Addis Ababa University

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School of Chemical and Bio Engineering

Synthesis and Characterization of Cellulose-Based Hydrogels Using Citric Acid as a Crosslinker

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School of Chemical and Bio Engineering

This is to certify that the thesis prepared by *Alula Gebregergs*, entitled "*Synthesis and Characterization of Cellulose-Based Hydrogels Using Citric Acid as a Crosslinker*" and submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering (Process Engineering) complies with the regulation of the University and meets the accepted standards with respect to originality and quality.

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Declaration

I, the undersigned, declare that this thesis is my original work, has not been presented for a degree in this or any other university, and all sources of materials used for the thesis have been fully acknowledged.

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This thesis has been submitted for examination with my approval as a university advisor.

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Abstract

Incorporation of synthetic polymers along with natural polymers to prepare hydrogels can improve the performance of these materials. The objective of this study was to synthesize and evaluate a hydrogel using sodium carboxymethyl cellulose (NaCMC), polyethylene glycol (PEG), and citric acid. The Fourier Transform Infrared analysis of these raw materials confirms that the functional groups involved in the crosslinking reaction are present. The effect of preparation conditions such as polymer composition, reaction temperature (65-95 ℃), reaction time (8-24 hours) and citric acid concentration (10-20%) on the swelling degree was evaluated. The results demonstrated that superabsorbent hydrogels were produced with swelling degree typically ranging from 215% to 5595%. The swelling degree was significantly influenced by the temperature, concentration of crosslinker, time and polymer composition. In addition to their high swelling capacity, Thermogravimetric analysis of NaCMC based hybrids that were prepared by blending with 20 wt.% PEG has shown good stability. Response surface methodology was used to optimize the synthesis process. The optimum hydrogel with swelling degree of 6748% was synthesized at 72.38 ℃ temperature, 8 hours of reaction time, 16.54% citric acid concentration, and 80% NaCMC and 20% PEG composition. Influence of ionic strength and pH of the external solution on the swelling behavior of the hydrogel was investigated. Urea as an agrochemical model was loaded onto the obtained hydrogel to study the slow release of the nutrient. The hydrogel was responsive to the variation of ionic strength and pH of the external solution. Due to its considerable slow urea release and good water retention capacity, it could be used in agricultural application.

***Keywords**: Carboxymethyl cellulose, Superabsorbent hydrogel, Slow release, Swelling*

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Acronyms and Abbreviations

ASTM	American Standards Testing Materials
ANOVA	Analysis of Variance
CA	Citric Acid
CCD	Central Composite Design
CMC	Carboxymethyl Cellulose
DSC	Differential Scan Calorimetry
DVS	Divinylsulphone
ECH	Epichlorohydrin
FTIR	Fourier-Transform Infrared
HEC	Hydroxyethyl Cellulose
IR	Infrared
NaCMC	Sodium Carboxymethyl Cellulose
NMR	Nuclear Magnetic Resonance
PEG	Polyethylene Glycol
PVA	Polyvinyl Alcohol
RSM	Response Surface Method
SAH	Superabsorbent Hydrogel
SAP	Superabsorbent Polymer
SEM	Scanning electron microscope
TGA	Thermogravimetric Analysis
WSC	Water Soluble Carbodiimide

Conc.	Concentration
Comp.	Composition
DS	Degree of Substitution
g	Gram
hr.	Hour
min.	Minute
NaCMC/ CA10	NaCMC Hydrogel Crosslinked with 10% (w/w) Citric acid
NaCMC/PEG20	Hydrogel with polymer composition of 80 wt.% NaCMC and 20 wt.% PEG
NaCMC/PEG40	Hydrogel with polymer composition of 60 wt.% NaCMC and 40 wt.% PEG
NaCMC/PEG20/CA10	NaCMC and PEG blended hydrogel crosslinked with 10% (w/w) Citric acid
Temp.	Temperature
wt.%	Weight percent

Chapter 1

Introduction

1.1. Background

Hydrogels are materials that exhibit a three-dimensional network of hydrophilic polymers, capable to swell and retain a considerable amount of water within its structure(Ullah et al., 2015). By virtue of their excellent hydrophilicity, permeability, and compatibility, polymer-based hydrogels have been used extensively as drug delivery, food, cosmetics, high water- absorbing resin, contact lenses, corneal, implant, substitutes for skin, tendons, ligaments, cartilage, and bone(Rimmer, 2011). Moreover, super porous hydrogels have been successfully used as soil improvers, slow-release fertilizers, pesticide release devices(Davidson et al., 2013).

Superabsorbent polymers (SAPs) are the most commercially thriving materials of the hydrogel class. The superabsorbent hydrogels (SAHs) with the capacity to absorb urine and blood are used in hygiene products, such as in baby diapers and feminine incontinence products(Sannino et al., 2004). SAHs are crosslinked hydrophilic polymers insoluble in water, but capable to absorb large amounts of water through a swelling process. Hydrogels swell to a volume much larger than their original size, with a weight of 10-1000 times higher than their initial one. For this feature, hydrogels have been widely used in many areas such as diapers and napkins for personal care, drug delivery systems in the pharmaceutical area, in catalysis, and in bio-sensing.

Petroleum-based chemicals, such as acrylic acid, acrylamide, and acrylonitrile have been the main ingredients for the manufacture of synthetic hydrogels. The incorporation of fillers, such as clay(Naghsh & Shams, 2017) and graphene oxide(Sadiku, 2017), in the polymer matrix can efficiently enhance the swelling ability, the gel strength, and the thermal stability of synthetic SAP. Despite their ability to absorb a large amount of water, acceptable gel strength, and low cost, synthetic hydrogels application can be limited by their poor biocompatibility and biodegradability. Therefore, research studies on bio-based SAP, such as cellulose(Kono & Fujita, 2012), starch(Xiao, 2012), chitosan(Yao et al., 2012), and proteins(Ni & Zhang, 2017), have been growing due to their non-toxicity, biocompatibility, and biodegradability(Nnadi & Brave, 2013). Furthermore, bio-based SAP composites and nanocomposites have been developed through the incorporation of organic and inorganic filler (Ni & Zhang, 2017).

Polysaccharide-based hydrogels behave as smart materials and offer a variety of properties that can be exploited in several applications. Cellulose is an environmentally friendly polysaccharide alternative to conventional materials and exhibit properties that make it very attractive in many applications. Nowadays, cellulose derivatives-based hydrogels have gained a great popularity in agriculture(Paulino et al., 2015) and pharmaceutical industry(Peppas et al., 2000), and become more and more imperative in these fields, owing to the production of new derivatives with extended applications.

Carboxymethylcellulose (CMC) and its sodium salt(NaCMC) are biopolymers derived from cellulose. It is a copolymer of ß-D-glucose and ß -D- glucopyranose 2-O-(carboxymethyl)-monosodium salt which is connected via ß -1,4-glycosidic bonds. It is widely used in food and pharmaceutical industry. The mechanical properties of NaCMC films can be improved by blending with other polymers(Muppalla et al., 2014). For instance, polyvinyl alcohol (PVA) and polyethylene glycol (PEG) are versatile polymer with many industrial applications, and it may be the only synthesized polymer whose backbone is mainly composed of C– C bonds that is absolutely biodegradable and regarded as safe(Zalipsky & Harris, 1997). They have a planar zigzag structure, which is water-soluble on account of its elevated polarity. PVA has great potential for application in the production of a biodegradable film(Salmawi, 2007).

1.2. Statement of Problem

Acrylic acid based superabsorbent polymers (SAP) production are strongly dependent on petroleum-derived chemical feedstocks. The partial and/or complete replacement of petroleum-based chemicals with their equivalent natural polymers is a growing international effort. Cellulose is one of the most abundant biopolymers provided by nature and that could impart improved or new physical properties through chemical functionalization. Sodium carboxymethyl cellulose, cellulose derivative, has imparted hydrophilic property and gel formation ability. This property makes it ideal for making natural polymer-based hydrogel with good swelling capacity(Pan & Ragauskas, 2012).

Conventional synthetic polymers used to prepare hydrogels are hydrophobic in nature and chemically stronger compared to natural polymers. Their mechanical strength results in slow degradation rate, but on the other hand, mechanical strength provides the durability as well. Hence to prepare cellulose-based hydrogels with good mechanical stability, biodegradable synthetic polymers such as polyethylene glycol and polyvinyl alcohol are incorporated as network modifiers and molecular spacers (Esposito et al., 2005). The mechanical stability, swelling ability, and biodegradability of cellulose-based hydrogels could be modulated by adjusting the ratio of sodium carboxymethyl cellulose (Adel et al., 2010) and through optimization of synthesis parameters.

Since most of the chemicals used for crosslinking hydrogels are toxic, unreacted chemicals are usually eliminated after crosslinking through extensive washing in distilled water. However, as a rule toxic crosslinkers should be avoided, in order to preserve the biocompatibility of the final hydrogel, as well as to ensure an environmentally sustainable production process. Citric acid, a crosslinking agent able to overcome toxicity was selected in this study.

Synthetic SAPs are being used as soil conditioners (providing nutrients and moisture) to aid plant establishment and growth in drought-prone growing media. The most widely employed polyacrylate based SAPs are reported to degrade at rates less than 10% per year. Because of their very low degradation rate, acrylic SAPs are regarded as potential pollutants in the soil. As a result, in the last decade, the increasing interest in environmental issues has led manufacturers and researchers to focus on the development of alternative, environmentally friendly superabsorbent polymers.

