food Science and Technology*, **48(3)**: 52-58.

Rajeev Jindal., Kaith B. S., and Mittal H. (2010). Superabsorbent hydrogels from poly(acrylamide-co-acrylonitrile) grafted Gum ghatti with salt, pH and temperature responsive properties. *Der Chemica Sinica*, **1(2)**: 92-103.

Raju K. M., Raju M. P., and Mohan Y. M. (2003). Synthesis of superabsorbent co-polymers as water manageable materials. *Polymer Internationals*, **52(3)**: 768-772.

Ramaswamy V., Vimalathithan R. M., and Ponnusamy V. (2010). Synthesis and characterizations of $BaSO_4$ nano particles using micro emulsions technique. *Journal of Advances in Applied Science Research*, **1(2)**: 197-204.

Rietjens M., and Steenbergen P. A. (2005). Crosslinking mechanism of boric acid with diols revisited. *European Journal of Inorganic Chemistry*, **6(3)**: 1162-1174.

Rizki A., Rahmi R., Julinawati J., and Hira H. (2020). Isolation and characterization of cellulose from rice husks waste and sawdust with chemical method. *Journal Natural*, **20(1)**: 6-9.

Rojas S. S., Yukimitu K., de Camargo A. S. S., Nunes L. A. O., and Hernandes A. C. (2006). Undoped and calcium doped borate glass system for thermoluminescent dosimeter. *Journal of Non-crystal Solids*, **352(19)**: 3608–3612.

Rosiak J. M., and Yoshii F. (1999). Hydrogels and their medical applications. *Nuclear Instrumental Methods Physical Research*, **151(13)**: 56–64.

Rosiak J. M., Ulanski P., and Rzeinicki A. (1995). Hydrogels for biomedical purposes. *Nuclear Instrumental Methods Physical Research*, **105(57)** 335–339.

Rowley J. A., Madlambayan G., and Mooney D. J. (1999). Alginate hydrogels as synthetic extracellular matrix materials. *Biomaterials*, **20(3)**: 45–53.

Rudzinski W. E., Dave A. M., Vaishnav U. H., Kumbar S. G., Kulkarni A. R., and Aminabhavi T. M. (2002). Hydrogels as controlled release devices in agriculture. *Designed Monomers and Polymers*, **5(4)**: 39-65.

Salmi T., Valtakari D., and Paatero E. (1994). Kinetic study of the carboxymethylation of cellulose. *Industrial Engineering Chemistry*, **33(2)**: 1454-1459.

Sannino A., Madaghiele M., Conversano F., Mele G., Maffezzoli A., Netti P. A., Ambrosio L., and Nicolais L. (2004). Cellulose derivativehyaluronic acid-based microporous hydrogels cross-linked through divinyl sulfone (DVS) to modulate equilibrium sorption capacity and network stability. *Biomacromolecules*, **5(1)**:92-96.

Sannino A., Demitri C., and Madaghiele M. (2009). Biodegradable cellulose-based hydrogels: Design and applications. *Materials Basel*, **2(2)**: 353-373.

Sara R., and Lo G. (2003). Characterization of the substitutuent in starch and cellulose derivatives, *Analytica Chemical Acta*, **497(76)**: 27-65.

Sevage A. B., Young A. E., and Maasberg A. T. (1954). *Ethers*. *In*: E. Ott, H. M. Spurlin, and M. W. Grafflin, eds. *Cellulose and Cellulose Derivatives Part II*. New York: Interscience Publishers, Inc., 882–954.

Sawsan D., Hussein A., Ragab E. A., Samir K., Mohamed S. A., and Mohamed E. (2018). Preparation and characterization of eco-friendly carboxymethylcellulose antimicrobial nanocomposite hydrogels. *Journal of Renewable Materials*, **6(5)**: 536-547.

Scurlock J. M. O., Dayton D. C, and Hames B. (2000). Bamboo: an overlooked biomass resource? *Biomass Bioenergy*, **19(1)**: 229–244.

Seiichi I., and Shosuke W.(2000). Neutral paper containing carboxymethylcellulose or carboxymethylcellulose and chitosan with increased yield of sizing agents and paper strengthening agents. J. P. Patent 98186280.

Sen M., Yolacan B., and Guven G. (2007). Radiation-induced degradation of galactomannan polysaccharides, Nuclear instruments methods physical research section. *Beam Interaction Materials Atoms*, **265(34)**: 429–433.

Sendur Kumaran, S., Natarajan S., Muthvel I. and Sathiayamurthy V.A. (2001). Efficacy of graded doses of polymers on processing quality of tomato cv. CO_3. *Journal of Madras Agriculture*, **88(6)**: 298-299.

Shafigh P., Mahmud B H., Jumaat Z., and Zargar M. (2014). Agricultural wastes as aggregate in concrete mixtures – A review. *Construction and Building Materials*, **53(4)**: 110–117.

Shang J., Shao Z., and Chen X. (2008). Chitosan-based electroactive hydrogel. *Polymer*, **49(25)**: 5520-5525.

Sharma P K, Asthana G S., and Asthana A. (2016). Hydrogel Advancement: A New Approach for Gastroretentive Drug Delivery. *International Journal of Pharmaceutical and Clinical Research*, **8(10)**: 1418-1422.

Shi Y., Li J., Shao J., Deng S., Wang R., Li N., Sun J., Zhang H., Zheng X., Zhou D., Huttermann A., and Chen S. (2010). Effects of stockosorband luquasorb polymers on salt and drought tolerance of populous popularis. *Science of Horticulture*, **124(34)**: 268-273.

Shooshtarian S., Abedi Koupai J., and Tehranifar A. (2011). Evaluation of application of superabsorbent polymers in green space of arid and semi-arid regions with emphasis on Iran. *Journal of Biodiversity and Ecological Sciences,* **1(2)**: 258-269.

Shukla S. K., Sagar, Naman, Deepika, Sundaram, Prateeksha, Ankur, Arun, Srishti, Vaishali, Rakesh, Rizwana, Bharadvaja A., and Dubey G. C. (2015). Extraction of cellulose micro sheets from rice husks: A scalable chemical approach. *DU Journal of Undergraduate Research and Innovation*, **(1)3**: 187- 194.

Silva D. A., De Pala R. C. M., Feitosa J. P. A., De Brito A. C. F., Maciel J. S and Paula H. C. B. (2004). Carboxymethylation of cashew tree exudate polysaccharide. *Carbohydrate Polymers*, **58(4)**: 163-171.

Singh R. K., and Singh A. K. (2013). Optimization of reaction conditions for preparing carboxymethyl cellulose from corn cobic agricultural waste. *Waste Biomass Valorization*, **4(2)**: 129-137.

Sorber J., Steiner G., Schulz V., Guenther M., Gerlach G., and Salzer R. (2008). Hydrogel-based piezoresistive pH sensors: Investigations using FTIR attenuated total reflection spectroscopic imaging. *Analytical Chemistry*, **80(8)**: 2957-2962.

Staudinger H. (1932). Die hochmolekularen organischen Verbindungen - Kautschuk und Cellulose. Springer Verlag.

Stigsson V., Kloow G., and Germgard U. (2001). An historical overview of carboxymethyl cellulose (CMC) production on an industrial scale. *Paper Asia,* **10(17)**: 16-21.

Suflet D. M., Chitanu G. C., and Popa V. I. (2006). Phosphorylation of polysaccharides: New results on synthesis and characterization of phosphorylated cellulose. *Reactive and Functional Polymers*, **66(22)**: 1240-1249.

Sun R., Fang J. M., Mott L., and Bolton J. (1999). Extraction and characterization of hemicelluloses and cellulose from oil palm trunk and empty fruit bunch fibres. *Journal of Wood Chemistry and Technology,* **19(2)**: 167-185.

Sunardi J., Tanabe F., Ishiguri J., Ohshima K., K Iizuka., and Yokota S. (2016). Changes in lignocellulolytic enzyme activity during the degradation of *Picea jezoensis* wood by the white-rot fungus *Porodaedalea pini*. *International Biodeterioration and Biodegradation*, **110(34)**: 108-112.

Sutiya B., Istikowati W. T., Rahmadi A., and Sunardi J. (2012). Kandungu kimia dan sifat alang-alang (*Imperata cylndrica*) sebagai gambaran bahan baku pulp dan kertas. *Bioscientiae,* **9(1)**: 8-19.

Takigami M., Nagasawa N., Hiroki A., Tagichi M., and Takigami S. (2012). Preparation of stable CMC-Acid Gel. *Gums Stabilisers Food Ind*, **16(2)**:175–182.

Tayel M. Y., and EL-Hady O. A. (1981). Super gel as a soil conditioner and its effects on some soil-water retentions. *Acta Horticulturae (ISHS)*, **119(22)**: 247-256.

Taylor K. C., and Halfacre R. G. (1986). The effect of hydrophilic polymer on media water retention and nutrient availability to *Ligustrum lucidum*. *Horticulture Science*, **21(5)**: 1159-1161.

Teodorescu M., Lungu A., and Stanescu P. O. (2009). Preparation and properties of novel slow-release NPK agrochemical formulations based on poly (acrylic acid) hydrogels and liquid fertilizers. *Industrial and Engineering Chemistry Research*, **48(10)**: 6527-6534.

Thakur G., Rodrigues F. C., and Singh K. (2018). Crosslinking biopolymers for advanced drug delivery and tissue engineering applications. *Advances in Experimental Medicine and Biology*, **1078(1)**: 213-231.

Togrul H., and Arslan N. (2003). Production of carboxymethylcellulose from sugar beet pulp cellulose and rheological behavior of carboxymethylcellulose. *Carbohydrate Polymers*, **54(9)**: 73-82.

Trksak R. M., and Ford P. J. (2008). Sago-based gelling starches, U. S. Patent 7,422,638, National Starch and Chemical Investment Holding Corporation, New Castle, DE.

Ugheoke I. B., and Mamat O. (2012). A critical assessment and new research directions of rice husks silica processing methods and properties. *Maejo International Journal of Science Technology*, **6(3)**:430–448.

Vanderck K., Cano-Odena A., Koeckelberghs G., Dedroog T., and Vankelecom I. (2010). A simplified diamine crosslinking method for PI nanofiltration membranes. *Journal of Membrane Science*, **353(23)**: 135–143.

Varaprasad K., Mohan Y. M., Ravindra S., Reddy N. N., Vimala K., Monika K., Sreedhar B., and Raju K. M. (2010). Hydrogel-silver nanoparticle composites: A new generation of antimicrobials. *Journal Applied Polymer Science*, **115(2)**: 1199-1207.

Varshney V. K., Gupta P. K., Naithani S., Khullar R., Bhatt A., and Soni P. L. (2006). Carboxymethylation of α-cellulose isolated from *Lantana camara* with respect to degree of substitution and rheological behavior. *Carbohydrate Polymers*, **63(9)**: 40–44.

Vempati R., Musthyala S., Molleh Y., and Cocke D. (1995). Surface analyses of pyrolysed rice husks using scanning force microscopy. *Water Research*, **11(7)**: 1722-1725.

Verraest D. L., Peters J. A., Kuzee H. C., Batelaan J. G. and Bekkum V. H.(1995). Carboxymethylation of inulin. *Carbohydrate Research*, **271(98)**: 101–112.

Viera R. G., Filho G. R., Assuncao R. M. N., Meireles C. S., Vieira J. G., and Oliveira G. S. (2007). Synthesis and characterization methylcellulose from sugarcane bagasse cellulose. *Carbohydrate Polymers,* **67(23)**: 182-189.

Viero P. W. M., Chiswell K. E. A., and Theron J. M. (2002). The effect of a soil-amended hydrogel on the establishment of a Eucalyptus grandis clone on a sandy clay loam soil in Zululand during winter. *The Southern African Forestry Journal,* **193(1)**: 65-75.

Vladimíra T., Krysztof P., Iva S., Alena Ž.,Vlasta S., and Anna E. (2008). Microwave-assisted synthesis of carboxymethylcellulose–based polymeric surfactants, *Polymer Bulletin,* **60(9)**: 15–25.

Volkamar K. M. and Chang C. (1995). Influence of hydrophilic gel polymers on water relations, growth and yield of barley and canola. *Canadian Journal of Plant Science*, **75(9)**: 605-611.

Wallace A., and Wallace G. A. (1986). Effect of polymeric soil conditioners on emergence of tomato seedlings. *Soil Science,* **141(5)**: 321-323.

Wan Rosli W. D., Rohaizu R., and Ghazali A. (2011). Synthesis and characterization of cellulose phosphate from oil palm empty fruit bunches. *Carbohydrate Polymers,* **84(6)**: 262-267.

Wan Rosli, W. D., Leh, C. P., Zainuddin, Z., and Tanaka R. (2004). The effects of prehydrolysis on the production of dissolving pulp from empty fruit bunches. *Journal of Tropical Forest Science,* **16(3)**: 343-349.

Wang C., and Chen C. (2005). Physical properties of the crosslinked cellulose catalyzed with nanotitanium dioxide under UV irradiation and electronic field. *Applied Catalysis A: General,* **293(12)**: 171-179.

Wang L., Zhang J. P., and Wang A. Q. (2008). Removal of methylene blue from aqueous solution using chitosan-g-poly (acrylic acid)/ montmorillonite superadsorbent nanocomposite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **322(12)**: 47-53.

Ward C., Torquebiau R., and Xie H. (2016). Improved Agricultural Water Management for Africa’s Drylands. World Bank Publications.

Wei S., Kumar V., and Banker G. S. (1996). Phosphoric acid mediated depolymerization and decrystallization of cellulose: preparation of low crystallinity cellulose- A new pharmaceutical excipient. *International Journal of Pharmaceutics*, **142(19)**: 175-181.

Wingerson A., and Richard C. (2002). Method of treating lignocellulosic biomass to produce cellulose, http://www.patentstorm.us/patents/6419788-description.html, US. Patent Issued on July 16.

Wong J. E., Díez-Pascual A. M., and Richtering W. (2009). Layer-by-layer assembly of polyelectrolyte multilayers on thermoresponsive p(NIPAM-co-MAA) microgel: Effect of ionic strength and molecular weight. *Macromolecules*, **42(12)**:1229-1238.

Wu D., Wang T., Lu B.; Xu X., Cheng S., and Jiang X. (2008). Fabrication of supramolecular hydrogels for drug delivery and stem cell encapsulation. *Langmuir*, **24(18)**: 10306-10312.

Xiao H-X, Lin Q-L, Liu G-Q, and Yu F. X. (2012). A comparative study of the characteristics of cross-linked, oxidized and dual-modified rice starches. *Molecules*, **17(9)**:10946–10957.

Xie J., and Hsieh Y. L. (2003). Thermosensitive poly(n-isopropylacrylamide) hydrogels bonded on cellulose supports. *Journal of Applied Polymer Science*, **89(7)**: 999-1006.

Xiudong Z., Linxin Z., Runcang S., Mingfei L., and Xinwen P. (2016). Microwave-assisted extraction of polysaccharides from bamboo (*Phyllostachys acuta*) leaves and their antioxidant activity. *Bioresources*, **11(2)**: 5100–5112.

Xu Y., Salmi J., Kloser E., Perrin F., Grosse S., and Denault J. (2013). Feasibility of nanocrystalline cellulose production by endoglucanase treatment of natural bast fibers. *Industrial Crops Production*, **51(12)**: 381-384.

Yan C., Altunbas A., Yucel T., Nagarkar R.P., Schneider J.P., and Pochan D. J. (2010). Injectable solid hydrogel: Mechanism of shear-thinning and immediate recovery of injectable β-hairpin peptide hydrogels. *Soft Matter*, **6(7)**: 5143–5156.

Yang X. H., and Zhu W. L. (2007). Viscosity properties of sodium carboxymethylcellulose solutions. *Cellulose*, **14(12)**: 409-417.

Yang X., Chen X., Ge Q., Li B., Tong Y., Zhang A., Li Z., Kuang T. and Lu C. (2006). Tolerance of photosynthesis to photo-inhibition, high temperature and drought stress in flag leaves of wheat: a comparison between a hybridization line and its parents grown under field conditions. *Plant Science*, **171(22)**: 389-397.

Yao X., ZhuY., TianY., Feng W., and Cao W. (2010). Exploring hyperspectral bands and estimation indices for leaf nitrogen accumulation in wheat. *International Journal of Applied Earth Observation and Geoinformation*, **12(9)**: 89-100.

Yazdani F., Allahdadi I., and Akbari G. A. (2007). Impact of superabsorbent polymer on yield and growth analysis of soybean (*Glycine max L.*) under drought stress condition. *Pakistan Journal of Biological Science*, **10(1)**: 4190-4196.

Yazdani F., Allhdadi I., Akbari Gh. A., and Behbahani M. R. (2007). Effect of different rates of superabsorbent polymer (Tarawat A200) on soybean yield and yield components (*Glycine max* L.). *Agronomy Journal of Pajouhesh and Sazandegi,* **75(3):**167-174.

Yeasmin M. S., and Mondal M. I. H. (2015). Synthesis of highly substituted carboxymethyl cellulose depending on cellulose particle size. *International Journal of Biological Macromolecules,* **80(5)**: 725-731.

Yoshimura T., Matsuo K., and Fujioka R. (2006). Novel biodegradable superabsorbent hydrogels derived from cotton cellulose and succinic anhydride: Synthesis and characterization. *Journal of Applied Polymer Science*, **99(12)**: 3251-3256.

Zhang G., Zhang L., Deng H., and Ping Sun. (2011). Preparation and characterization of sodium carboxymethylcellulose from cotton stalk using microwave heating. *Journal of Chemical Technology Biotechnology,* **86(22)**: 584–589.

Zhan F., Liu M., and Wu L. M. (2004). Preparation of superabsorbent polymer with slow-release phosphate fertilizer. *Journal of Applied Polymer Science,* **92(5)**: 3417-3421.

Zhao D., Liao G., Gao G., and Liu F. (2006). Influences of intramolecular cyclization on structure and cross-linking reaction processes of PVA hydrogels. *Macromolecules*, **39(8)**: 1160-1164.

Zhao H., Cheng F., Li G. F and Zhang J. W. (2003). Optimization of a process for carboxymethylcellulose (CMC) preparation in mixed solvents. *International Journal of Polymeric Materials*, **52(7)**: 749-759.

Zhao X., Li Q., and Mi Y. (2013). Optimization of reaction conditions for preparing carboxymethylcelluloseguaze. *Advanced Materials Research,* **709(43)**: 40-44.

Zhou J., and Zhang L. (2000). Solubility of cellulose in NaOH/urea aqueous solution. *Polymer Journal,* **32(12)**: 866–870.

Zohuriaan-Mehr, M. J., and Kabiri, K. (2008). Superabsorbent polymer materials: a review. *Iranian Polymer Journal,* **17(6)**: 451-456.

APPENDICES

Appendix 1: Optimization conditions for synthesis of carboxymethylcellulose

1A: Optimum concentration of NaOH required for maximum yield

To determine the optimum concentration of sodium hydroxide (NaOH) for maximum percentage yield of carboxymethylcellulose, the synthesis was conducted under varied concentration of NaOH that is 10 - 40 % at intervals of 5. In a typical synthesis, 5.00 g of the extracted cellulose was added to 250 mL Erlenmeyer flask containing 100 mL of distilled water followed by 10 mL of 10 % of sodium hydroxide solution added drop wise. The alkalization process was carried out by shaking the content for 60 minutes at 25 ^{o}C on a fitted shaker. Then 5.00 g of MCA was added to the mixture (etherification) and the mixture was heated in a microwave oven at power output of 2 (140 watts) for 2 minutes. It was allowed to cool to room temperature and then filtered. The residue obtained was soaked in 100 mL of methanol for 24 hours, after which it was neutralized using 100 mL glacial acetic acid. The mixture was filtered again and the residue was dried in an oven at 60 ^{o}C to maintain a constant weight. Each synthesis was carried out in triplicate and average product was calculated.

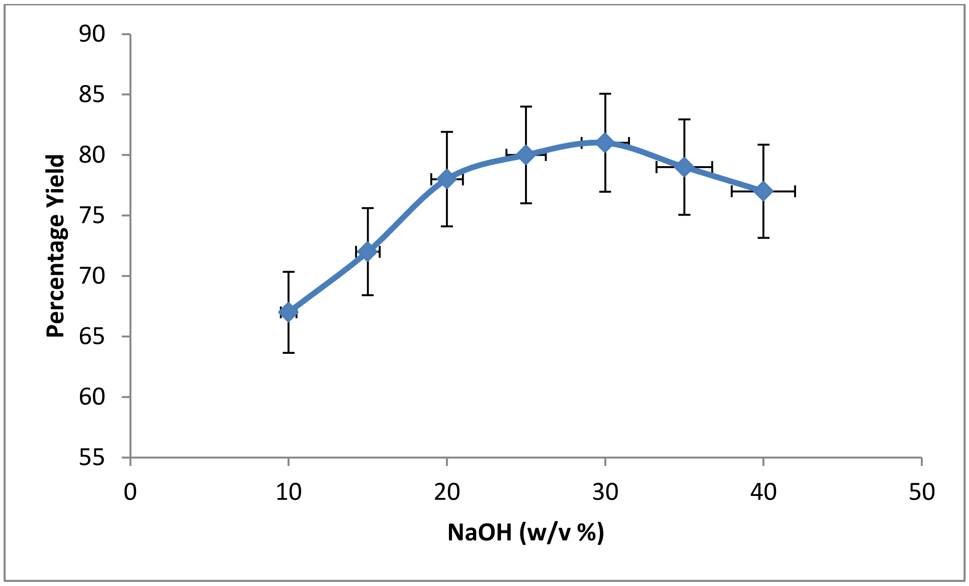


Figure 1A: Percent yield of sodium carboxymethylcellulose synthesized at various alkali concentration (at power output 4 equivalent to 280 Watts, 5.00 g of MCA, 2 minutes)

The optimum of NaOH concentration required for maximum percentage yield of carboxymethylcellulose was evaluated by varying its concentration while keeping the other reagents constant and determining corresponding yield of product obtained. Figure 1A shows how the percentage yield of CMC changed as concentration of NaOH was varied. As shown, the percentage yield (%) of CMC increased with NaOH concentration reaching a maximum yield of 81 % at an alkali concentration of 30 % (optimum). At the concentration of 10 - 20 %, the yield of Na-CMC was sharply increasing, however, after 25 % only a slight increase was observed.

1B Optimization of concentration of NaOH for best degree of substitution

The optimum concentration of sodium hydroxide (NaOH) required for optimum degree of substitution in CMC was established by determining the degree of substitution in all the carboxymethylcellulose products obtained in the above appendix 1A, by potentiometric titration as described in section 3.6.1. The results are summarized in in figure 1B.

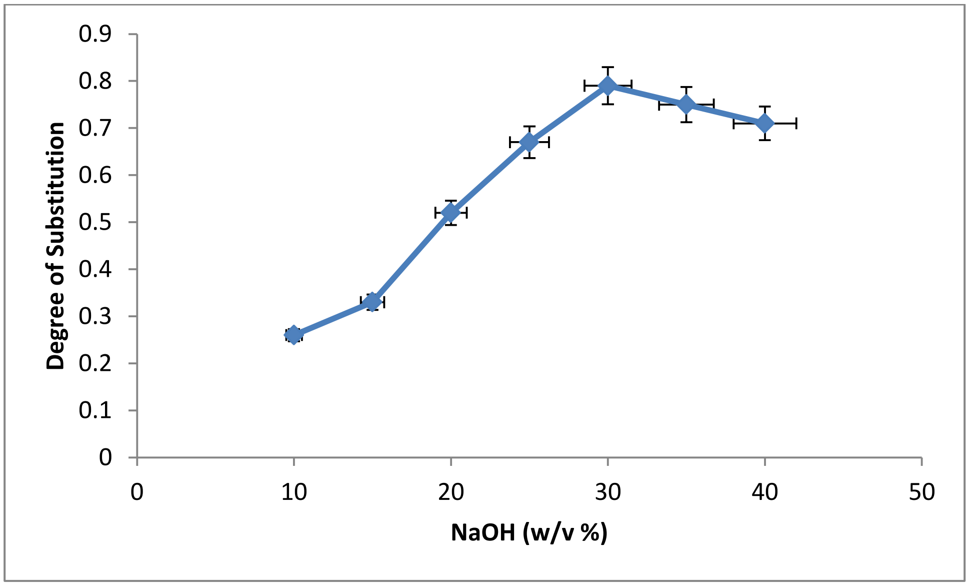


Figure 1B: Variation of degree of substitution with NaOH concentration (at power output 4 equivalent to 280 Watts, 5.00 g of MCA, 2 minutes)

It was observed that the DS in CMC increased with NaOH concentration. A maximum DS was attained at an alkali concentration of 30 % (w/v). This was taken as the optimum NaOH concentration for synthesis of CMC.

1C Optimization of amount of monochloroacetic acid required for optimum degree of substitution

To determine the optimum of MCA amount required to give optimum degree of substitution. In CMC, the CMC was prepared under varied amounts of MCA that is. 2.00, 3.00, 4.00, 5.00, 6.00, and 7.00 g, while all other conditions were maintained constant and the degree of substitution in each product were determined. In a typical synthesis, 5.00 g of the extracted cellulose was added to 250 mL Erlenmeyer flask, containing 100 mL of distilled water followed by 10 mL of 30 % sodium hydroxide (NaOH) added drop wise. The mixture was shaken on a fitted shaker for 1 hour at 25 ^{o}C to undergo alkalization. After 1 hour, 2.00 g of MCA was added to the mixture which was then heated in a microwave oven at power output of 2 (140 watts) for 2 minutes. The mixture was allowed to cool to room temperature and filtered. The obtained residue was soaked in 100 mL of methanol for 24 hours, and then neutralized using glacial acetic acid. The degrees of substitutions were determined using potentiometric titration as described in section 3.6.1.andthe results are summarized in figure 1C.

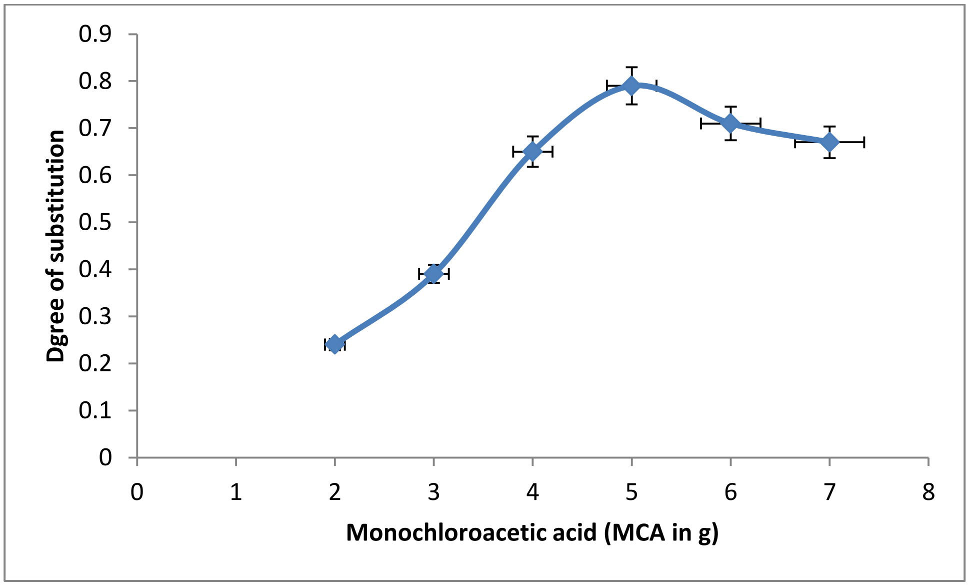


Figure 1C: Variation of degree of substitution with amount of monochloroacetic acid (at power output 4 equivalent to 280 Watts, 5.00 g of MCA, 2 minutes)

Figure 1C shows how the degree of substitution changed as amount of MCA was varied. As shown in Figure 1C, the DS of carboxymethylcellulose increased with an increase in MCA and a maximum DS of 0.79 at 5.00 g was obtained. Thus, 5.00 g of MCA was chosen as optimum amount for use in synthesis of CMC.

1D Optimization of microwave oven power out-put on the degree of substitution

This was achieved by synthesizing CMC under varying the power output from 2, 4, 6, 8 and 10 (which corresponds to 140, 280, 420, 560 and 700 watts), and determining degree of substitution attained. Typically, 5.00 g of extracted cellulose was taken in each product, 250 mL Erlenmeyer flask containing 100 mL of distilled water. Then, 10 mL of 30 % of sodium hydroxide (NaOH) concentration was added drop wise. The alkalization process was carried out by shaking the content for 60 minutes at 25 ^{o}C on a fitted shaker. At the end of the set time 5.00 g of MCA was added and the mixture heated in a microwave at power of 2, for 2 minutes. The mixture was allowed to cool to room temperature and then filtered. The obtained residue was soaked in 100 mL of methanol for 24 hours, and then neutralized using glacial acetic acid. The procedure was repeated at microwave power output of 4, 6, 8, and 10 respectively for 2 minutes. The degrees of substitution were determined using potentiometric titration as described in section 3.5.2. The results are displayed in figure 1D.