Hence this thesis work will provide a means to produce a hydrogel with water sorption capability. These hydrogels will be synthesized using renewable, environmentally friendly cellulose derivative and sustainable procedure. Potential of these hydrogels in the agricultural sector to improve water use and nutrient delivery will also be investigated. To the best of my knowledge, there is no scientific report that used citric acid as a crosslinker for NaCMC/PEG hydrogel that was used for agricultural application.

1.3. Objective of the Research

1.3.1. General Objective

The general objective of this work was to synthesize cellulose-based hydrogel using citric acid as a crosslinker and evaluate its water retaining capability.

1.3.2. Specific Objectives

The specific objectives are:

- To synthesize superabsorbent hydrogel using different ratio of carboxymethyl cellulose and polyethylene glycol
- To characterize chemical properties of the product
- To study swelling property and water holding capacity of these different superabsorbent hydrogels with a specific focus on water sorption application
- To determine the optimal operating conditions for the synthesis of the hydrogel with maximum water sorption capacity and to study the main effect and interaction effect of the factors that are involved in the synthesis of the hydrogel
- To investigate the effectiveness of citric acid as crosslinking agent for synthesis of hydrogel

1.4. Significance of the Study

Importance of exploring hydrogel application in the agriculture sector in Ethiopia which is continuously influenced by scarcity of water is crucial. The water management problem could be resolved through measures that increase the soil moisture retention capacity and the water use efficiency. The employment of superabsorbent hydrogels can increase the capacity of the soil to store and release water under stress. These superabsorbent hydrogels could also be used for slow release of agrochemicals which prevent leaching into soil and improve the accessibility of the nutrients to the plants.

It is worth noting that, being acrylate-based, most commercial superabsorbent products are not biodegradable. Cellulose-based hydrogels fit perfectly in the current trend to develop environmentally friendly alternatives to acrylate-based superabsorbent hydrogels.

In general, the significance of this research can be seen from different perspectives.

1. Provide a means to exploit and manage local resources (cellulose)
2. Finding an environmentally friendly alternative to acrylate-based superabsorbent with almost the same performance
3. Provide alternative biodegradable raw material to the hygiene industries that produce diapers, feminine napkins, and hospital bed sheets
4. Serve as a starting material for further research studies on the application cellulose and cellulose derivate based hydrogels in the agricultural sector in Ethiopia where the paucity of water is a common problem

1.5. Scope of the Study

The thesis work generally covers synthesis of cellulose-based hydrogel and characterization of used raw materials and the prepared hydrogel. The hydrogel is based on sodium carboxymethyl cellulose backbone, polyethylene glycol spacer which is regarded as safe, and citric acid crosslinker. Furthermore, factors (i.e. polymer composition, reaction temperature, reaction period and crosslinker concentration) that affect the hydrogel synthesis are studied, and the hydrogel synthesis process is also optimized. Effect of ionic strength and pH of the external solution on the swelling behavior of the obtained hydrogel is examined. To explore the agricultural application of the hydrogel; water holding capacity, and urea loading and release potential is investigated.

Chapter 2

Literature Review

Hydrogels are, mainly, structures formed from polymers and/or polyelectrolytes, and contain large amounts of trapped water. Concerning definitions of hydrogel types, according to the source, hydrogels can be divided into those formed from natural polymers and those formed from synthetic polymers. On the basis of the cross-linking method, the hydrogels can be divided into chemical gels and physical gels. Physical gels are formed by molecular self-assembly through ionic or hydrogen bonds, while chemical gels are formed by covalent bonds.

Synthetic polymer-based hydrogels have been reported such those formed by cross-linking poly(ethylene glycol), poly(vinyl alcohol), poly(amido-amine), poly(N-isopropylacrylamide), polyacrylamide, and poly(acrylic acid) and their copolymers(Laftah et al., 2011). Synthetic hydrogels like PEG-based hydrogels have advantages over natural hydrogels, such as the ability for photopolymerization, adjustable mechanical properties, and easy control of scaffold architecture and chemical compositions. A number of polysaccharides have similar properties to PEG in terms of biocompatibility and low protein and cell adhesion, and they can be biodegraded to nontoxic products that are easily assimilated by the body or by the soil(Esposito et al., 2005)

Various hydrogels from natural polymers have been fabricated using alginate, starch, gelatin, chitosan, cellulose and their derivatives showing their potential in biomaterials application because of their safety, hydrophilicity, biocompatibility, and biodegradability.

Cellulose, the most abundant renewable resource on earth, will become the main chemical resource in the future(Chang & Zhang, 2011). Moreover, numerous new functional materials from cellulose are being developed over a broad range of applications, because of the increasing demand for environment-friendly and biocompatible products. Cellulose having abundant hydroxyl groups can be used to prepare hydrogels easily with fascinating structures and properties. There is a need to study cellulose-based hydrogels in both fundamental research and industrial application because of superabsorbent materials application range from personal hygienic products to water reservoir systems for agriculture.

2.1. Cellulose-based Hydrogels

Outstanding biocompatibility of the cellulose and cellulose derivatives define their extensive usage in different applications, such as in pharmaceutical compounded and industrialized products. Cellulose esters and cellulose ethers are two main groups of cellulose derivatives with different physicochemical and mechanical properties.

Cellulose esters are water-insoluble polymers with good film-forming characteristics which find a variety of applications, as classical material-coatings and controlled-release systems, hydrophobic matrices, and semipermeable membranes for applications in pharmacy, agriculture, and cosmetics. Moreover, cellulose esters (e.g., cellulose acetate (CA), cellulose acetate phthalate (CAP), cellulose acetate butyrate (CAB), cellulose acetate trimelitate (CAT), hydroxypropylmethyl cellulose phthalate (HPMCP)) are used extensively as binders, fillers, and laminate layers in composites and laminates, as excellent material for photographic films, and as membrane-forming materials(Lee et al., 2015) applicable for gas separation, water purification, food and beverage processing, and biomedical applications.

In contrast, cellulose ethers which exhibit a good solubility, high chemical resistance, non-toxic nature, and low cost are utilized in drilling technology and building materials, as additives for drilling fluids and processing of plaster systems, as well as stabilizers in food, pharmaceutical, and cosmetics formulations as the main component. Moreover, cellulose ethers are widely used as important excipients for designing matrix tablets. The most commonly used cellulose ethers are methyl cellulose (MC), ethyl cellulose (EC), hydroxyethyl cellulose (HEC), carboxymethylcellulose (CMC), sodium carboxymethyl cellulose (NaCMC), hydroxypropyl cellulose (HPC) and hydroxypropylmethyl cellulose (HPMC).

Cellulose ethers are generally hydrophilic and convert to hydrogel after exposing to water. Both types of soluble and insoluble cellulose ethers can absorb water and form a gel. Matrix tablets made from the soluble cellulose ethers form hydrogels which gradually dissolve in water until it disappears (dissolution-controlled drug delivery system). However, the insoluble cellulose ether coatings remain as a viscose gel around tablets allowing the diffusion of drug molecules within this layer (diffusion-controlled drug delivery system)(Sahu et al., 2013).

Among the abovementioned cellulose ethers, only sodium carboxymethyl cellulose is a polyelectrolyte, and thus a 'smart' cellulose derivative which shows sensitivity to pH and ionic strength variations. Indeed, the presence of sodium carboxymethyl cellulose in a cellulose-based hydrogel provides the hydrogel itself with electrostatic charges anchored to the network, which have a double effect on the swelling capability. On one side, the electrostatic repulsion established between charges of the same sign forces the polymer chains to a more elongated state than that found in a neutral network, thus increasing the swelling. On the other hand, the counterions that are present in the gel to ensure macroscopic electrical neutrality induce more water to enter the network. The polyelectrolyte nature of sodium carboxymethyl cellulose makes it ideal for the development of superabsorbent hydrogels with a smart behavior(Sannino et al., 2009).

Furthermore, a composite of cellulose and some cellulose derivatives can play vital roles in the enhancement of the performance of absorbent products. Cellulose itself, in the form of cellulosic fibers or nano-fibers, can provide water-holding capacity and channeling of fluids over a wide dimensional range(Pan & Ragauskas, 2012). Also, for obtaining the hydrogels with specific properties, cellulose can be combined with synthetic or natural polymers. Cellulose composite hydrogel was prepared from cellulose and polyvinyl alcohol (PVA) in 6/4/90 NaOH/urea/water (w/w) aqueous solution using both physical and chemical crosslinking methods(Chang et al., 2008).

2.2. Application of Cellulose-based Hydrogels

2.2.1. Hygiene

Special hydrogels, as superabsorbent materials, are widely employed in the hygienic domain (disposable diapers and female napkins). It is estimated that the majority of parents in industrialized countries, along with thousands of hospitals and group care centers around the world, use disposable diapers containing a superabsorbent polymer (SAP). Several medical studies have provided clear evidence that disposable diapers play an important role in reducing the risk of spread of gastrointestinal illnesses and are significantly more effective than double cloth diapers and plastic overpants. With the superabsorbent materials, a new generation of high-performance diapers was created. Not only did the diapers become thinner but also they had improved retention performance which helped reduce leakage and diaper rash(Sannino et al., 2004). Different attempts have been made to produce disposable diapers, napkins, hospital bed sheets, sanitary towels and other similar products.

Hydrogels, based on sodium carboxymethyl cellulose and hydroxyethyl cellulose crosslinked with divinyl sulphone (DVS), possess swelling capabilities comparable with those displayed by SAP, and high-water retention capacities under centrifugal loads. Such hydrogels are able to absorb up to one liter of water per gram of dry material, without releasing it under compression. The hydrogel can be produced both in form of powder or of a bulk material with a well-defined shape and a strong memory of its shape after swelling.