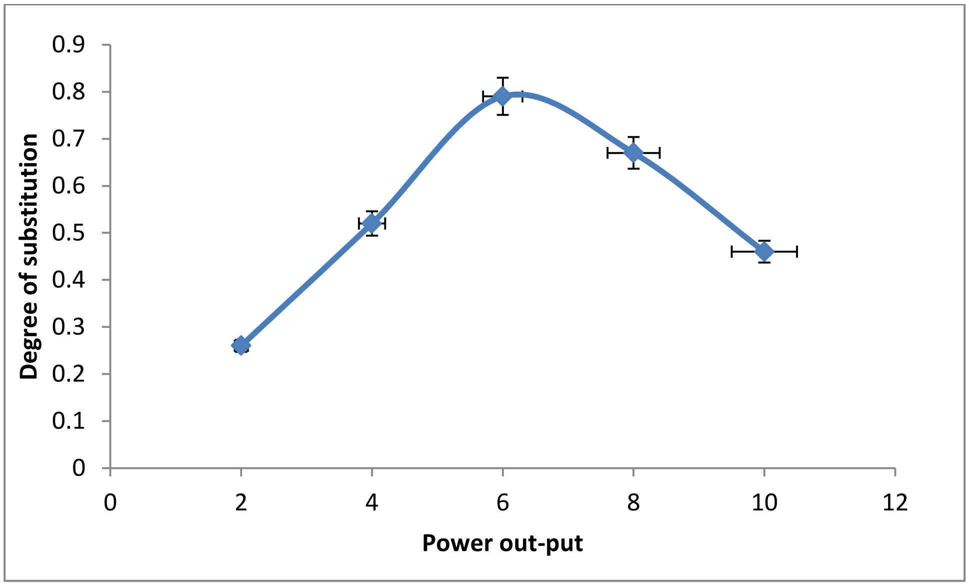


Figure 1D: The variation of degree of substitution DS with microwave oven power out-put (at 30% concentration of NaOH, 5.00 g of MCA, 2 minutes)

A maximum degree of substitution of 0.79 was obtained at the power of 6. This was taken as the optimum operating power out-put for the microwave oven.

1E Optimization of reaction time

To determine the optimum time required to give optimum degree of substitution, the CMC was prepared under varied time that is 1, 2, 3, 4, and 5 minutes while other condition were kept constant and degree of substitution of each product was determined. In a typical synthesis, 5.00 g of the extracted cellulose was added to 250 mL Erlenmeyer flask containing 100 mL of distilled water. Then 10 mL of 30 % concentration of sodium hydroxide solution was added drop-wise. The alkalization process was carried out by shaking the content for 60 minutes at 25 ^{o}C on a fitted shaker. Then 5.00 g of MCA was added to the mixture (etherification) and heated in a microwave oven at power output of 2 (140 watts) for 1, 2, 3, 4, and 5 minutes, the mixture was filtered. The obtained residue was soaked in 100 mL of methanol for 24 hours, and was neutralized using glacial acetic acid. The degrees of substitutions were determined using potentiometric titration as described in section 3.6.1. and results are summarized in figure 1E.

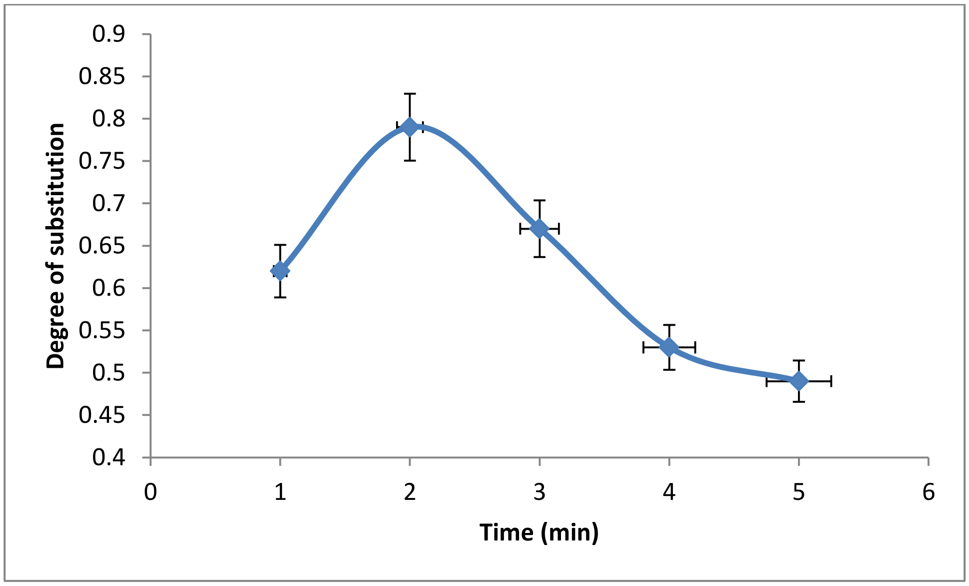


Figure 1E: The variation of degree of substitution with time (DS) (at 30% concentration of NaOH, power out-put of 280 Watts, 5.00 g of MCA)

The variation of the degree of substitution, with reaction period, revealed that the degree of substitution values increased rapidly in the first hour and then decreased. The DS was decreased after 2 minutes, probably due to degradation of cellulose structure when the time is prolonged (Heinze and Pfeiffer, 1999).

Appendix 2: Optimization of reaction conditions for synthesis of SAH by crosslinking CMC with ethane-1,2-diol

Reaction time, microwave oven power out-put, and amount of cross-linker required were optimized by determining the percentage swelling of SAH prepared under varied condition as described below.

2A Optimum reaction time

To determine the optimum reaction for completion of the reaction, the ethane-1,2-diol SAH was prepared under varied reaction time that is 1 – 7 minutes while other condition were kept constant and percentage swelling of each product were determined. The reaction time that gave the product with highest percentage swelling was taken as the optimum reaction time. In typical synthesis, 2.00 g of carboxymethylcellulose (DS = 0.79) was added to 30 mL of distilled water into 200 mL beaker. The mixture was dissolved by stirring at room temperature using a magnetic stirrer for 24 hours. The resulting solution was treated with 10 mL ethane-1,2-diol and heated in a microwave at a power output of 280 watts for 1 minute. The reaction mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled water, then, was dried in an oven at 40 ^{o}C to a constant weight. The results are summarized in figure 2A.

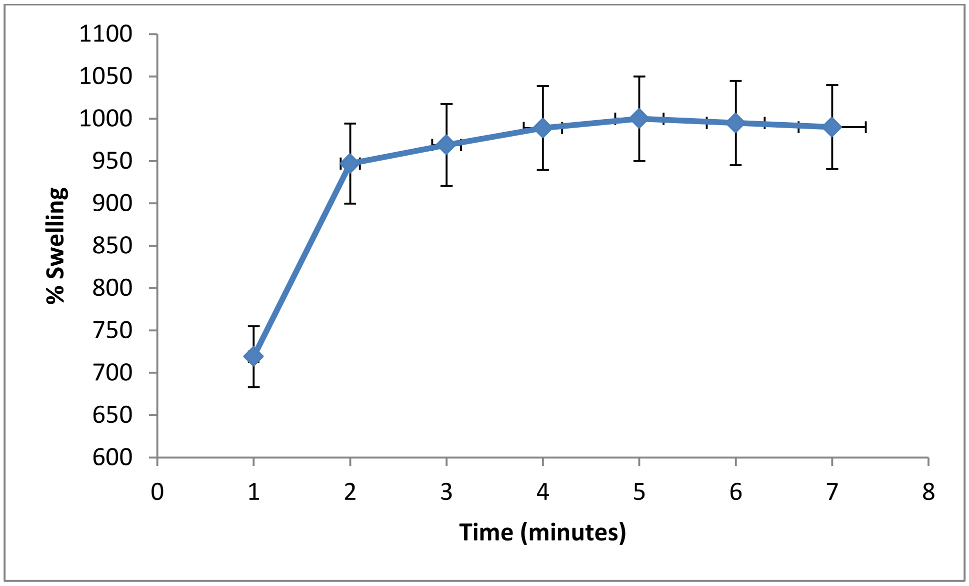


Figure 2A: Variation of percentage of swelling with reaction time (at power output 4 equivalent to 280 Watts, 10 mL of 1, 2-ethanediol, 2.00 g of CMC).

It can be seen from Figure 2A, that the percentage swelling increased with time up to a maximum swelling (1000 %) after 5 minutes. Thus, on heating at one minute intervals for 5 minutes in the microwave and monitoring the swelling rate of the SAH, it was observed that the percentage swelling increased rapidly from 719 % in the first minute to 947 % in the second minute after which the increment was gradual to 1000 % in the fifth minute. The optimum percentage swelling was taken at 5 minutes.

2B Optimization of microwave power out-put

To determine the optimum microwave power out-put required for synthesis of the ethane-1,2-diol SAH, percentage swelling of the product prepared under varied microwave power out-put that is 2 – 10 while other condition were kept constant and percentage swelling of each product were determined. The microwave power out-put that gave the product with highest percentage swelling was taken as the optimum reaction time. In typical synthesis, 2.00 g of carboxymethylcellulose (DS = 0.79) was added to 30 mL of distilled water into 200 mL beaker. The mixture was dissolved by stirring at room temperature using a magnetic stirrer for 24 hours. The resulting solution was treated with 10 mL ethane-1,2-diol and heated in a microwave at a power output of 140 watts for 5 minute. The reaction mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled water, then, was dried in an oven at 40 ^{o}C to a constant weight. The experiments were carried out in triplicates. The results are summarized in figure 2B.

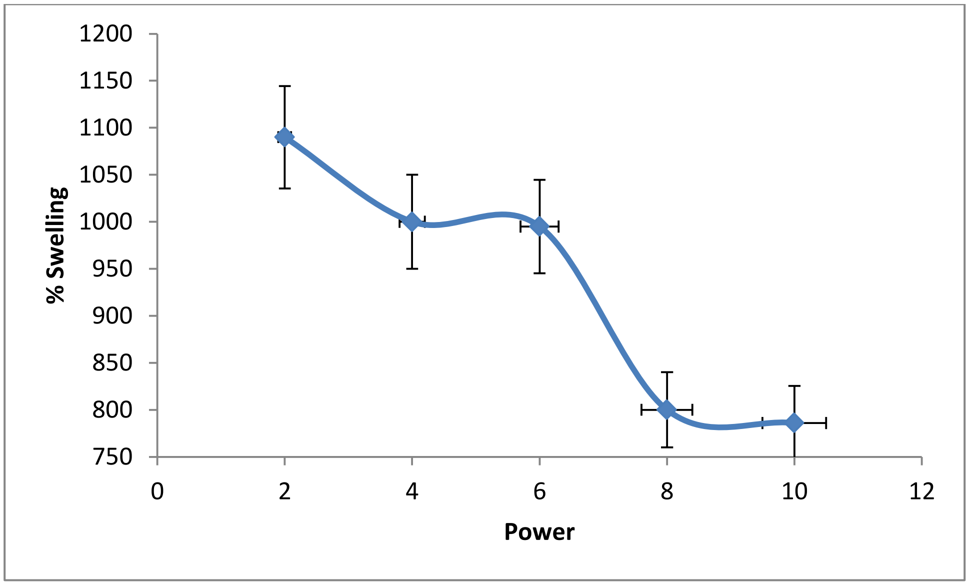


Figure 2B: Variation of percentage of swelling with power out-put of microwave (at 5 minutes, 10mL of ethane-1,2-diol, 2.00 g of CMC)

It was observed that initially, the percentage swelling was high at the power of 2, a further increase in the power out-put resulted in the decrease in percentage swelling from 1090 to 786 % which is statistically significant. This might be as a result of inadequate entropy and internal energy, leading to low rate of diffusion of water molecules into the hydrogel. Perhaps the hydrogels decomposed by the high power.

2C Optimization of the amount of cross-linker required for the reaction

To determine the optimum amount of cross-linker for completion of the reaction, the ethane-1,2-diol SAH was prepared under varied amount of cross-linker that is 3, 4, 5, 10, 15, 20, and 25 mL of ethane-1,2-diol while other condition were kept constant and percentage swelling of each product were determined. The amount of cross-linker that gave the product with highest percentage swelling was taken as the optimum. In typical synthesis, 2.00 g of carboxymethylcellulose (DS = 0.79) was added to 30 mL of distilled water into 200 mL beaker. The mixture was dissolved by stirring at room temperature using a magnetic stirrer for 24 hours. The resulting solution was treated with 5 mL ethane-1,2-diol and heated in a microwave at a power output of 280 watts for 5 minute. The reaction mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled water, then, was dried in an oven at 40 ^{o}C to a constant weight. The experiments were carried out in triplicates. The results are summarized in figure 2C.

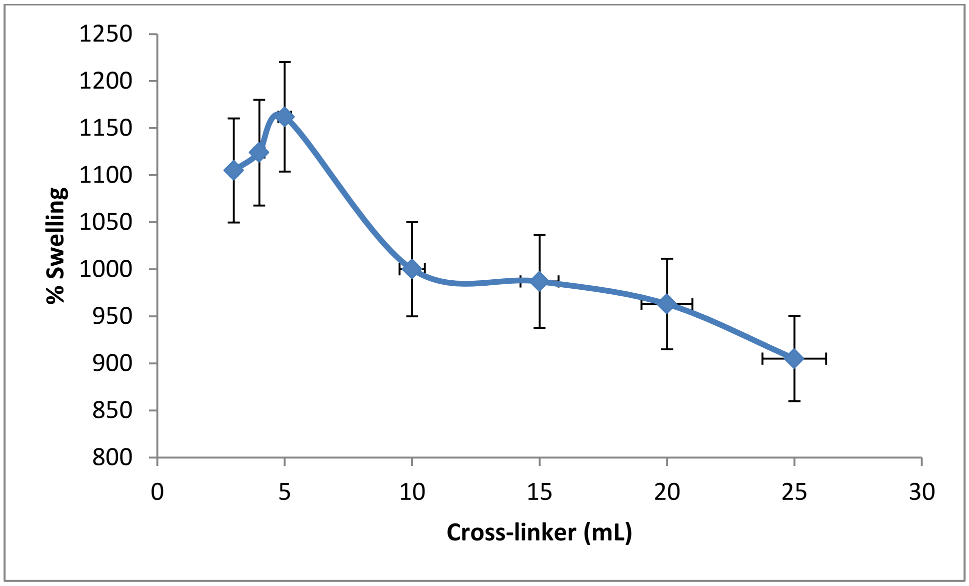


Figure 2C: Variation of percentage of swelling with amount of cross-linker (at Power output 4 equivalent to 280 Watts, 5 minutes, 2.00 g of CMC)

It is clear from Figure 2C, that the initial percentage swelling was high when 5 mL of the cross-linker was used (1162 %), further increase in the amount of cross-linker resulted to decrease in percentage swelling from 1162 % to 905 % which is statistically significant. Thus, 5 mL of ethane-1,2-diol is taken as the optimum.

Appendix 3: Optimization of reaction conditions for synthesis of SAH by crosslinking CMC with ethane-1,2-diamine

Reaction time, microwave oven power out-put, and amount of cross-linker required were optimized by determining the percentage swelling of SAH prepared under varied condition as described below.

3A Optimization of reaction time

To determine the optimum reaction for completion of the reaction, the ethane-1,2-diamine SAH was prepared under varied reaction time that is 1 – 7 minutes while other condition were kept constant and percentage swelling of each product were determined. The reaction time that gave the product with highest percentage swelling was taken as the optimum reaction time. In typical synthesis, 2.00 g of carboxymethylcellulose (DS = 0.79) was added to 30 mL of distilled water into 200 mL beaker. The mixture was dissolved by stirring at room temperature using a magnetic stirrer for 24 hours. The resulting solution was treated with 10 mL ethane-1,2-diamine and heated in a microwave at a power output of 280 watts for 5 minutes. The reaction mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled water, then, was dried in an oven at 40 ^{o}C to a constant weight. The results are summarized in figure 3A.

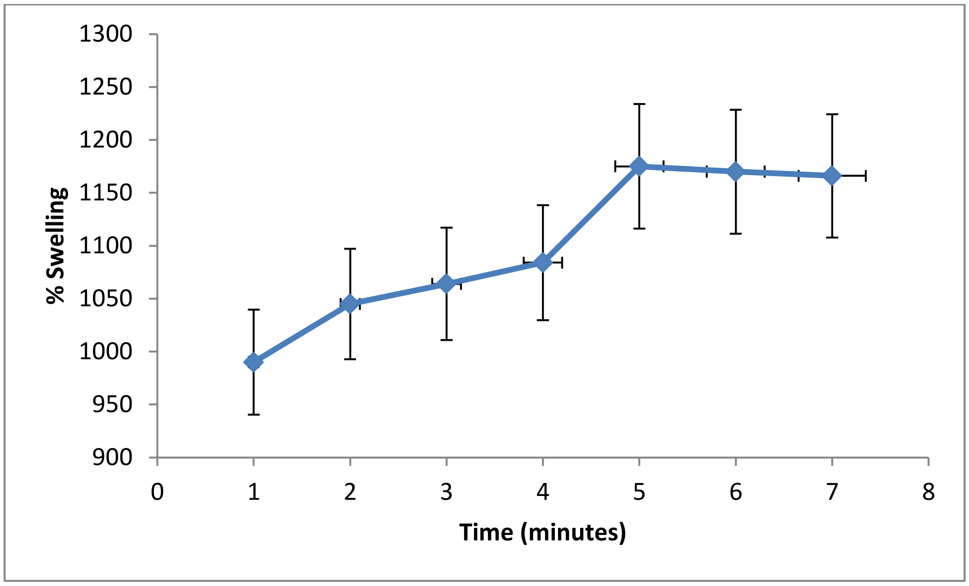


Figure 3A: Variation of percentage swelling with reaction time (at Power output 4 equivalent to 280 Watts, 10 mL of ethane-1,2-diamine, 5 minutes, 2.00 g of CMC)

The percentage swelling was about 990 % at 1 minute; it further increases to 1045, 1064, 1084 and 1175 % at 2, 3, 4 and 5 minutes, respectively. The percentage swelling increases with time, this can be as a result of increases in H^+ and OH^- ions which binds to the hydrophilic groups in the superabsorbent hydrogel. ($CONH_2$ being hydrophilic can easily absorb adequate of water). Due to the presence of $CONH_2$ in the polymer network, it creates a distance between the matrixes; which allows the hydrogel to absorb a lot of water, and there are free available sites where water molecules can be attached to the superabsorbent hydrogel.

3B Optimization of microwave power out-put for synthesis

To determine the optimum microwave power out-put required for synthesis of the ethane-1,2-diamine SAH, percentage swelling of the product prepared under varied microwave power out-put that is 2 – 10 while other conditions were kept constant and percentages swelling of each product were determined. The microwave power out-put that gave the product with highest percentage swelling was taken as the optimum reaction time. In typical synthesis, 2.00 g of carboxymethylcellulose (DS = 0.79) was added to 30 mL of distilled water into 200 mL beaker. The mixture was dissolved by stirring at room temperature using a magnetic stirrer for 24 hours. The resulting solution was treated with 10 mL ethane-1,2-diamine and heated in a microwave at a power output of 140 watts for 5 minute. The reaction mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled water, then, was dried in an oven at 40 ^oC to a constant weight. The experiments were carried out in triplicates. The results are summarized in figure 3B.

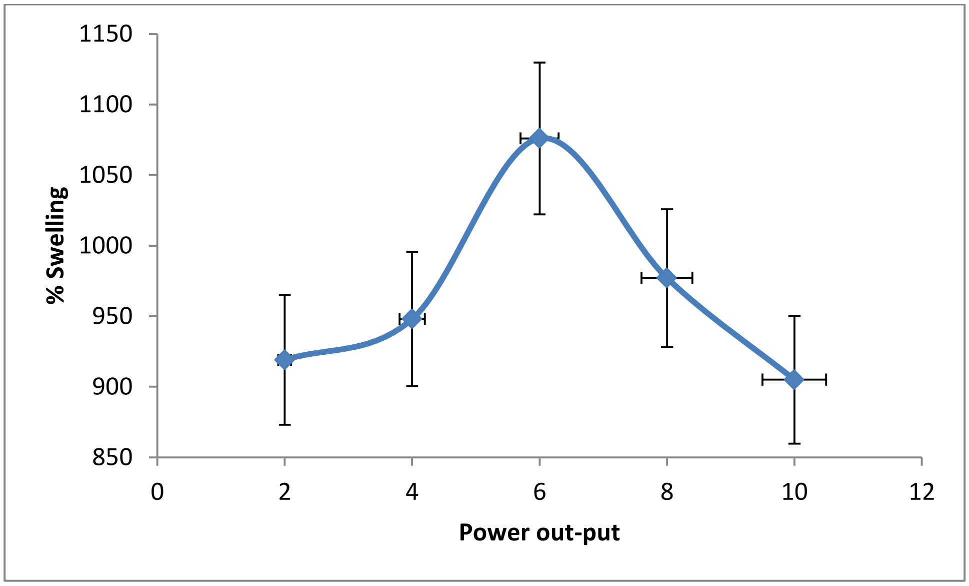


Figure 3B: Variation of percentage swelling with power out-put (at 5 minutes, 10mL of ethane-1,2-diamine, 2.00 g of CMC)

It can be seen from the Figure that the highest percentage swelling of 1076 occurred at a power output of 6 (420 watts) and this was recorded as optimum reaction power output.

The percentage swelling increased from 919 – 1076 %, when the power out-put was increase from 2 - 6, this is equivalent to 140 - 420 watts respectively. An increase in the power output from 6 – 10, which corresponds to 420 – 700 watts, resulted in a decrease in percentage swelling from 1076 - 905.

3C Optimization of amount of cross-linker (mL) used in synthesis

To determine the optimum amount of cross-linker for completion of the reaction, the ethane-1,2-diamine SAH was prepared under varied amount of cross-linker that is 2, 4, 6, 8, 10, 12, and 14 mL of ethane-1,2-diamine while other condition were kept constant and percentage swelling of each product were determined. The amount of cross-linker that gave the product with highest percentage swelling was taken as the optimum. In typical synthesis, 2.00 g of carboxymethylcellulose (DS = 0.79) was added to 30 mL of distilled water into 200 mL beaker. The mixture was dissolved by stirring at room temperature using a magnetic stirrer for 24 hours. The resulting solution was treated with 2 mL ethane-1,2-diamine and heated in a microwave at a power output of 280 watts for 5 minute. The reaction mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled water, then, was dried in an oven at 40 ^{o}C to a constant weight. The experiments were carried out in triplicates. The results are summarized in figure 3C.

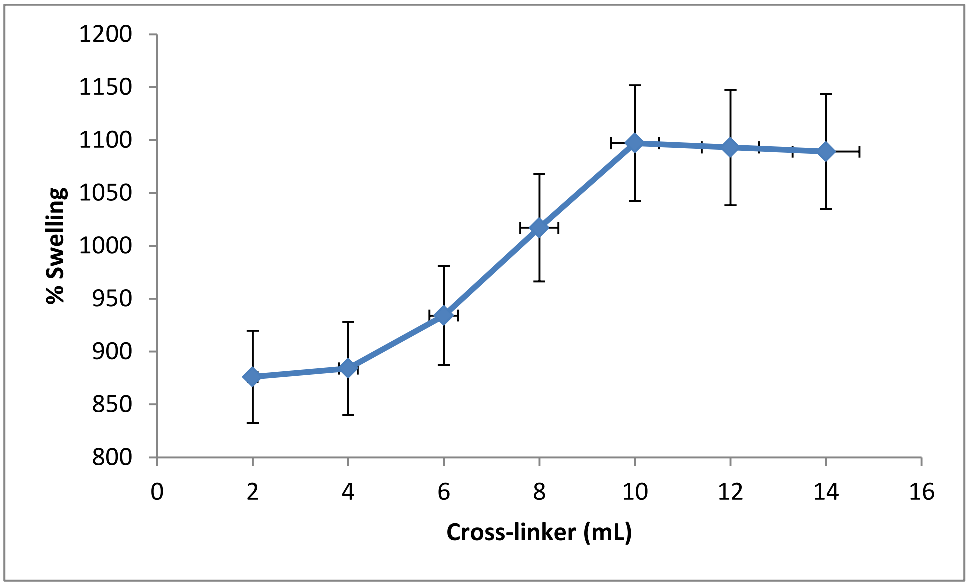


Figure 3C: Variation of percentage swelling with amount of cross-linker (at 5 minutes, power out-put of 4 equivalent to 280 Watts, 2.00 g of CMC)

The percentage swelling was about 876 % at 2 mL; there was an increase gradually to 884, 934, 1017 and 1097 % at 4, 6, 8, and 10 mL, respectively. An increase in crosslinking agent leads to an increase in the density of crosslinking and proper interaction of functional groups in the polymer. Above 10 mL the percentage swelling decrease, therefore, 10 mL is considered as the optimum.

Appendix 4: Optimization of reaction conditions for synthesis of SAH by crosslinking cellulose with phosphoric acid

Reaction time, microwave oven power out-put, and amount of cross-linker required were optimized by determining the percentage swelling of SAH prepared under varied condition as described below.

4A Optimization of reaction time for the cross-linking of cellulose with phosphoric acid

To determine the optimum reaction for completion of the reaction, the phosphoric acid SAH was prepared under varied reaction time that is. 1 to 5 minutes while other conditions were kept constant and percentage swelling of each product was determined. The reaction time that gave the product with highest percentage swelling was taken as the optimum reaction time. In typical synthesis, 2.00 g of cellulose was added to 30 mL of distilled water into 200 mL beaker. The mixture was dissolved by stirring at room temperature using a magnetic stirrer for 24 hours. The resulting solution was treated with 10 mL phosphoric acid and heated in a microwave at a power output of 280 watts for 5 minutes. The reaction mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled water, then, was dried in an oven at 40 ^{o}C to a constant weight. The results are summarized in figure 4A.

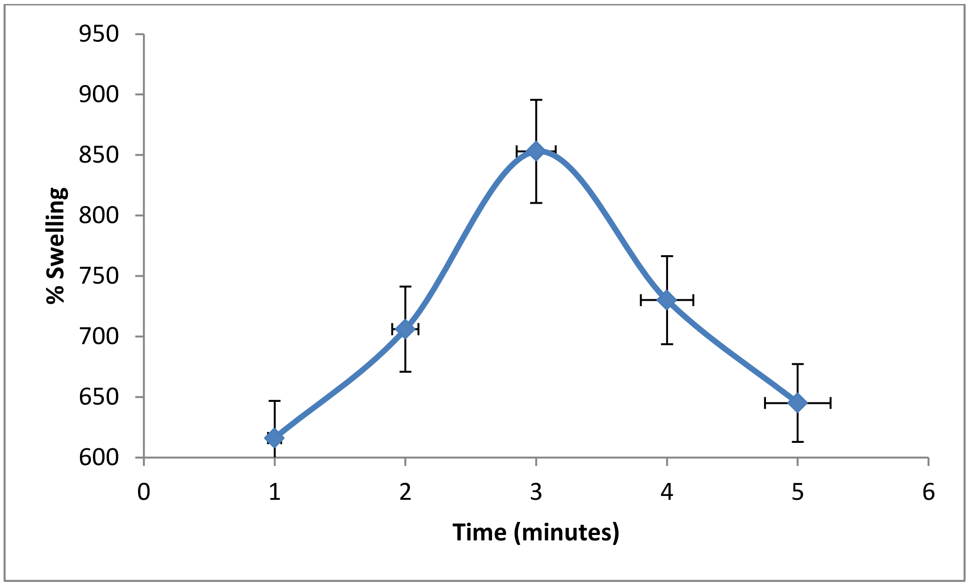


Figure 4A: Variation of percentage of swelling with reaction time

There is an increase in the percentage swelling from 616 to 853 % when the time varied from 1 to 3 minutes as shown in Figure 4A. As the time increased from 3 to 5 minutes, the percentage of swelling decreased from 853 to 645 %. The percentage swelling of the superabsorbent reached its maximum at 3 minutes of reaction time which was 853 %. Takigami *et al*. (2012) reported that the amount of crosslinking increases with an increase with incubation time. The decrease in percentage swelling after 3 minutes of reaction can be due to saturation. As shown in Figure 4A, the percentage of swelling depends on the reaction time.