These significant results have been achieved by inducing a microporous structure in the hydrogel, by means of a phase inversion desiccation technique in acetone (i.e., a non-solvent for cellulose), which increased the water absorption, as well as the swelling kinetics, due to capillarity effects. The scanning electron microscopy (SEM) images of an acetone-dehydrated and air-dried cellulose-based hydrogel revealed the surface of the former displays foldings and voids, whereas the latter shows a smooth and dense surface(Sannino et al., 2009).

2.2.2. Biomedical

Another application of hydrogels is wound dressings which are designed to promote healing while protecting the wound from infection. This is particularly important in cases of chronic wounds (e.g., ulcers), which fail to heal properly. Since a moist environment encourages rapid healing, hydrogels are optimal candidates for the development of wound dressings, either as sheets or in amorphous form. Amorphous hydrogels should be designed to maintain the right moisture balance in the wound bed, by hydrating the wound surface and/or absorbing the wound exudates. They also provide non-adherent dressings which can be easily removed without any damage to the wound bed. Hydrogel transparency is a further advantage in this application, as wound healing can be easily monitored. The most advanced hydrogel dressings include antimicrobial agents, such as silver ions, in their formulation(Ma et al., 2015).

Regenerative medicine is an interdisciplinary field which deals with the induced regeneration of tissues and organs in vivo, by means of a scaffolding material or template that guide and support the cells during the synthesis of new tissues(Amlizan & Wui, 2011). Due to their large water content, hydrogels are highly biocompatible, possess rubbery mechanical properties close to those of soft tissues and usually allow the incorporation of cells and bioactive molecules during the gelling. Moreover, although cells do not readily attach to highly hydrophilic surfaces, the bulk or surface chemistry of hydrogels can be easily modified with extracellular matrix domains, which promote cell adhesion as well as specific cell functions. Hydrogels are thus likely to be ideal platforms for the design of biomimetic scaffolds for tissue regeneration.

The use of cellulose and its derivatives as biomaterials for the design of tissue engineering scaffolds has received increasing attention, due to the excellent biocompatibility of cellulose and its good mechanical properties(Onofrei & Filimon, 2012). Ideally, for optimal tissue regeneration, the scaffold should be biodegradable, with a biodegradation rate matching that of the biological process of interest, but practically a slow degradation is often preferred, in order to minimize the risks associated to a premature resorption of the scaffold. In spite of its durability, cellulose is thus a candidate biomaterial for the design of tissue engineering scaffolds.

2.2.3. Agriculture

Moreover, there is an increasing interest in using superabsorbent hydrogels in agriculture. This is mainly due to the need to reduce water consumption and optimize water resources in agriculture and, horticulture and has a role in the promotion of a novel approach of human habit and culture towards water, to be treated as a benefit to save and not as an excess to waste.

In agricultural applications, superabsorbent polymers (SAP) granules are mixed with the soil in given amounts. After watering, the granules absorb the water by swelling, and then release it slowly through a diffusive mechanism, as the soil gets dry. In this way, irrigated water is not lost through drainage or evaporation while being efficiently supplied to the plant roots when needed. Furthermore, SAP granules increase their size upon swelling, thus enhancing soil porosity and providing a better oxygenation to the roots. A further advantage of SAPs in agriculture is that they can be loaded with nutritional substances and phytopharmaceuticals, which are then gradually released to the plants(Cannazza et al., 2014).

To prove the feasibility and the efficacy of the proposed technology, a pilot scale production plant was developed to produce the amount of hydrogel necessary for some studies being carried out in experimental greenhouses in the South of Italy, where the paucity of water is a common problem(Demitri et al., 2013). Preliminary results show great promise. The soil with the addition of small quantities of the product is able to remain humid for periods more than four times longer with respect to the soil watered without the presence of the hydrogel. A similar study of Polyelectrolyte cellulose-based hydrogel application for the cultivation of bean crop, typical of Southern Italy, was investigated in a pilot study(Satriani et al., 2018). The result showed that the combination of deficit irrigation and soil amendment hydrogel leads to a maximization of the crop productivity and water use efficiency.

2.3. Crosslinking Methods

Cellulose-based hydrogels can be achieved by the chemical or physical stabilization of cellulosic materials in aqueous solutions. Moreover, can be employed a number of crosslinking agents and catalysts to form hydrogels. Thus, the most widely used crosslinkers for cellulose derivatives are epichlorohydrin (ECH), aldehydes, aldehyde-based reagents, urea derivatives, carbodiimides and, multifunctional carboxylic acids. The crosslinking reactions between the cellulose chains activated by chemical agents may occur in water solution, organic solvents or even in the dry state.

2.3.1. Divinyl Sulphone (DVS)

A small difunctional molecule of DVS was used to form biodegradable cellulose-based hydrogels by creating intermolecular covalent bonds among polymer chains (Esposito et al., 1996). The swelling properties of these materials are comparable with those displayed by acrylate-based products(Lionetto et al., 2005). The DVS molecule presents two carbon-carbon (C=C) double bonds that can be opened and linked to the OH^- groups of the cellulose molecules. The polymerization is thus characterized by the first addition of DVS carbon-carbon double bond to the cellulose chain and a second addition. Only the latter leads to a crosslinked network.

Aqueous solutions of sodium carboxymethyl cellulose (NaCMC) and hydroxyethyl cellulose (HEC) was employed to form a hydrogel using DVS as a cross-linking agent(Capitani et al., 2000). The presence of HEC is necessary to promote quantitatively intermolecular rather than intramolecular cross-linking (Esposito & Mensitieri, 1996). In fact, poor cross-linking efficiency is reported if only NaCMC is used, seemingly due to the electrostatic repulsion between charged macromolecules and to the fact that few hydroxyl groups remain available for reaction at C_6, the most reactive position Nevertheless, due to its toxicity, DVS requires appropriate safety measurements during the production process and strict quality controls on the final product (i.e. all unreacted DVS has to be extracted from the gel before it can be applied).

2.3.2. Water Soluble Carbodiimide (WSC)

WSC does not chemically bind to polysaccharide molecules but seems to mediate ester bonds formation between carboxyl and hydroxyl groups belonging to different polysaccharide molecules. WSC can be found as a by-product of the reaction, in the form of a urea derivative, which displays a very low degree of cytotoxicity. The presence of WSC induces the intramolecular or intermolecular formation of an acid anhydride between two carboxyl groups, changing the WSC itself into a urea derivative; this anhydride is then responsible for the reaction with a hydroxyl group, to yield an ester bond between two polysaccharide molecules. However, the initial reaction of WSC with carboxyl groups is dependent on pH, the optimal pH ranging from 3.5 to 4.5.

Hydrogels based on hydroxyethyl cellulose (HEC), sodium carboxymethyl cellulose (NaCMC) and hyaluronic acid (HA) have been crosslinked with a water-soluble carbodiimide, which is both non-toxic and a ‘zero-length’ crosslinker (Sannino et al., 2005). The carbodiimide, which is washed out from the polymer network after the synthesis, is well-known to induce the formation of ester bonds among polysaccharide molecules without taking part in the linkage.

2.3.3. Esterification

Carboxylic acid was used as a crosslinking agent in various cellulose derivative systems and different mechanisms have been proposed to explain the crosslinking reaction of cellulose polymers with a carboxylic acid. The attachment of the polyfunctional carboxylic acids via esterification with a cellulosic hydroxyl group and its esterification with another cellulosic hydroxyl group produce crosslinked cellulose chains. This mechanism is based on an anhydride intermediate formation. Attachment of the carboxylic acid moiety to cellulose's hydroxyl group via esterification reaction of the first cyclic anhydride would expose a new carboxylic acid unit in carboxylic acid, which has the proper chemical connectivity to form a new intramolecular anhydride moiety with the adjacent carboxylic acid unit. Further reaction with a cellulose hydroxyl of another chain can then lead to crosslinking. The effectiveness of such carboxylic acids increases with their functionality in the order 1,2,3,4-butanetetra- carboxylic acid (BTCA) > tricarballylic acid (TCA) > succinic acid(Zhou et al., 1995).

Other literature data reveal new methods have been reported for obtaining cellulose-based hydrogels, namely by radiation(Borsa, 2014) and by absorption a monomer solution into a dried porous cellulose network, followed by the crosslinking inside the network(Cuadro et al., 2015).

2.4. Hydrogel Synthesis using Citric Acid

Cellulose-based hydrogels crosslinked with citric acid have been recently reported, which combine good swelling properties with biodegradability and absolute safety of the production process (Coma et al., 2003) (Demitri et al., 2008).

2.4.1. Citric Acid

Citric acid which is widely used in food and drug industry is an excellent crosslinking agent. Citric acid, extensively wide-spread in nature, is prepared commercially by fungal fermentation of glucose. Citric acid and its salts, with a good affinity for metal ions, are used in soft drinks, as an anti-oxidant in the food industry, as a sequestering agent for metal ions, as a cleaning, and polishing agent for metals, and as a mordant in dyeing.

Recently, citric acid was used as crosslinking agent in various cellulose derivative systems and different mechanisms have been proposed in the literature to explain the crosslinking reaction of cellulose polymers or cellulose derivative polymers with Citric acid(Rimmer, 2011)(Cuadro et al., 2015)(Demitri et al., 2008)(Capanema et al., 2018).

2.4.2. Reaction Mechanism

Since cellulose contains three hydroxyl groups per monomer and polyethylene glycol (PEG) has hydroxylated end groups, cross-linking by citric acid may occur between sodium carboxymethyl cellulose (NaCMC) with itself (Figure 2.3), PEG with NaCMC (Figure 2.4), and PEG with itself. When citric acid is heated, it will dehydrate to yield cyclic anhydride intermediate (Figure 2.2), that reacts with free hydroxyl groups of NaCMC or PEG.