4B Optimization of microwave oven power out-put for synthesis

To determine the optimum microwave power out-put required for synthesis of the phosphoric acid SAH, percentage swelling of the product prepared under varied microwave power out-put that is 2 – 10 while other condition were kept constant and percentage swelling of each product were determined. The microwave power out-put that gave the product with highest percentage swelling was taken as the optimum power out-put. In typical synthesis, 2.00 g of cellulose was added to 30 mL of distilled water into 200 mL beaker. The mixture was dissolved by stirring at room temperature using a magnetic stirrer for 24 hours. The resulting solution was treated with 10 mL phosphoric acid and heated in a microwave oven at a power output of 140 watts for 5 minutes. The reaction mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled water, then, was dried in an oven at 40 ^{o}C to a constant weight. The experiments were carried out in triplicates. The results are summarized in figure 4B.

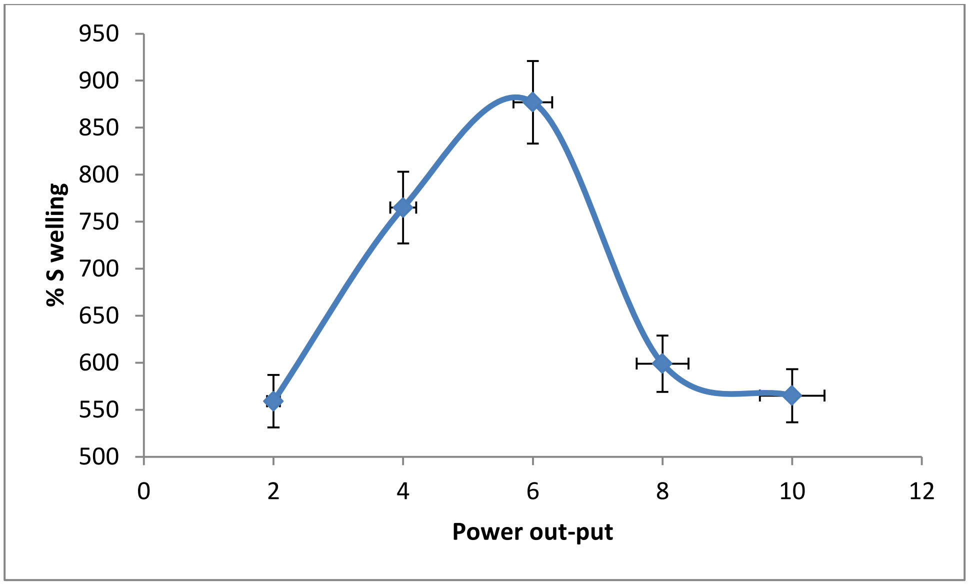


Figure 4B: Variation of percentage swelling with power out of microwave

There is an increase in the percentage swelling from 559 to 877 % when the time varied from 1 to 3 minutes as shown in Figure 9. As time increased from 3 to 5 minutes, the percentage of swelling decreased from 877 to 565 %. The graph shows that there is an increase in percentage swelling as the power out-put increases; this can be as a result of the acceleration of the formation of superabsorbent and promoting the hydrogen bond formation (Takigami *et al*., 2012). The power output of 3 was considered as optimum. At higher power out-put, hydrogen bond formation caused a tighter crosslinking network, and Leafs few voids for penetration of water, leads to a decrease in the percentage swelling.

4C Optimization of amount of cross-linker (mL) used in synthesis

To determine the optimum amount of cross-linker for completion of the reaction, the phosphoric acid SAH was prepared under varied amount of cross-linker that is 2, 4, 6, 8, 10, 12, and 14 mL of phosphoric acid while other conditions were kept constant and percentage swelling of each product were determined. The amount of cross-linker that gave the product with highest percentage swelling was taken as the optimum. In typical synthesis, 2.00 g of cellulose was added to 30 mL of distilled water in a 200 mL beaker. The mixture was dissolved by stirring at room temperature using a magnetic stirrer for 24 hours. The resulting solution was treated with 2 mL phosphoric acid and heated in a microwave oven at a power output of 280 watts for 5 minute. The reaction mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled water, and dried in an oven at 40 ^{o}C to a constant weight. The experiments were carried out in triplicates and results are summarized in figure 4C.

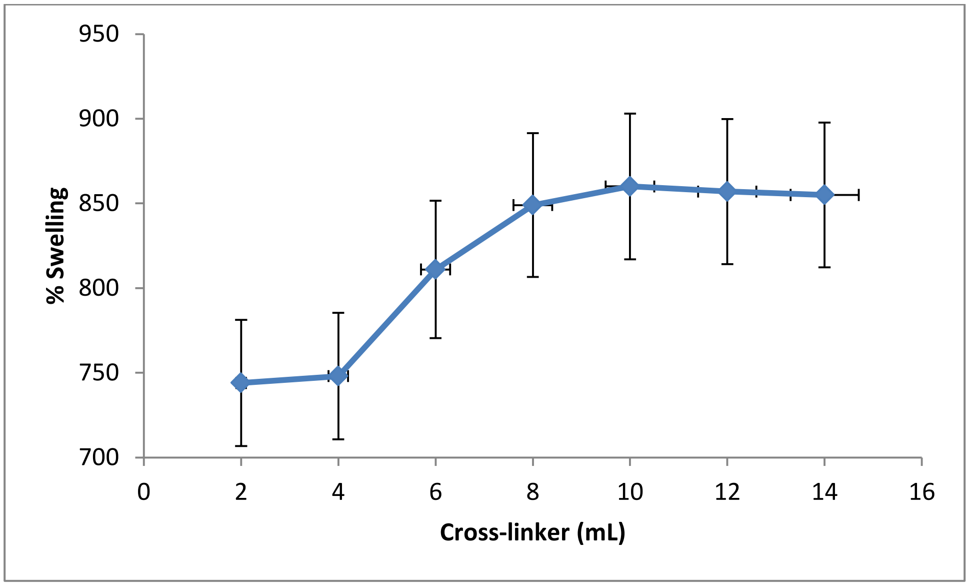


Figure 4C: Variation of percentage swelling with amount of cross-linker

The percentage swelling increased from 744 to 860 % corresponding to 2 to 10 mL of phosphoric acid. At a low concentration of the cross-linker (phosphoric acid), the percentage of swelling is a bit low. The increase in percentage swelling was due to an increase in the amount of phosphoric acid, it reaches optimum at 10 mL. An adequate amount of phosphoric acid leads to effective crosslinking between the OH group of cellulose and the phosphate group leading to the formation of a superabsorbent hydrogel. A similar result was observed by Xiao *et al*. (2012) that a high degree of cross-linker in the polymer network, reduces the percentage of swelling because water molecules find it difficult to penetrate.

Appendix 5: Optimization of reaction conditions for synthesis of SAH by crosslinking cellulose with boric acid

Reaction time, microwave oven power out-put, and amount of cross-linker required were optimized by determining the percentage swelling of SAH prepared under varied conditions as described below.

5A Optimization of reaction time

To determine the optimum reaction for completion of the reaction, the boric acid SAH was prepared under varied reaction time that is 1 to 5 minutes while other conditions were kept constant and percentage swelling of each product was determined. The reaction time that gave the product with highest percentage swelling was taken as the optimum reaction time. In typical synthesis, 2.00 g of cellulose was added to 30 mL of distilled water in a 200 mL beaker. The mixture was dissolved by stirring at room temperature using a magnetic stirrer for 24 hours. The resulting solution was treated with 1.00 g boric acid and heated in a microwave at a power output of 280 watts for 5 minutes. The reaction mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled water, then, was dried in an oven at 40 ^{o}C to a constant weight. The results are summarized in figure 5A.

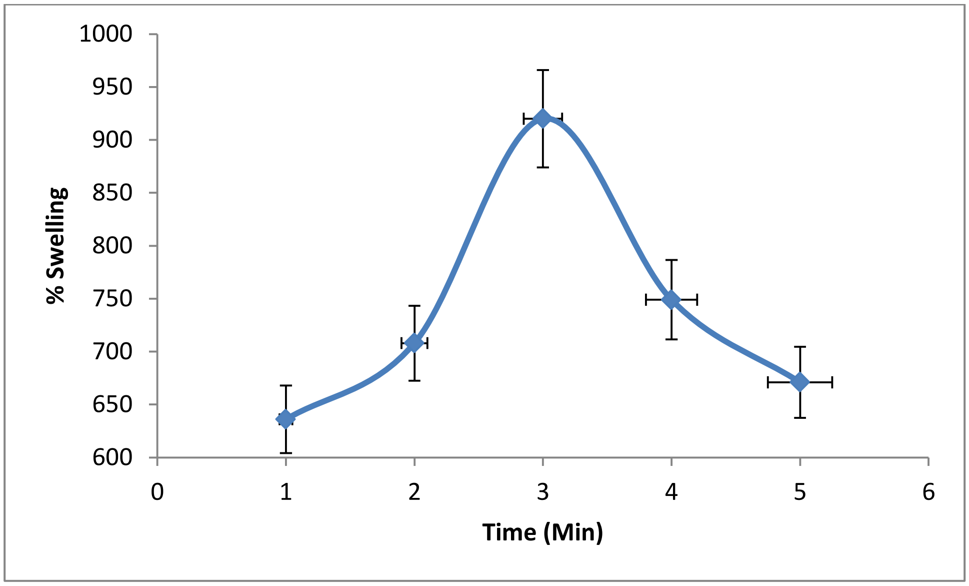


Figure 5A: Variation of percentage swelling with reaction time (at power out-put of 6 equivalent 420 Watts, 1.0 g of boric acid, 2.00 g of cellulose)

There is an increase in percentage swelling from 636 – 920 % when the time was varied from 1 to 3 minutes as shown in Figure 5A. As time increased from 3 to 5minutes, the percentage of swelling of superabsorbent decreases 920 – 671 %. The increase in percentage swelling can be as a result of the formation of hydrogen bonding between the functional groups on the superabsorbent hydrogel and water molecules.

5B Optimization of microwave power out-put for synthesis

To determine the optimum microwave power out-put required for synthesis of the boric acid SAH, percentage swelling of the product prepared under varied microwave power out-put that is 2 to 10 while other conditions were kept constant were determined. The microwave power out-put that gave the product with highest percentage swelling was taken as the optimum reaction time. In a typical synthesis, 2.00 g of cellulose was added to 30 mL of distilled water in a 200 mL beaker. The mixture was dissolved by stirring at room temperature using a magnetic stirrer for 24 hours. The resulting solution was treated with 1.0 g boric acid and heated in a microwave at a power output of 140 watts for 5 minute. The reaction mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled water, then, was dried in an oven at 40 °C to a constant weight. The experiments were carried out in triplicates. The results are summarized in figure 5B.

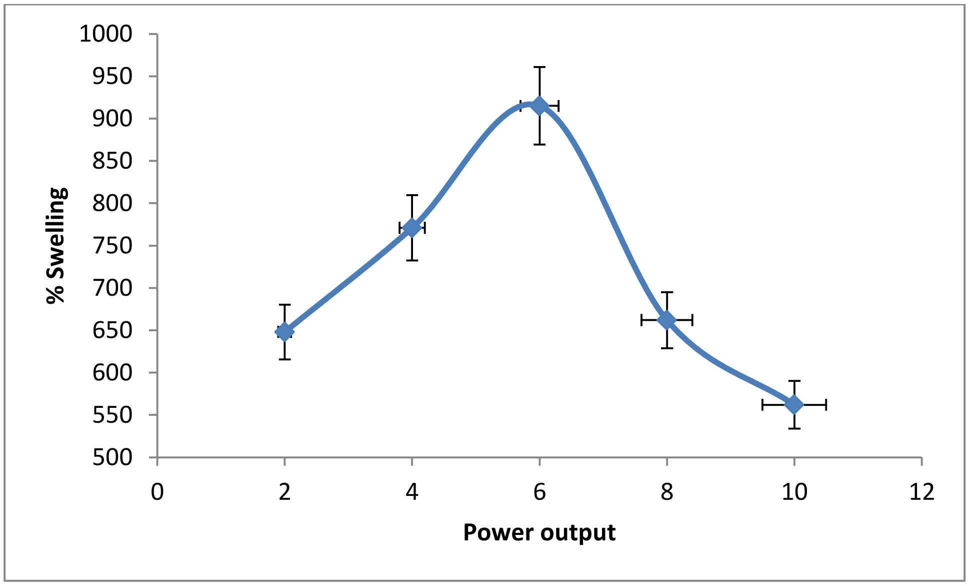


Figure 5B: Variation of percentage swelling with power-output (at 3 minutes, 1.0 g of boric acid, 2.00 g of cellulose)

The percentage swelling increased from 648 – 915 %, when the power out-put was increased from 2 – 6; this is equivalent to 140 - 420 watts, respectively. An increase in the power output from 6 – 10 which corresponds to 420 – 700 watts was accompanied by a decrease in percentage of swelling. The highest percentage of swelling occurred at a power output of 6 (420 watts) and recorded as optimum. As the power output increases, there is destruction between the hydrogen bonding existing in polymer, thus the percentage swelling increases. Consequently, an increase in power output enhances the swelling capacity. The decrease in the percentage swelling might be a result of inadequate entropy and internal energy, leading to a low rate of diffusion of water molecules into the hydrogel.

5C Optimization of amount of cross-linker (g) used in synthesis

To determine the optimum amount of cross-linker for completion of the reaction, the phosphoric acid SAH was prepared under varied amount of cross-linker that is 0.5, 0.6, 0.7, 0.8, 1.0, 1.1 and 1.2 g boric acid while other condition were kept constant and percentage swelling of each product were determined. The amount of cross-linker that gave the product with highest percentage swelling was taken as the optimum. In typical synthesis, 2.00 g of cellulose was added to 30 mL of distilled water into 200 mL beaker. The mixture was dissolved by stirring at room temperature using a magnetic stirrer for 24 hours. The resulting solution was treated with 2 mL phosphoric acid and heated in a microwave at a power output of 280 watts for 5 minute. The reaction mixture was allowed to cool to room temperature and then filtered. The residue was washed several times with distilled water, then, was dried in an oven at 40 ^{o}C to a constant weight. The experiments were carried out in triplicates. The results are summarized in figure 5C.

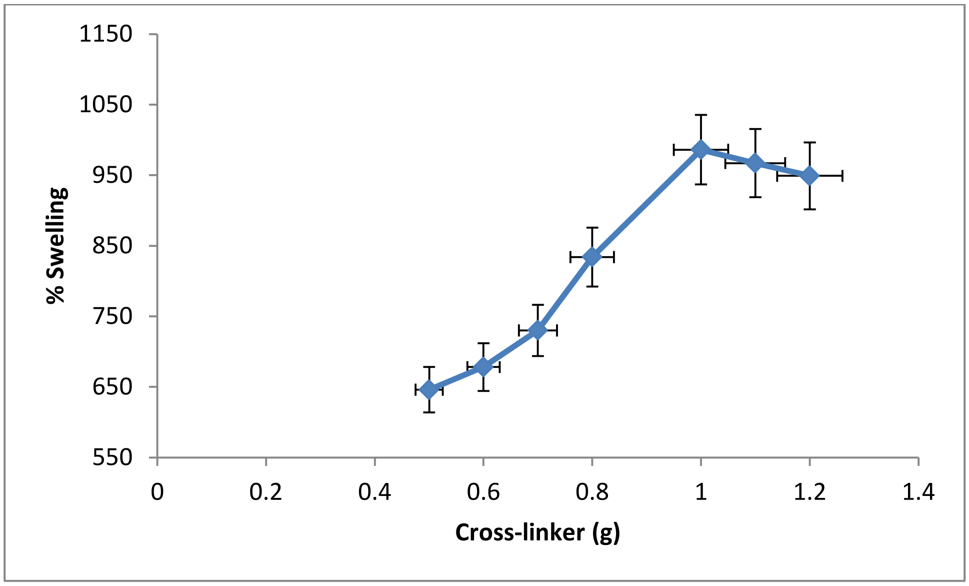


Figure 5C: Variation of percentage swelling with amount of cross-linker (Boric acid) (at power out-put of 6 equivalent 420 Watts, 3 minutes, 2.00 g of cellulose)

It was observed that the percentage of swelling increased with an increase in the amount of cross-linker (Boric acid). The percentage of swelling increased from 646 – 986 % when the amount of cross-linker (Boric acid) was increased from 0.5 – 1.0 g. The graph indicated that a low amount of cross-linker led to less percentage swelling of the superabsorbent hydrogel, in comparison with the number of OH groups in cellulose, only a few were able to crosslinked, due to inadequate amount of boric acid, while other OH remain vacant. The extent of the formation of complex (crosslinking) will be small, due to inadequate amount of boric is inadequate. The crystallinity also reduced when there is less amount of cross-linker.

Appendix 6: Optimization of conditions for synthesis of superabsorbent hydrogels

					SAH crosslinked with ethane-1,2-diamine Mean±SD	**SAH crosslinked with ethane-1,2-diol Mean±SD**	**SAH crosslinked with boric acid Mean±SD**	**SAH crosslinked with phosphoric acid Mean±SD**
Time (min)	1				99.00±1.00^{a}	719.00±1.00^{a}	635.00±1.00^{a}	616.00±1.00^{a}
	2				1045.00±1.00^{b}	947.00±1.00^{b}	708.00±1.00^{b}	706.33±0.57^{b}
	3				1065.00±1.00^{c}	968.66±0.57^{c}	919.00±1.00^{c}	853.33±0.57^{c}
	4				1084.00±1.00^{d}	988.00±1.00^{d}	749.00±1.00^{d}	730.00±1.00^{d}
	5				1175.00±0.00^{e}	999.00±1.00^{e}	671.00±1.00^{e}	645.00±1.00^{e}
Power out-put	2				919.00±1.00^{a}	1089.00±1.00^{a}	648.00±1.00^{a}	559.00±1.00^{a}
	4				948.00±1.00^{b}	1000.33±0.57^{b}	771.33±0.57^{b}	765.33±0.57^{b}
	6				1076.00±1.00^{c}	995.00±1.00^{c}	914.33±0.57^{c}	877.00±1..00^{c}
	8				1016.66±0.57^{d}	799.00±1.00^{d}	662.00±1.00^{d}	599.33±0.57^{d}
	10				1097.33±0.57^{e}	785.00±1.00^{e}	562.00±1.00^{e}	565.00±1.00^{e}
Cross-linker	Dm	Dl	B	P				
	2	5	0.5	2	876.00±1.00^{a}	1161.00±1.00^{a}	646.00±1.00^{a}	744.00±1.00^{a}
	4	10	0.6	4	884.00±0.00^{b}	1001.00±1.00^{b}	678.00±0.00^{b}	748.33±0.57^{b}
	6	15	0.7	6	934.00±1.00^{c}	986.00±1.00^{c}	730.00±1.00^{c}	811.00±1.00^{c}
	8	20	0.8	8	1016.66±0.57^{d}	962.00±1.00^{d}	834.00±1.00^{d}	849.00±1.00^{d}
	10	25	1.0	10	1097.33±0.57^{e}	904.00±1.00^{e}	986.00±0.57^{e}	860.33±0.57^{e}
Dose (g)	1				920.00±1.00^{a}	956.00±1.00^{a}	818.00±1.00^{a}	840.00±1.00^{a}
	2				1078.33±0.57^{b}	1000.00±1.00^{b}	886.00±0.57^{b}	846.00±1.00^{b}
	3				1098.00±1.00	1046.00±1.00^{c}	775.00±1.00	615.33±0.57

	c		c	c
4	786.00±1.00^{d}	741.00±1.00^{d}	651.00±1.00^{d}	571.00±1.00^{d}
5	691.00±1.00^{e}	606.00±1.00^{e}	522.00±1.00^{e}	504.00±1.00^{e}

Means that do not share a letter are significantly different ($p < 0.05$)

Appendix 7: Pre-harvest studies

Plant height

Weeks	SAH Dose	SAH crosslinked with ethane-1,2-diamine Mean±SD	SAH crosslinked with ethane-1,2-diol Mean±SD	SAH crosslinked with boric acid Mean±SD	SAH crosslinked with phosphoric acid Mean±SD
3	Control	27.69±1.60^{a}	29.20±1.11^{a}	28.57±0.54^{a}	29.53±0.70^{a}
	1g	28.21±2.22^{a}	29.23±1.47^{a}	29.12±0.76^{a}	28.76±0.49^{a}
	2g	27.52±1.83^{a}	28.61±0.61^{a}	29.02±0.63^{a}	28.95±0.67^{a}
	3g	27.88±1.80^{a}	28.43±0.51^{a}	29.24±0.93^{a}	29.55±0.88^{a}
	4g	28.48±2.10^{a}	29.19±0.84^{a}	29.47±0.89^{a}	28.90±0.98^{a}
	5g	28.97±2.49^{a}	29.14±0.93^{a}	29.43±0.67^{a}	29.50±0.67^{a}
6	Control	40.06±0.97^{e}	40.20±0.84^{f}	39.44±0.68^{f}	38.93±0.35^{f}
	1g	87.46±0.69^{d}	75.71±0.87^{e}	55.48±0.97^{e}	52.43±0.11^{e}
	2g	88.32±1.24^{d}	81.44±1.40^{d}	59.42±0.65^{d}	61.34±1.32^{d}
	3g	100.57±0.71^{c}	88.78±1.42^{c}	68.29±1.35^{c}	68.79±0.88^{c}
	4g	108.58±1.07^{b}	100.86±1.70^{b}	87.45±1.92^{b}	78.16±0.61^{b}
	5g	119.00±3.11^{a}	111.28±1.24^{a}	100.76±2.01^{a}	83.25±0.17^{a}
9	Control	42.21±0.41^{f}	42.46±0.10^{f}	41.98±1.00^{f}	41.83±0.25^{f}
	1g	156.71±1.23^{e}	150.54±1.29^{e}	147.92±0.09^{e}	126.20±1.16^{e}
	2g	168.25±1.15^{d}	161.04±1.20^{d}	156.46±1.67^{d}	134.25±1.37^{d}
	3g	179.05±1.10^{c}	175.33±0.95^{c}	163.44±0.62^{c}	143.11±1.02^{c}
	4g	191.40±1.38^{b}	186.16±1.72^{b}	175.18±1.40^{b}	154.65±0.97^{b}
	5g	201.44±1.05^{a}	195.05±1.62^{a}	186.08±1.07^{a}	163.69±0.84^{a}
12	Control	43.24±0.56^{e}	42.77±0.25^{f}	42.24±0.83^{f}	42.94±0.08^{f}
	1g	219.50±1.32^{d}	224.23±1.31^{e}	208.33±1.20^{e}	192.81±1.75^{e}
	2g	221.74±1.99^{d}	234.39±0.77^{d}	218.48±0.73^{d}	204.59±1.20^{d}
	3g	243.39±2.62^{c}	247.24±1.31^{c}	228.88±1.28^{c}	214.13±1.06^{c}
	4g	260.41±1.02^{b}	256.18±1.24^{b}	242.35±0.94^{b}	224.20±1.63^{b}
	5g	270.23±2.28^{a}	265.54±0.68^{a}	256.77±1.45^{a}	232.96±1.85^{a}

Means that do not share a letter are significantly different ($p < 0.05$)

Number of Leafs

Weeks	**SAH Dose**	**SAH crosslinked with ethane-1,2-diamine Mean±SD**	**SAH crosslinked with ethane-1,2-diol Mean±SD**	**SAH crosslinked with boric acid Mean±SD**	**SAH crosslinked with phosphoric acid Mean±SD**
3	Control	5.66±1.52^{a}	5.00±1.00^{a}	5.33±0.57^{a}	4.00±1.00^{a}
	1g	5.00±1.00^{a}	5.00±1.00^{a}	5.66±1.52^{a}	4.66±0.15^{a}
	2g	5.00±1.00^{a}	6.33±0.57^{a}	5.66±1.52^{a}	4.33±0.57^{a}
	3g	5.00±1.00^{a}	6.66±0.57^{a}	5.00±0.00^{a}	4.00±1.00^{a}
	4g	5.33±0.57^{a}	5.33±0.57^{a}	5.00±1.00^{a}	4.33±0.57^{a}
	5g	6.00±1.00^{a}	6.00±1.00^{a}	5.66±0.57^{a}	5.00±1.00^{a}
6	Control	5.66±0.57^{d}	6.23±0.57^{d}	5.00±0.57^{d}	5.00±1.00^{d}
	1g	6.66±0.57^{d}	7.66±0.52^{c}	5.66±0.57^{d}	5.33±0.57^{d}
	2g	7.33±0.57^{cd}	8.66±0.57^{b}	6.00±1.00^{c}	6.33±0.57^{cd}
	3g	8.66±0.57^{bc}	8.66±0.57^{a}	6.33±0.57^{bc}	7.66±0.15^{bc}
	4g	9.00±1.00^{ab}	10.00±1.00^{a}	8.00±1.00^{ab}	7.33±0.57^{ab}
	5g	10.66±0.57^{a}	10.33±0.57^{a}	8.33±0.52^{a}	8.00±1.00^{a}
9	Control	8.33±0.57^{d}	7.66±0.57^{e}	6.33±0.52^{e}	6.00±1.00^{b}
	1g	10.00±1.00^{c}	9.00±1.00^{d}	9.33±0.52^{d}	6.33±0.57^{b}
	2g	12.66±0.57^{b}	11.66±1.51^{c}	10.33±0.51^{c}	7.33±0.57^{a}
	3g	14.33±0.57^{a}	14.33±1.52^{b}	13.00±1.00^{b}	7.66±1.52^{a}
	4g	15.66±0.57^{a}	15.33±0.52^{b}	14.00±1.00^{b}	8.66±1.52^{a}
	5g	27.33±0.57^{a}	15.33±0.57^{a}	15.66±0.57^{a}	9.33±0.57^{a}
12	Control	8.33±0.57^{d}	8.66±0.57^{e}	8.33±0.57^{d}	6.00±1.00^{d}
	1g	12.66±1.15^{c}	12.33±0.57^{d}	10.66±1.52^{c}	8.00±1.00^{c}
	2g	13.66±1.52^{bc}	13.33±0.57^{c}	12.00±1.00^{b}	9.66±1.15^{bc}
	3g	15.00±1.00^{ab}	15.33±0.57^{b}	12.66±1.52^{b}	10.00±1.00^{ab}
	4g	17.66±1.15^{a}	16.33±0.57^{a}	15.66±1.52^{a}	11.00±1.00^{a}
	5g	18.33±0.57^{a}	17.00±1.00^{a}	16.66±1.52^{a}	12.66±1.52^{a}

Means that do not share a letter are significantly different ($p < 0.05$)

Leaf length (cm)

Weeks	SAH Dose	SAH crosslinked with ethane-1,2-diamine Mean±SD	SAH crosslinked with ethane-1,2-diol Mean±SD	SAH crosslinked with boric acid Mean±SD	SAH crosslinked with phosphoric acid Mean±SD
3	Control	29.21±2.54^{bc}	28.69±0.68^{d}	26.67±3.36^{a}	28.69±0.68^{a}
	1g	27.09±0.73^{c}	26.24±1.46^{cd}	27.94±2.54^{a}	27.09±2.93^{a}
	2g	31.75±1.27^{ab}	30.05±0.73^{bc}	30.06±1.94^{a}	27.94±2.54^{a}
	3g	34.71±0.73^{a}	32.59±0.73^{ab}	26.24±1.46^{a}	28.36±0.73^{a}
	4g	32.17±1.19^{ab}	30.90±0.73^{bc}	25.40±0.00^{a}	31.33±1.94^{a}
	5g	33.02±1.27^{b}	34.29±1.27^{a}	30.48±2.54^{a}	31.75±1.27^{a}
6	Control	31.82±1.42^{e}	30.18±0.20^{e}	30.25±0.14^{e}	30.18±0.20^{d}
	1g	33.60±2.54^{d}	43.18±0.00^{d}	41.06±0.73^{d}	39.37±1.27^{c}
	2g	45.72±0.00^{c}	44.02±0.73^{cd}	43.18±0.00^{c}	40.97±0.57^{bc}
	3g	50.37±0.73^{b}	45.29±0.73^{bc}	45.29±0.73^{b}	42.75±0.73^{ab}
	4g	52.91±0.73^{b}	46.99±1.27^{b}	45.72±0.00^{b}	44.02±0.73^{a}
	5g	55.88±1.27^{a}	50.80±0.00^{a}	48.26±0.00^{a}	44.87±1.46^{a}
9	Control	34.32±0.65^{e}	32.17±0.05^{d}	32.10±0.37^{e}	32.17±0.05^{e}
	1g	78.74±2.20^{d}	76.20±0.00^{c}	66.04±2.54^{d}	59.69±1.27^{d}
	2g	80.52±0.66^{cd}	77.47±1.20^{c}	71.12±0.00^{c}	62.23±1.27^{c}
	3g	82.55±1.27^{bc}	79.58±0.73^{b}	71.96±1.46^{bc}	66.04±0.00^{b}
	4g	84.24±0.73^{ab}	81.28±0.00^{b}	74.93±1.27^{ab}	68.58±0.00^{a}
	5g	86.36±0.00^{a}	84.24±0.73^{a}	76.20±0.00^{a}	69.42±0.73^{a}
12	Control	35.06±0.82^{e}	33.42±0.39^{e}	32.93±0.73^{d}	33.40±1.73^{a}
	1g	81.70±0.73^{d}	81.70±0.73^{d}	71.12±0.00^{c}	66.46±0.73^{a}
	2g	84.06±0.92^{c}	83.82±0.00^{c}	74.50±1.46^{b}	68.58±0.00^{a}
	3g	86.36±0.00^{b}	84.24±0.73^{c}	77.89±1.46^{a}	71.12±0.00^{a}
	4g	88.90±0.00^{a}	87.20±0.73^{b}	79.58±1.46^{a}	73.66±1.27^{a}
	5g	90.50±0.81^{a}	88.90±0.00^{a}	80.42±1.45^{a}	75.35±1.46^{a}