The reaction mechanism involves attachment of the carboxylic acid moiety to cellulose's building block (glucose) hydroxyl group via esterification reaction. The first condensation of the anhydride with cellulose O-H leads to a fast disappearance of the anhydride C=O groups. Then the carboxylate groups of the citric acid linked to the polymer are capable of forming another intramolecular anhydride moiety. Further reaction of this anhydride with a cellulose hydroxyl of another chain can then lead to crosslinking. This second reaction is slower because it involves groups linked to large macromolecules and hence more sterically hindered as also reported for other cellulose crosslinking processes(Rimmer, 2011). However, the second reaction of citric acid could occur with the hydroxyl group of PEG forming NaCMC/ PEG composite network.

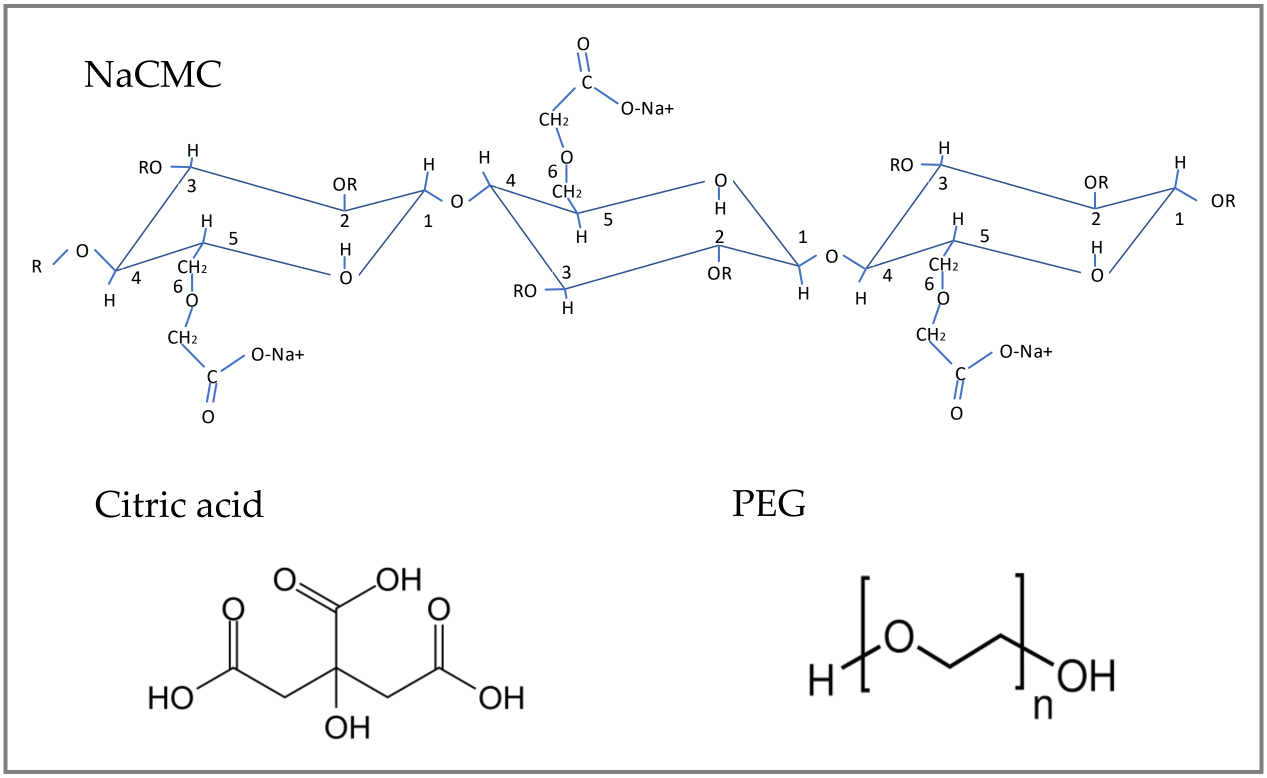

Figure 2.1 Schematic representation of sodium carboxymethyl cellulose(NaCMC[1]), Polyethylene Glycol(PEG) and Citric acid

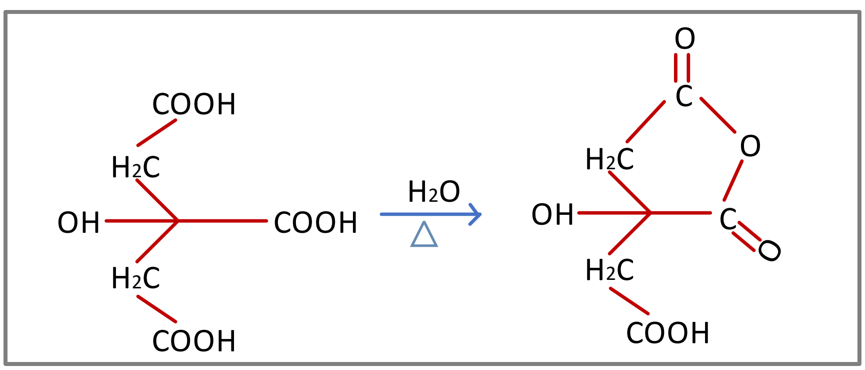

Figure 2.2 Formation of cyclic anhydride from citric acid

[1] R could be H or CH_2COO^- Na^+ substituent

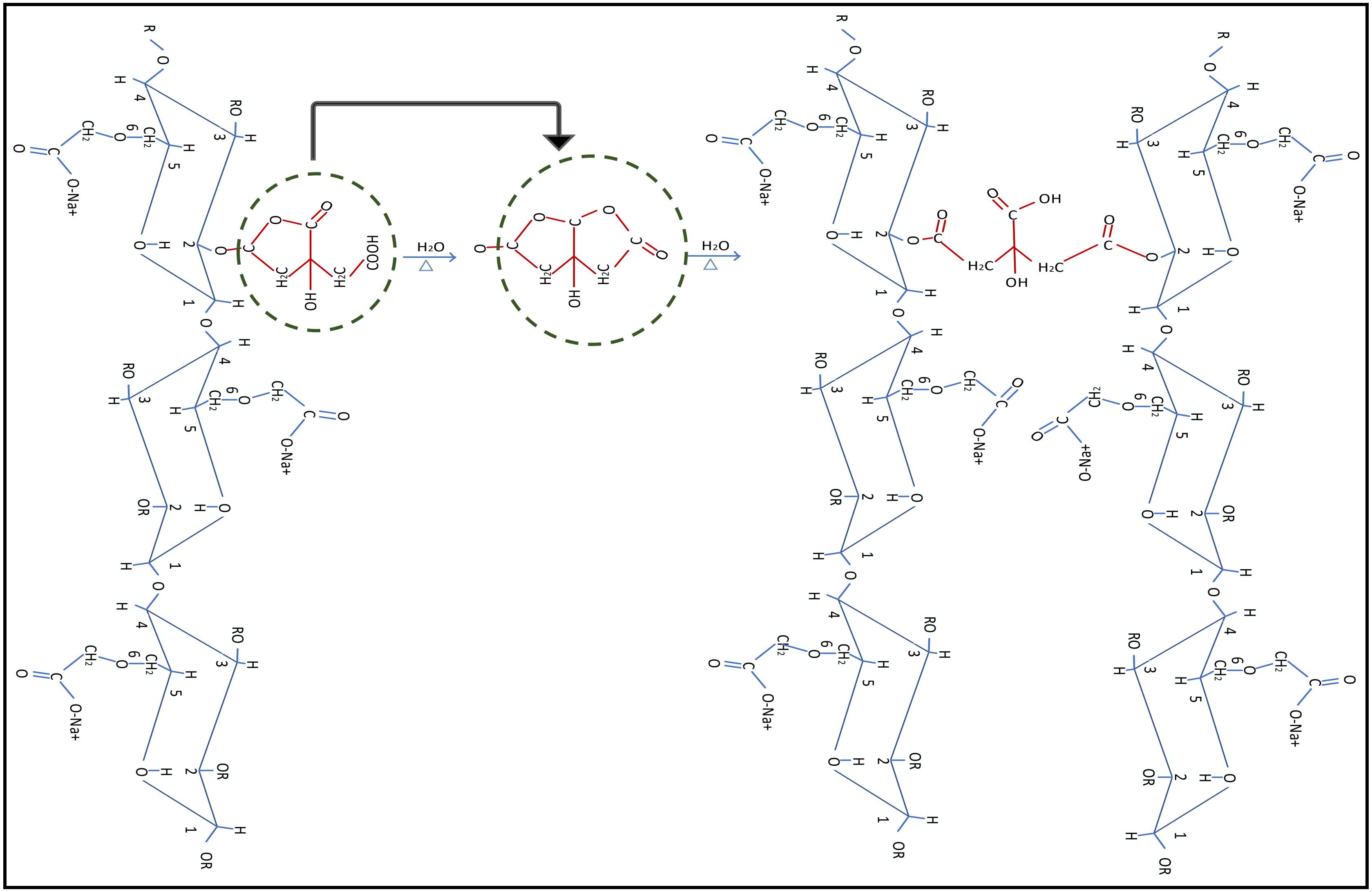

Figure 2.3 Citric acid anhydride reaction with sodium carboxymethyl cellulose (NaCMC)