Means that do not share a letter are significantly different ($p < 0.05$)

Leaf diameter

Weeks	**SAH Dose**	**SAH crosslinked with ethane-1,2-diamine Mean±SD**	**SAH crosslinked with ethane-1,2-diol Mean±SD**	**SAH crosslinked with boric acid Mean±SD**	**SAH crosslinked with phosphoric acid Mean±SD**
3	Control	2.36 ± 0.15^{b}	2.28 ± 0.00^{bc}	2.02 ± 0.25^{b}	2.28 ± 0.00^{b}
	1g	2.18 ± 0.13^{b}	2.19 ± 0.14^{c}	2.28 ± 0.25^{a}	2.28 ± 0.25^{b}
	2g	3.63 ± 0.15^{a}	3.46 ± 1.05^{ab}	3.63 ± 0.15^{b}	2.70 ± 0.38^{b}
	3g	3.63 ± 0.15^{a}	3.63 ± 0.15^{a}	2.19 ± 0.14^{b}	2.96 ± 0.38^{ab}
	4g	3.30 ± 0.67^{a}	3.72 ± 0.15^{a}	2.28 ± 0.25^{b}	3.63 ± 0.15^{a}
	5g	3.72 ± 0.15^{a}	3.72 ± 0.15^{a}	2.96 ± 0.81^{a}	3.46 ± 0.14^{a}
6	Control	2.63 ± 0.05^{e}	2.55 ± 0.03^{d}	2.54 ± 0.07^{d}	2.55 ± 0.03^{c}
	1g	4.57 ± 0.00^{d}	4.82 ± 0.25^{c}	3.97 ± 0.14^{c}	3.46 ± 0.14^{b}
	2g	4.91 ± 0.29^{cd}	5.33 ± 0.28^{bc}	4.31 ± 0.25^{bc}	3.55 ± 0.00^{b}
	3g	5.33 ± 0.25^{bc}	5.75 ± 0.15^{ab}	4.82 ± 0.51^{ab}	3.80 ± 0.25^{ab}
	4g	5.83 ± 0.25^{b}	6.09 ± 0.25^{a}	5.33 ± 0.25^{a}	3.80 ± 0.25^{ab}
	5g	6.43 ± 0.14^{a}	6.00 ± 0.14^{a}	4.99 ± 0.38^{ab}	4.22±0.14a
9	Control	2.70 ± 0.01^{d}	2.65 ± 0.01^{c}	2.67 ± 0.00^{c}	2.69 ± 0.01^{b}
	1g	6.64 ± 0.07^{b}	6.00 ± 0.14^{b}	5.07 ± 0.25^{b}	5.07 ± 0.25^{a}
	2g	6.72 ± 0.12^{b}	6.43 ± 0.14^{b}	6.00 ± 0.14^{a}	5.51 ± 0.31^{a}
	3g	7.09 ± 0.02^{b}	6.35 ± 0.00^{b}	6.00 ± 0.14^{a}	5.58 ± 0.25^{a}
	4g	7.35 ± 0.01^{a}	6.52 ± 0.14^{b}	6.43 ± 0.38^{a}	5.58 ± 0.25^{a}
	5g	7.44 ± 0.15^{a}	7.19 ± 0.39^{a}	6.60 ± 0.25^{a}	5.66 ± 0.15^{a}
12	Control	2.72 ± 0.01^{e}	2.69 ± 0.02^{c}	2.68 ± 0.01^{d}	2.69 ± 0.02^{c}
	1g	6.85 ± 0.00^{d}	6.93 ± 0.15^{b}	5.16 ± 0.14^{c}	4.31 ± 0.00^{b}
	2g	7.06 ± 0.07^{cd}	7.27 ± 0.14^{ab}	5.83 ± 0.25^{b}	4.56 ± 0.25^{b}
	3g	7.27 ± 0.14^{bc}	7.44 ± 0.15^{a}	5.84 ± 0.00^{b}	4.56 ± 0.25^{b}
	4g	7.44 ± 0.15^{b}	7.44 ± 0.15^{a}	6.00 ± 0.14^{ab}	5.41 ± 0.14^{a}
	5g	7.78 ± 0.14^{a}	7.44 ± 0.15^{a}	6.34 ± 0.25^{a}	5.66 ± 0.15^{a}

Means that do not share a letter are significantly different ($p < 0.05$)

Leaf area

Weeks	SAH Dose	SAH crosslinked with ethane-1,2-diamine Mean±SD	SAH crosslinked with ethane-1,2-diol Mean±SD	SAH crosslinked with boric acid Mean±SD	SAH crosslinked with phosphoric acid Mean±SD
3	Control	52.10±7.57^{b}	48.03±1.91^{c}	40.72±8.20^{b}	48.03±1.91^{b}
	1g	44.33±1.60^{b}	43.38±4.60^{bc}	47.74±4.87^{b}	46.77±1.08^{b}
	2g	86.77±6.78^{a}	78.60±25.4^{ab}	82.17±8.14^{b}	56.61±8.08^{b}
	3g	94.75±3.27^{a}	89.03±4.91^{a}	43.38±4.60^{b}	62.90±6.83^{b}
	4g	79.09±2.83^{a}	86.37±4.76^{a}	43.54±4.84^{ab}	85.56±6.77^{a}
	5g	92.33±6.88^{a}	95.88±7.01^{a}	68.70±23.5^{a}	82.74±6.51^{a}
6	Control	60.93±1.2^{e}	58.57±0.46^{e}	57.95±1.52^{d}	58.57±0.46^{d}
	1g	156.80±0.06^{c}	156.29±8.23^{d}	122.58±5.92^{c}	102.57±7.32^{c}
	2g	177.71±10.59^{cd}	176.20±10.97^{cd}	139.83±8.23^{bc}	109.51±1.96^{bc}
	3g	201.61±12.81^{c}	195.64±8.11^{bc}	164.10±19.50^{ab}	122.24±9.99^{abc}
	4g	228.93±9.29^{b}	214.99±14.76^{ab}	179.19±13.79^{a}	125.88±9.25^{ab}
	5g	269.75±11.91^{a}	290.03±5.58^{a}	182.90±8.71^{a}	142.58±9.50^{a}
9	Control	63.76±1.00^{d}	59.67±8.38^{d}	60.68±0.05^{e}	60.41±1.03^{d}
	1g	392.53±13.64^{c}	343.54± 8.38^{c}	251.60±21.80^{d}	227.58±16.21^{c}
	2g	408.22±11.04^{c}	373.78±4.36^{bc}	311.61±13.55^{c}	252.98±11.66^{bc}
	3g	439.29±8.37^{b}	379.02±3.49^{bc}	324.51±12.59^{bc}	176.77±12.58^{ab}
	4g	464.76±2.94^{a}	397.41±8.94^{b}	361.70±24.30^{ab}	287.41±13.07^{a}
	5g	482.57±9.50^{a}	454.80±8.24^{a}	377.41±14.52^{a}	295.40±9.59^{a}
12	Control	64.59±0.64^{f}	61.60±0.54^{d}	60.94±0.48^{e}	61.62±0.57^{c}
	1g	420.24±3.77^{e}	425.48±12.85^{c}	275.48±7.82^{d}	215.24±2.37^{b}
	2g	446.69±7.39^{d}	457.74±9.22^{b}	326.29±9.24^{c}	235.16±13.07^{b}
	3g	471.61±9.50^{c}	470.80±13.41^{ab}	341.28±6.42^{bc}	243.87±13.55^{b}
	4g	496.77±9.78^{b}	487.33±12.18^{a}	358.26±13.35^{ab}	294.80±19.10^{a}
	5g	528.78±13.45^{a}	496.77±9.78^{a}	383.20±21.60^{a}	320.64±12.63^{a}

Means that do not share a letter are significantly different ($p < 0.05$)

Appendix 8: Post harvest studies

Number of cobs

SAH Dose	SAH crosslinked with ethane-1,2-diamine Mean±SD	SAH crosslinked with ethane-1,2-diol Mean±SD	SAH crosslinked with boric acid Mean±SD	SAH crosslinked with phosphoric acid Mean±SD
Control	$0.33±0.57^{d}$	$0.33±0.57^{c}$	$0.33±0.57^{c}$	$0.00±00^{c}$
1g	$1.00±0.00^{cd}$	$0.66±0.57^{c}$	$1.00±0.00^{bc}$	$0.66±0.57^{bc}$
2g	$1.66±0.57^{bcd}$	$1.33±0.57^{bc}$	$1.00±0.00^{bc}$	$1.33±0.57^{ab}$
3g	$2.33±0.57^{abc}$	$2.00±0.00^{ab}$	$1.66±0.57^{ab}$	$2.00±0.00^{a}$
4g	$2.66±0.57^{ab}$	$2.33±0.57^{ab}$	$2.33±0.57^{a}$	$2.00±0.00^{a}$
5g	$3.33±0.57^{a}$	$3.00±0.00^{a}$	$2.66±0.57^{a}$	$2.33±0.57^{a}$

Means that do not share a letter are significantly different ($p < 0.05$)

Cob length

SAH Dose	SAH crosslinked with ethane-1,2-diamine Mean±SD	SAH crosslinked with ethane-1,2-diol Mean±SD	SAH crosslinked with boric acid Mean±SD	SAH crosslinked with phosphoric acid Mean±SD
Control	$2.77±4.79^{c}$	$2.73±4.73^{d}$	$0.00±0.00^{e}$	$0.00±0.00^{e}$
1g	$11.06±0.81^{b}$	$9.78±1.53^{c}$	$8.87±0.01^{d}$	$8.72±0.16^{d}$
2g	$13.27±0.83^{ab}$	$11.48±0.45^{bc}$	$10.94±0.07^{c}$	$10.30±0.15^{c}$
3g	$16.24±0.95^{ab}$	$13.71±0.68^{abc}$	$11.16±0.85^{c}$	$11.08±0.46^{bc}$
4g	$17.76±0.58^{a}$	$16.29±0.89^{ab}$	$14.84±1.39^{b}$	$12.10±0.22^{b}$
5g	$18.53±1.33^{a}$	$18.09±1.16^{a}$	$17.54±0.44^{a}$	$13.79±0.95^{a}$

Means that do not share a letter are significantly different ($p < 0.05$)

Cob diameter

SAH Dose	SAH crosslinked with ethane-1,2-diamine Mean±SD	SAH crosslinked with ethane-1,2-diol Mean±SD	SAH crosslinked with boric acid Mean±SD	SAH crosslinked with phosphoric acid Mean±SD
Control	$0.66±1.55^{c}$	$0.66±1.55^{c}$	$0.00±0.00^{e}$	$0.00±0.00^{f}$
1g	$2.42±0.58^{b}$	$2.25±0.22^{b}$	$1.98±0.15^{d}$	$1.42±0.03^{e}$
2g	$2.78±0.15^{b}$	$2.53±0.02^{ab}$	$2.08±0.07^{d}$	$1.75±0.21^{d}$
3g	$3.07±0.13^{ab}$	$2.69±0.07^{ab}$	$2.45±0.11^{c}$	$2.14±0.57^{c}$
4g	$3.20±0.20^{ab}$	$3.08±0.11^{ab}$	$2.82±0.13^{b}$	$2.40±0.02^{b}$
5g	$3.80±0.11^{a}$	$3.29±0.18^{a}$	$3.36±0.10^{a}$	$2.67±0.08^{a}$

Means that do not share a letter are significantly different ($p < 0.05$)

Cob weight

SAH Dose	SAH crosslinked with ethane-1,2-diamine Mean±SD	SAH crosslinked with ethane-1,2-diol Mean±SD	SAH crosslinked with boric acid Mean±SD	SAH crosslinked with phosphoric acid Mean±SD
Control	$0.00±0.00^{f}$	$0.00±0.00^{e}$	$0.00±0.00^{f}$	$0.00±0.00^{f}$
1g	$112.67±4.04^{e}$	$100.67±4.51^{d}$	$45.67±2.51^{e}$	$24.67±5.51^{e}$
2g	$126.00±1.73^{d}$	$112.33±2.50^{c}$	$64.33±3.21^{d}$	$37.33±3.21^{d}$
3g	$135.33±3.79^{c}$	$124.33±3.21^{b}$	$78.33±4.04^{c}$	$48.00±1.73^{c}$
4g	$154.67±4.04^{b}$	$141.00±9.00^{a}$	$96.67±2.89^{b}$	$59.67±4.04^{b}$
5g	$180.00±5.57^{a}$	$148.33±1.52^{a}$	$107.33±7.37^{a}$	$83.33±1.58^{a}$

Means that do not share a letter are significantly different ($p < 0.05$)

Number of grain per cob

SAH Dose	SAH crosslinked with ethane-1,2-diamine Mean±SD	SAH crosslinked with ethane-1,2-diol Mean±SD	SAH crosslinked with boric acid Mean±SD	SAH crosslinked with phosphoric acid Mean±SD
Control	0.00±0.00^{f}	0.00±0.00^{e}	0.00±0.00^{f}	0.00±0.00^{f}
1g	242.67±2.52^{e}	207.67±15.95^{d}	46.67±2.08^{e}	23.67±4.73^{e}
2g	294.67±3.79^{d}	289.67±3.51^{c}	111.33±8.02^{d}	41.00±3.00^{d}
3g	324.33±3.21^{c}	315.00±5.57^{b}	160.33±5.69^{c}	67.67±3.51^{c}
4g	380.00±4.58^{b}	320.67±3.06^{b}	221.00±5.57^{b}	102.67±5.69^{b}
5g	418.67±8.08^{a}	350.00±2.00^{a}	247.67±3.06^{a}	165.00±9.17^{a}