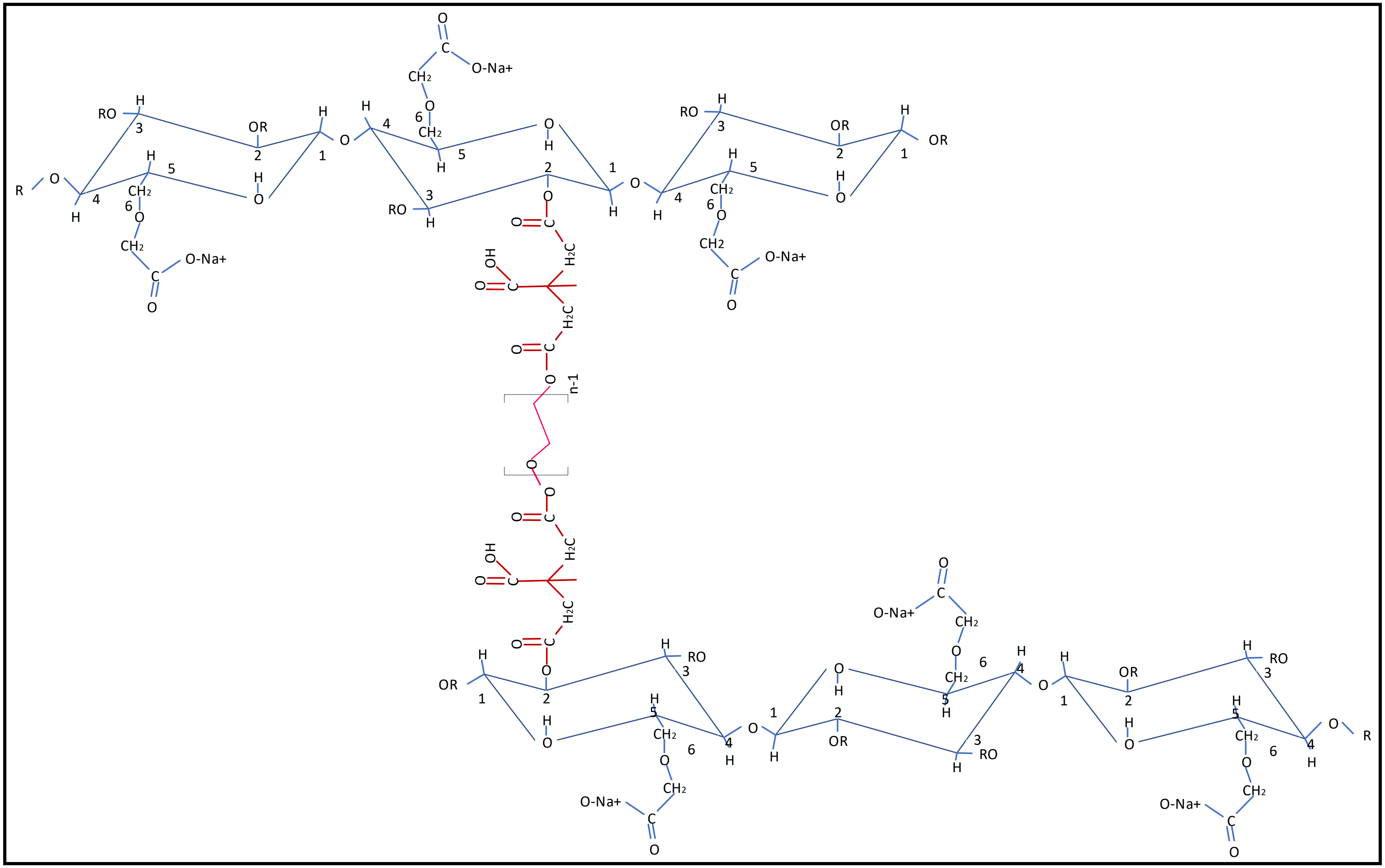

Figure 2.4 Sodium carboxymethyl cellulose (NaCMC) and polyethylene glycol (PEG) crosslinked with citric acid

2.4.3. Effect of Temperature on the Synthesis of Hydrogel

According to Demitri et al. work, the Differential Scan Calorimetry(DSC) analysis of citric acid shows that the anhydride forms when the temperature is raised above 60 ℃ (Demitri et al., 2013)(Demitri et al., 2008). Temperature about 60 ℃, attributed to a water loss process associated with the dehydration leading to the formation of cyclic anhydride intermediate. A complete degradation of citric acid starts at about 160 ℃. Moreover, the DSC analysis of neat sodium carboxymethyl cellulose (NaCMC) powder indicates a possible degradation peak above 100 ℃. Hence NaCMC is thermally stable below 100 ℃. Consequently, the synthesis temperature was varied between 65 ℃ and 95 ℃ to ensure citric acid crosslinking through the formation of cyclic anhydride intermediate without degrading the carboxymethyl cellulose sodium salt.

Chapter 3

Materials and Methods

3.1. Materials and Equipment

Chemicals used during the study were general purpose reagent NaCMC (BDH, England), PEG (HIMEDIA, India), $CaCl_2$ (BDH, England), NaCl (Merck, Germany), Citric acid (neolab, India), urea (neolab, India), NaOH (Merck, Germany), HCl (Merck, Germany), ethanol (BDH, England), Methyl red indicator and pure cellulose (for comparison). Solution with different pH were prepared using HCl(0.1N), NaOH(0.1N), andH_2SO_4(0.1N). All synthesis reactions were carried out using distilled water.

Synthesis and characterization of the hydrogels involve various equipment. Major equipment that were used during the experiments are electronic microbalance (Sartorius), graduated cylinder, Glass beakers, magnetic stirrer, polystyrene petri dish (diameter 60 mm), oven (DAS 42000, 224.2007), pH meter, pipette, water bath and Muffle furnace. All of the swelling measurements, both in distilled water and in water solutions, were carried out at room temperature using an electronic microbalance (Sartorius) with an accuracy of $\pm 10^{-5}$ g.

Perkin Elmer FTIR spectrometer (Perkin Elmer, 65, USA), X-ray diffraction (miniflex 300/600, Japan), and Thermogravimetric Analysis equipment (TA instrument, model: SDT Q600) were used to characterize the raw material and the synthesized hydrogel.

The overall structure of the experimental works is shown in Figure 3.1.

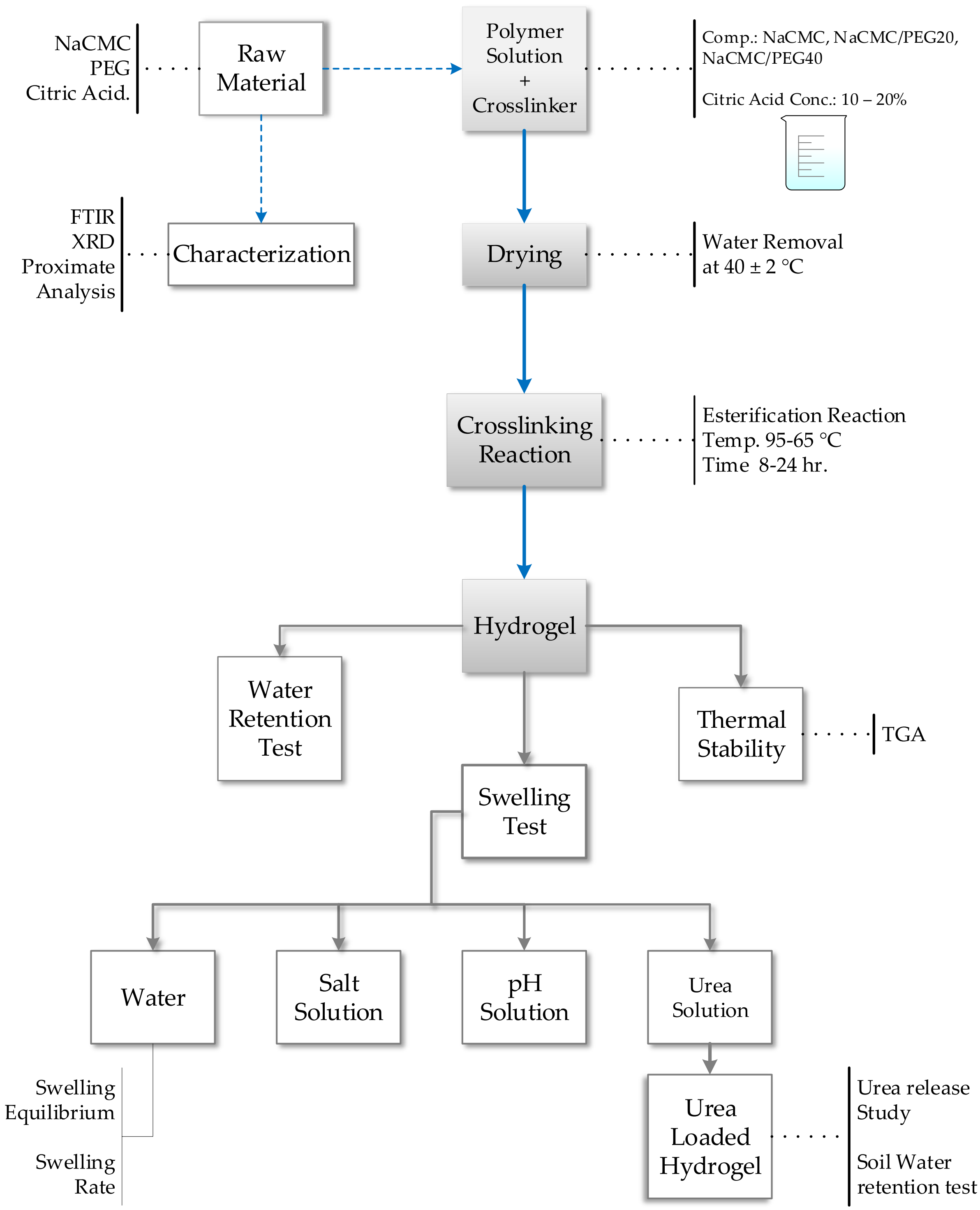

Figure 3.1 Framework of the experiment

3.2. Raw Material Characterization

The raw materials that were used for the synthesis of the hydrogel are NaCMC, PEG, and Citric acid.