Means that do not share a letter are significantly different ($p < 0.05$)

Grain weight

SAH Dose	SAH crosslinked with ethane-1,2-diamine Mean±SD	SAH crosslinked with ethane-1,2-diol Mean±SD	SAH crosslinked with boric acid Mean±SD	SAH crosslinked with phosphoric acid Mean±SD
Control	0.00±0.00^{f}	0.00±0.00^{f}	0.00±0.00^{f}	0.00±0.00^{f}
1g	93.67±3.51^{e}	79.67±4.16^{e}	24.00±1.00^{e}	12.33±2.52^{e}
2g	105.66±1.52^{d}	94.33±2.52^{d}	43.67±2.52^{d}	20.67±2.08^{d}
3g	116.33±2.52^{c}	103.67±2.08^{c}	58.33±2.08^{c}	30.33±2.52^{c}
4g	133.33±1.52^{b}	116.00±2.00^{b}	75.67±3.51^{b}	41.00±2.65^{b}
5g	158.33±2.08^{a}	124.00±4.36^{a}	84.00±3.61^{a}	61.67±3.06^{a}

Means that do not share a letter are significantly different ($p < 0.05$)

Appendix 9: Comparison on efficacy of SAHs on pre-harvest studies

Weeks	SAH Dose	Plant height	Number of Leafs	Leafs lengths	Leafs diameter	Leaf area
Ethane-1,2-diamine SAH	5g	270.23±2.28^{d}	18.33±0.57^{c}	90.50±0.81^{c}	7.78±0.14^{b}	528.78±13.45^{d}
Ethane-1.2-diol SAH		265.54±0.68^{c}	17.00±1.00^{bc}	88.90±0.00^{c}	7.44±0.15^{b}	496.77±9.78^{c}
Boric acid SAH		256.77±1.45^{b}	16.66±1.52^{b}	80.42±1.45^{b}	6.34±0.25^{a}	383.20±21.60^{b}
Phosphoric acid SAH		232.96±1.85^{a}	12.66±1.52^{a}	75.35±1.46^{a}	5.66±0.15^{a}	320.64±12.63^{a}

Means that do not share a letter are significantly different ($p < 0.05$)

Comparison on efficacy of SAHs on post-harvest studies

Weeks	SAH Dose	Number of cob	Length of cob	Diameter of cob	Weight of cob	Number of grain	Grain weight
Ethane-1,2-diamine SAH	5g	3.33±0.57^{a}	18.53±1.33^{b}	3.08±0.11^{b}	180.00±5.57^{d}	418.67±8.08^{d}	158.33±2.08^{d}
Ethane-1.2-diol SAH		3.00±0.00^{a}	18.09±1.16^{b}	3.29±0.18^{b}	148.33±1.52^{c}	350.00±2.00^{c}	124.00±4.36^{c}
Boric acid SAH		2.66±0.57^{a}	17.54±0.44^{b}	3.36±0.10^{b}	107.33±7.37^{b}	247.67±3.06^{b}	84.00±3.61^{b}
Phosphoric acid SAH		2.33±0.57^{a}	13.79±0.08^{a}	2.67±0.08^{a}	83.33±1.58^{a}	165.00±9.17^{a}	61.67±3.06^{a}

Means that do not share a letter are significantly different ($p < 0.05$)

Appendix 10: Additional images

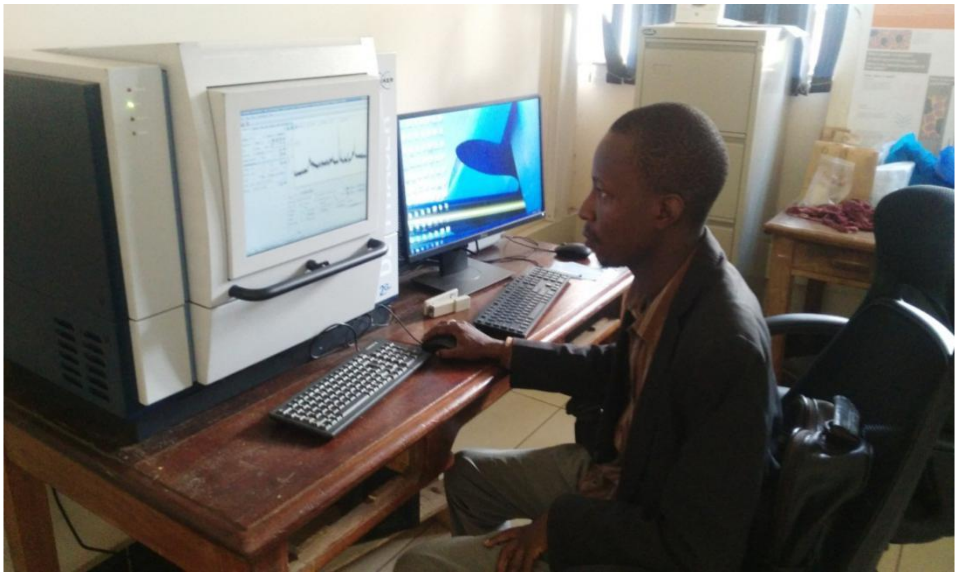


Figure 10A: Researcher during xrd characterization

Figure 10B: Pot containing 1 g boric acid SAH

Figure 10C: Cob of 5 g ethane-1,2-diamine SAH

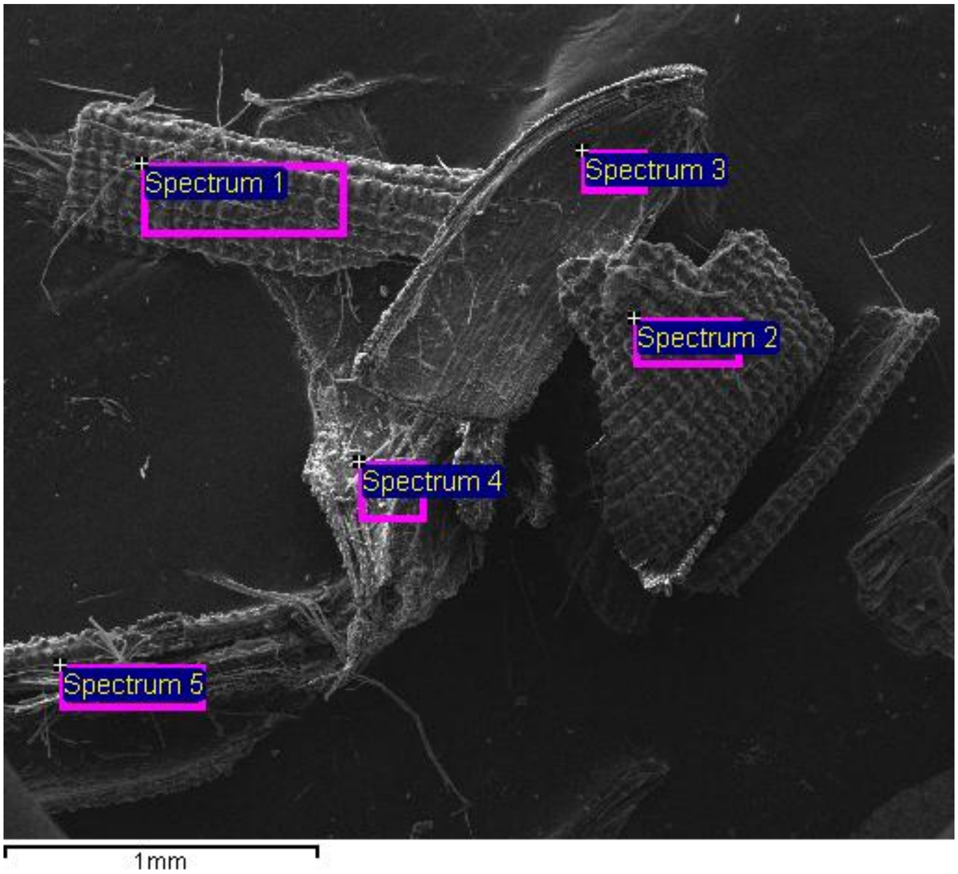
Figure 10D: Harvested maize from ethane-1,2-diamine SAH

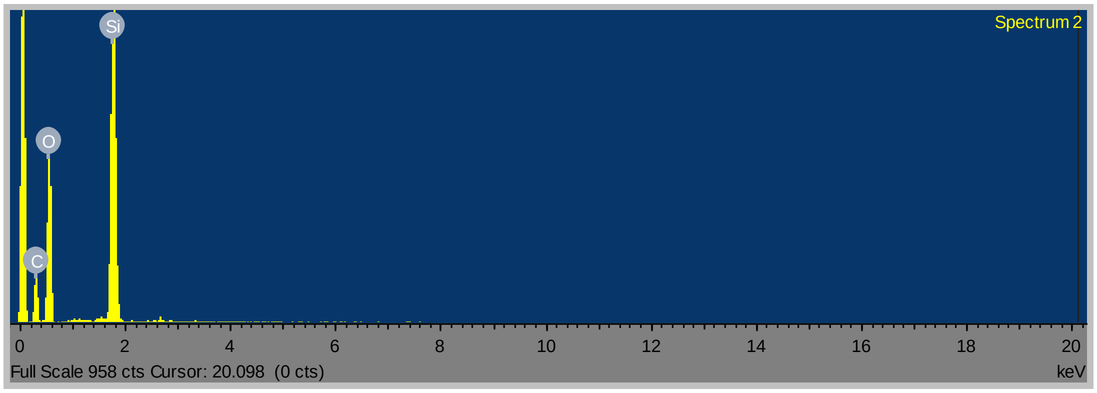
Figure 10E: Researcher during post-harvest studies

Appendix 11: EDX of cellulose

Elemental composition in weight %

Spectrum	Carbon	Oxygen	Silicon	Total
1	32.78	46.72	20.50	100
2	29.67	50.29	20.04	100
3	35.73	49.32	14.95	100
4	44.86	43.04	12.10	100
5	42.63	49.75	7.62	100
Mean	37.13	47.82	15.05	100
Std dev.	6.45	3.01	5.44	
Max	44.86	50.29	20.5	
Min	29.67	43.04	7.62	

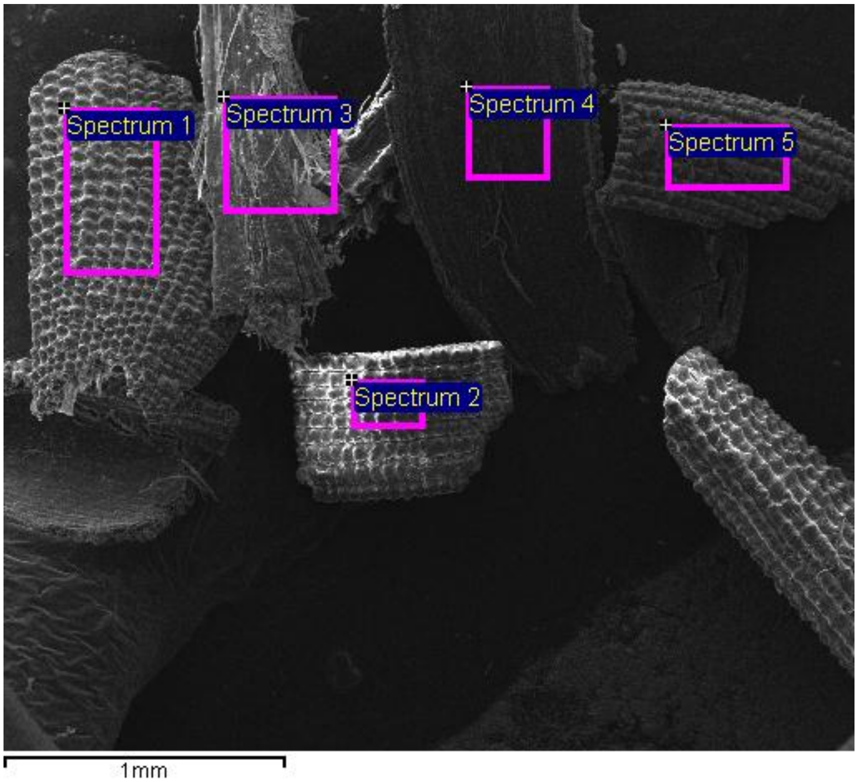


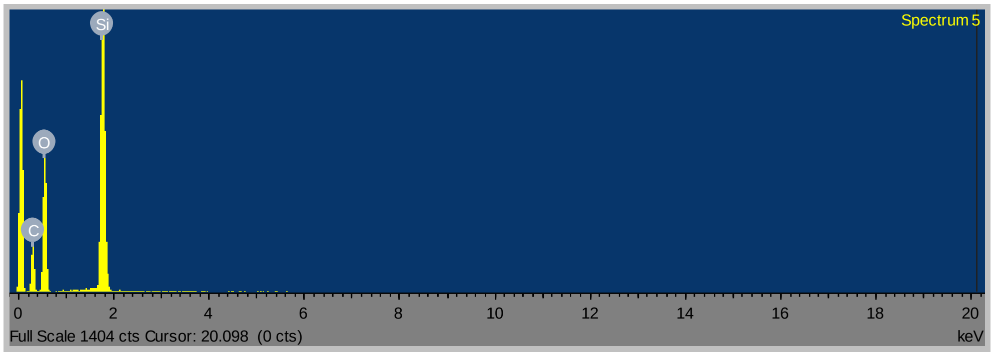

Spectrum 2
Si
O
C
0
2
4
6
8
10
12
14
16
18
20
keV
Full Scale 958 cts Cursor: 20.098 (0 cts)

Appendix 12: EDX of CMC

Elemental composition of CMC in weight %

Spectrum	Carbon	Oxygen	Silicon	Total
1	29.94	49.82	20.24	100
2	26.92	48.76	24.32	100
3	42.65	51.09	6.26	100
4	43.62	52.79	3.59	100
5	31.95	48.71	19.34	100
Mean	35.02	50.23	14.75	100
Std dev.	7.63	1.73	9.21	
Max	43.62	52.79	24.32	
Min	26.92	48.71	3.59	




Si
O
C
Spectrum 5
0
2
4
6
8
10
12
14
16
18
20
Full Scale 1404 cts Cursor: 20.098 (0 cts)
keV