3.2.1. Sodium Carboxymethyl Cellulose(NaCMC) Characterization

The moisture content and purity of the crude NaCMC was determined using standard test methods for Sodium Carboxymethylcellulose (ASTM D 1439 – 03). The measurement was done three times and the average was taken to increase the accuracy.

3.2.1.1. Moisture Content

3 g of the sample was weighed to the nearest 0.001 g and covered in weighing bottle. Then the bottle was placed in an oven at 105 ℃ for 2 hrs. with the cover removed followed by cooling the bottle in a desiccator, the cover was replaced and weighed. The sample was replaced in the oven for 30 mins., cooled, and reweighed until the mass loss was not more than 5 mg for 30 mins. drying time. Equation 3.1 was used to calculate the moisture content of NaCMC.

$$Moisture\ content(\%) = \frac{W_0 - W_f}{W_0} \times 100 \qquad (3.1)$$

Where W_0 : initial weight(g)

W_f : final weight(g)

3.2.1.2. Purity

First, the loss of mass was calculated as the percent of moisture in the sample using the above procedure.

3 g NaCMC was weighed, in the “as-received” condition, and mixed with 150 mL of ethanol (80%) that has been heated to 65 ℃, then it was immediately placed in a water bath adjusted at 60 ℃. The beaker was covered as completely as possible with a lid that will permit mechanical stirring. After 10 min stirring, to provide good agitation, the undissolved matter was allowed to settle with the beaker still in the bath. Then the hot supernatant was decanted and filtered, and 150 ml of ethanol (80%) that was heated at 65℃ was added to the undissolved matter and placed in the water bath.

After decanting the supernatant liquid, the insoluble matter was transferred to the crucible with the aid of ethanol (80%) at 65 ℃ in a wash bottle. The insoluble residue was first washed with 100 ml of ethanol (80%) at 65 ℃ followed by 50 mL of ethanol (95%) at room temperature, and finally with of ether at room temperature.

Then the crucible was placed in an oven at 105 °C for 1 hr. and the contents of the crucible was stirred break up the cake and facilitate complete drying and the crucible was placed in a desiccator. The crucible was dried for additional 1 hr. until the change in mass during the drying was less than 3 mg.

Then the percent sodium carboxymethylcellulose, P, on the dry basis was calculated as follows:

$$P = \frac{A \times 10000}{B \times (100 - C)} \tag{3.2}$$

Where A = mass of dried residue, g,

B = mass of specimen used, g, and

C = moisture in the specimen as received, %.

3.2.1.3. Ash Content

The crucible was preheated in a furnace at 600℃ for about 10 mins. to remove its moisture content and any physically adsorbed material and the crucible was placed inside a desiccator for 1 hr. Then, the crucible was weighed with and without the NaCMC. The furnace temperature was increased from 25 to 550 ℃ for 20 min and 550 to 600 ℃ for 30 mins. The sample was held at 600 ℃ for 4 hrs. Finally, it was cooled at room temperature. The weight of the sample before heating (W_1) and after heating (W_2) was used to determine the amount of ash content present in the sample. In this test, the amount of residual substance is equal to the ash present in the sample. The percentage of ash in the sample was calculated using equation (3.3).

$$Ash\ Content(\%) = \frac{W_2}{W_1} \times 100 \qquad (3.3)$$

Where $W_1 = W_{Crucible+Sample} - W_{Crucible}$

$W_2 = W_{Crucible+Ash} - W_{Crucible}$

3.2.1.4. Degree of Substitution

The DS was determined using a calcination-titration method as described by Mansouri et al. (Mansouri et al., 2015). A mass(m) of the NaCMC was weighed into a ceramic crucible and then it was mineralized inside a furnace at a maximum temperature of 600 ℃. The furnace temperature was increased from 25 to 550 ℃ for 20 min and 550 to 600 ℃ for 30 min. The sample was held at 600 ℃ for 4 h. Finally, it was cooled at room temperature. Ash containing Na_2O and possibly traces of NaCl, was dissolved in 100 mL of hot distilled water (80 ℃). 20 mL of this solution was titrated with 0.1 N Sulphuric acid (H_2SO_4) using methyl red as an indicator. The red methyl indicator was added to the solution which turned to yellow. The solution is then dosed with 0.1 N H_2SO_4 (0.05 M) until a red color appeared (the first endpoint). The reddish solution is heated to remove the dissolved CO_2 until the yellow coloration regenerates. A second titration is performed with 0.1 N H_2SO_4 to a sharp end point. DS was calculated using the following equation:

$$DS = \frac{0.162 \times \frac{0.1 \times A}{m}}{1 - 0.08 \times \frac{0.1 \times A}{m}} \tag{3.4}$$

where: 162 is the molecular weight of the anhydrous glucose unit and

80 the net increment in the anhydrous glucose unit for every substituted carboxymethyl group.

A: the volume (mL) of 0.1 N H_2SO_4 added and

m: mass of NaCMC, g.

3.2.2. Fourier Transform Infrared (FTIR) Spectroscopy

The functional group analysis of the raw materials used was carried out using FTIR spectroscopy. The FTIR spectra were recorded on spectrum 65 FT-IR (perkinElmer) equipped with KBr beam splitter. The sample was mixed with pre-dried KBr and the mixture was compressed to form a transparent pellet that was analyzed using transmission method of 400-4000 cm^{-1} at a spectral resolution of 4 cm^{-1}.

3.2.3. X-ray Diffraction (XRD)

Evaluation of the phase and morphology of raw material was conducted using miniflex 300/600, Japan at 40 kV and a current of 15 mA with Cuka radiation (1.54059-1.54441). The samples were placed on a sample holder made up of silicon wafer and the measurements were taken continuously from 10° to 70° angles.

3.3. Synthesis of Crosslinked Hydrogel

Sodium carboxymethyl cellulose (NaCMC) solution (2% w/v) was prepared by adding NaCMC powder (2.0 g) to 100 mL of distilled water and stirring at room temperature until complete solubilization occurred. After dissolution, the crosslinking agent, citric acid (CA), was added under stirring at concentrations of 10%, 15%, and 20% weight of the NaCMC polymer and homogenized for 20 mins. Then, 40 mL of the solutions were poured into plastic molds (polystyrene petri dish, diameter = 60 mm) and was allowed to dry at 40 ± 2 ˚C for 24 hrs. to remove water. Lastly, the samples were kept at 65 ± 2, 80 ± 2, and 95 ± 2 ℃ for 8, 16 and 24 hrs. for the crosslinking reaction (slow evaporation method) to take place. As a reference, a sample without CA (NaCMC/CA 0%) was also prepared and dried following the same thermal treatment.

To produce sodium carboxymethyl cellulose (NaCMC) and polyethylene glycol (PEG) blend, NaCMC/PEG solutions were prepared by adding 1.6 g of NaCMC and 0.4 g PEG (NaCMC/PEG20)[b] and 1.2 g of NaCMC and 0.8 g of PEG (NaCMC/PEG40)[c] to 100 mL of water and stirring at room temperature until complete solubilization occurred. After dissolution, the crosslinking agent, CA was added under stirring at concentrations of 10%, 15%, and 20% (W/W) to the NaCMC/PEG polymer and homogenized for 20 mins. Afterwards, the solutions were casted in plastic molds (polystyrene petri dish, diameter = 60 mm) and dried as described in the aforementioned section.

[b] Blend of 80 wt.% NaCMC and 20 wt.% PEG
[c] Blend of 60 wt.% NaCMC and 40 wt.% PEG

3.4. Experimental Design

The experiment was designed using response surface methodology where different synthesis parameters (i.e. raw material composition, citric acid concentration, time and temperature of crosslinking reaction) were varied and their effect on the hydrogel was analyzed. Randomization of the experimental runs and analysis of the experimental data was carried out using Design Expert 7.0.0. Face-centered Central Composite Design was used to determine the optimal conditions for the synthesis of the cellulose-based hydrogel.

The central composite method uses least squares regression to fit the data to a certain model. The adequacy of the model was determined by evaluating the lack of fit, obtained from ANOVA that was generated from it. Statistical significance of the model and the model variables were also determined at 5% probability level ($\alpha = 0.05$).

Table 3.1 Experimental factors and levels

Design Summary								
Study Type	Response Surface			**Runs**	60			
Initial Design	Central Composite			**Blocks**	No Blocks			
Design Model	Quadratic			**Levels**	3			
Factor	**Name**	**Units**	**Type**	**Low Actual**	**High Actual**	**Low Coded**	**High Coded**	**Mean**
A	Temp.	℃	Numeric	65.00	95.00	-1.000	1.000	80.000
B	Time	hr.	Numeric	8.00	24.00	-1.000	1.000	16.000
C	CA Conc.	%	Numeric	10.00	20.00	-1.000	1.000	15.000
D	Comp. (PEG content)	%	Categoric	0 [d]	40 [e]			20[f]

[d] Polymer composition of 100% NaCMC
[e] Polymer composition of 60% NaCMC and 40% PEG
[f] Polymer composition of 80% NaCMC and 20% PEG

3.5. Characterization and Analysis of the Hydrogel

3.5.1. Swelling Measurements

Hydrogel samples were prepared to study the effect of both the chemical composition and gelation procedures applied. Since it is difficult to characterize hydrogels analytically, swelling measurement was employed to understand the effect of synthesis parameter on the hydrogel. To reach the swelling equilibrium, the samples were incubated in distilled water for 24 hrs. at 20 ℃ (Chang et al., 2008). The equilibrium swelling was determined experimentally and percentage of swelling was expressed using equation (3.5).

$$Swelling\ (\%) = \frac{W_s - W_0}{W_0} \times 100 \tag{3.5}$$

Where W_s is the weight of the swollen gel at 25℃

W_0 is the weight of the gel at dry state

3.5.2. Swelling Kinetics

Water holding capacity and the sorption rate of the hydrogel are both important for the envisaged application, consequently swelling kinetics of the hydrogel was also studied.

After determining the optimum hydrogel, the sorption rate of the optimum hydrogel was assessed by monitoring the weight gain of the samples after immersion in distilled water for different time lengths (10, 20, 30, 60, 120, 180, and 300 minutes) and expressed as swelling ratio (SR) variations.

$$SR = \frac{W_s}{W_0} \tag{3.6}$$

3.5.3. Moisture Retention Capability

Pre-weighed CMC/PEG hydrogel discs with a thickness of 2 mm were allowed to swell at room temperature in a petri dish containing distilled water. The samples were weighed initially (M_0) and at different time intervals (M_t). Moisture retention capability was measured using the equation:

$$Moisture\ retention(\%) = \frac{M_t}{M_0} \times 100 \tag{3.7}$$

Where w_t : Weight of the swollen gel in distilled water at time t at 20°C

3.5.4. Hydrogel Swelling in Salt Solution

Equilibrium swelling studies at different ionic strength were also performed, by preparing three water solutions of NaCl and $CaCl_2$ at concentrations of 10^{-2}, 10^{-1}, and 1M. The dry samples were weighed and immersed in the aqueous solution until equilibrium attainment and were expressed in swelling ratio.

3.5.5. Hydrogel Swelling in Different pH Solutions

The same procedure was adopted for the analysis of the swelling capacity at different pH (in the range of pH values 2–10). In this case, a proper amount of NaCl was added to the buffer solutions used, in order to obtain the same value of ionic strength (0.04M).

3.5.6. Fourier Transform Infrared Spectroscopy

The functional group of the synthesized hydrogel was analyzed using Fourier-Transformed Infrared (FTIR) spectroscopy. FTIR analysis was recorded on a Perkin Elmer FTIR Spectrophotometer, using the potassium bromide disk technique, in the range of 4000–400 cm^{-1}. The disk was prepared from grounded samples (2 mg) and KBr (45 mg) using 400 kg/cm^2 pressure for 10 min.

3.5.7. Thermogravimetric Analysis (TGA)

Thermogravimetric analyzer (TA instrument, model: SDT Q600) was used to determine the thermal stability of the hydrogels with and without PEG using temperature programming from atmospheric temperature to 400 ℃ at the heating rate of 10 ℃/min. Testing was carried out under inert atmosphere (N_2) with a flow rate of 100 mL/min to remove all corrosive gases and avoid thermoxidative degradation. The thermal degradation onset temperature and the thermal degradation weight loss of composites were recorded and analyzed.

3.6. Agricultural Application

Hydrogels derived from cellulose exhibit unique properties such as biodegradability and biocompatibility which could be beneficial for bioengineering and agricultural purposes. Hence investigation of slow release capability and moisture retention capacity of the hydrogel was carried out.

3.6.1. Loading and Release of Urea

Urea loading was carried out by immersing pre-weighed dry NaCMC/ PEG (80:20) hydrogels into the different concentration of urea solution (5, 10, 15, 20, 30, 50 g/L) for 24 hours(Raafat et al., 2012). Thereafter, the swollen gels were dried at room temperature for 3 days. The loading percentage was calculated using equation (3.8).

$$Loading(\%) = \frac{M_l - M_0}{M_0} \times 100 \qquad (3.8)$$

where, M_0 and M_l are the weights of unloaded and loaded dry hydrogels, respectively.

To study the release of the fertilizer, 0.5 g of crushed urea-loaded hydrogel (without water) of known composition was placed into 100 mL of distilled water under unstirred condition at room temperature. A 2 mL amount of solution was collected from the liquid surface at different time intervals, and the amount of fertilizer released was determined gravimetrically by completely removing the water in an oven at 60 °C until a constant weight was obtained(Senna et al., 2015).

The percentage of the fertilizer released was determined according to the following equation.

$$Urea\,release(\%) = \frac{(\Delta W)_n \times \frac{[100-(n-1)\times 2]}{2} + \sum_{i=1}^{n-1}(\Delta W)_i}{W_0} \quad (3.9)$$

Where $(\Delta W)_i$: the amount of urea released found in the i^{th} 2 mL sample

W_0: the initial amount of urea contained by the hydrogel sample analyzed

3.6.2. Hydrogel Water Retention in Soil

The predominant soil used in this study was classified as a Typical Red. The soil collection was performed in the city of Addis Ababa, Ethiopia. The soil characterization was performed from a sub-collection of 4 soil samples from the study area that were taken at depths of 0–0.2 m and were combined to yield a composite sample, which was analyzed for its pH and electrical conductivity. Before analysis, the soil was air dried for three days up to constant weight.

3.6.2.1. Soil Characterization

This procedure was used to determine pH and electrical conductivity of the soil that was used in the study of water retention capability of the hydrogel in the soil.

Soil pH is one of the most common measurements in soil laboratories. It reflects whether a soil is acid, neutral or alkaline. Hence to determine pH of the soil, 50 g air-dried soil with less than 2 mm particle size was weighed and placed in a beaker and 50 mL distilled water was mixed with the soil to form 1:1(soil: water) suspension. Then the solution was mixed well and allowed to stand for 30 mins. and the suspension was stirred every 10 mins. After 1 hr., the combined electrode was placed in the suspension (about 3 cm deep) and the reading was taken after 30 seconds(Ryan et al., 2001).

The salinity in the soil was measured by electrical conductivity using a conductivity bridge. The total salt content of the soil can be estimated from this measurement. To determine electrical conductivity of the soil a 1:1 (soil: water) suspension was prepared and filtered using Whatman filter paper with the help of vacuum pump. The filtration was continued until the soil on the Buchner started to crack. The conductivity cell was used to determine the clear filtrate solutions conductivity(Ryan et al., 2001).

3.6.2.2. Water Retention Test

A 0.8 g sample of the gel was well-mixed with 40 g of dry soil and kept in a plastic tube and then 30 g of distilled water was slowly added into the tube and weighed (W_0). A controlled experiment, without gel, was also carried out. The samples were placed in an oven with air circulation at a temperature regulated precisely in 40 ℃ and from time to time the sample was removed and weighed (W_1). The same procedure was used for hydrogel loaded with urea fertilizer(Senna et al., 2015). The water evaporation ratio of soil was calculated using equation (3.10).

$$Water\ evaporation(\%) = \frac{W_0 - W_1}{W_0} \times 100 \tag{3.10}$$

Chapter 4

Results and Discussion

Esterification crosslinking of sodium carboxymethyl cellulose (NaCMC) and polyethylene glycol (PEG) blend using citric acid shows promise for preparation of hydrogel. Using synthetic polymers such as PEG as network modifier of NaCMC hydrogel has led to the formation of hydrogel matrixes with many exceptional properties for utilization.

4.1. Raw Material Characterization

4.1.1. Sodium Carboxymethyl Cellulose (NaCMC)

4.1.1.1. Moisture Content

The moisture content of the NaCMC used was 9.8%. The moisture content describes the volatile content of NaCMC. The moisture content by extension implies the total solids in the sample; and, by common usage, all materials volatile at this test temperature are designated as moisture. Moisture analysis (along with purity) is used to estimate the amount of active polymer in the material.

4.1.1.2. Purity

The purity of the NaCMC that was used for the synthesis of the hydrogel is 95.26%. The purity justifies the percent of active ingredient in the NaCMC which was used as the main raw material in the synthesis of the hydrogel.

4.1.1.3. Ash Content

Ash content of the NaCMC was 16.15%. The ash content of a NaCMC is the amount of non-carbon components (compounds containing sodium) present after combustion. Moreover, NaCMC ash obtained from calcination is used to estimate the COO^- content to determine the degree of substitution.

4.1.1.4. Degree of Substitution

The NaCMC used has 0.55 degree of substitution. The degree of substitution explains the number of substituent groups added to the cellulose backbone. The degree of substitution greatly affects solution properties, rheology, viscosity, hygroscopicity, salt tolerance, and many other properties of the polymer.

4.1.2. Fourier Transform Infrared Spectroscopy

Functional groups of Sodium carboxymethyl cellulose (NaCMC), polyethylene glycol (PEG), and citric acid are characterized using FTIR spectroscopy. As a general trend common to both polymers (NaCMC and PEG), the broadband in the 3700–3000 cm^{-1} region assigned to O−H vibrations and the peaks at 3000-2800 cm^{-1} related to C−H bands are present.

For NaCMC, the major vibrational bands related to carboxylates (COO^-) asymmetric (1603 cm^{-1}) and symmetric (1416 cm^{-1} and 1324 cm^{-1}) stretches exist, overlapped with the band of adsorbed water (1630-1650 cm^{-1}). It is worth to note that the presence of strong absorption band at 1,603 cm^{-1} is due to the ($-COO^-$) group generated from ($-COO^-Na^+$) structure. The acid form of NaCMC is not detected in the powder sample due to the absence of the characteristic bands of carboxyl groups (–COOH) usually observed at 1715-1730 and 1240-1250 cm^{-1}, which are assigned to antisymmetric stretching vibration of C=O and C−O stretching, respectively. C−O vibrations from primary and secondary alcohols appear at 1110 cm^{-1} (C2−OH), 1060 cm^{-1} (C3−OH), and 1024 cm^{-1} and 995 cm^{-1} (C6−OH). ß1-4 glycoside bonds between glucose units are detected at 898 cm^{-1}.

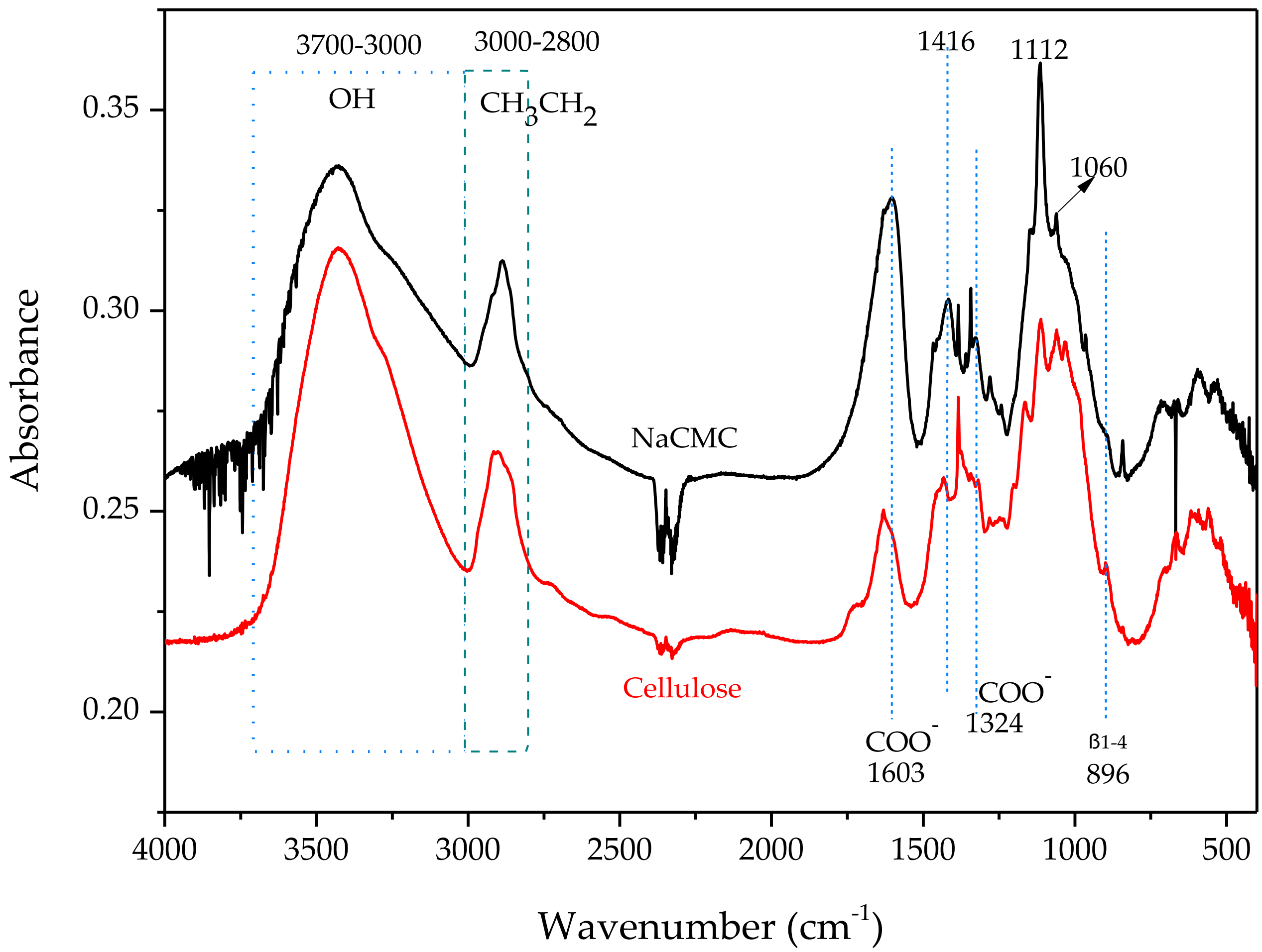

Figure 4.1 FTIR spectra of pure cellulose and sodium carboxymethyl cellulose (NaCMC)

The degree of substitution (DS) by carboxymethylation of cellulose is related to the -CH_2COOH group that can be attached to every of the three hydroxyl groups of the cellulose monomer unit. Theoretically, the DS value can reach 3 but usually does not exceed 2. This is an important parameter to characterize because the functionalization renders water-soluble and biocompatible cellulose derivative (NaCMC) with numerous applications. FTIR is not only used for characterizing the NaCMC but also to further evaluate the relative DS values. The band at 1603 cm^{-1} is predominantly associated with the contribution of carboxymethyl groups inserted in the cellulose polymer chain. By taking the ratio of the absorbance of this band (A_{1600}) and the reference band of ß1-4 glycoside bond at 898 cm^{-1} (A_{896}), A_{1600}/A_{898}, the calculated values is 1.245. Thus, this result indicates that the band at 1603 cm^{-1} is relatively stronger for NaCMC with DS of 0.55 due to the carboxymethyl substitution.

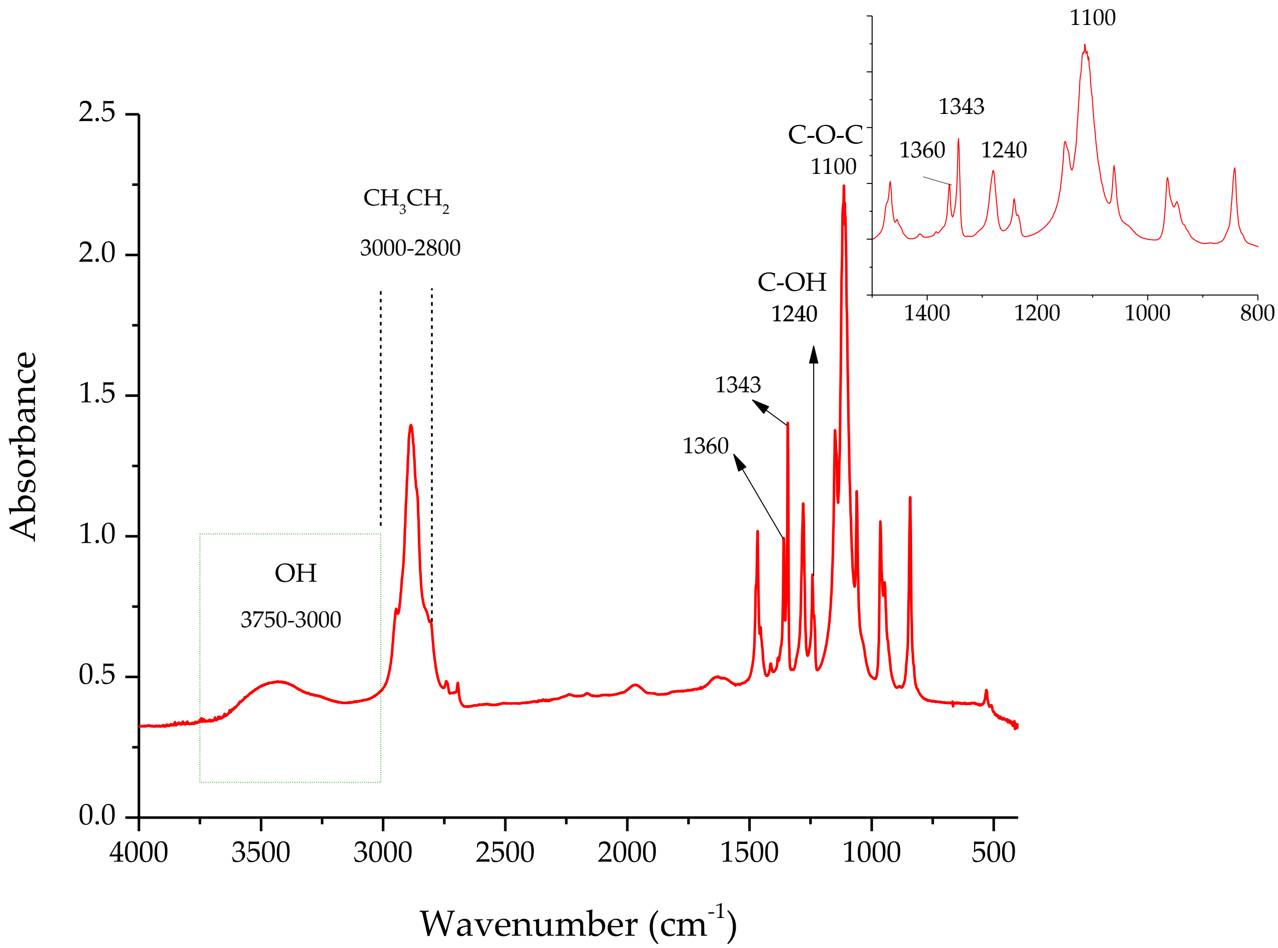

Figure 4.2 FTIR spectra of polyethylene glycol (PEG)

The peaks associated with C−O (alcohol) and C−O−C of PEG polymer are displayed in the IR spectrum at 1240 cm^{-1} and 1100 cm^{-1}, respectively. In addition, in the CH_2 wagging region of the spectrum (1320-1380 cm^{-1}), PEG shows two bands at 1360 cm^{-1} and 1343 cm^{-1}, that characterize the crystalline phase of this polymer.

The FTIR spectroscopy of citric acid show characteristic bands of carboxyl groups (−COOH) usually observed at 1715-1730 and 1240-1250 cm^{-1}, which are assigned to antisymmetric stretching vibration of C=O and C−O stretching, respectively. Moreover, the strong band at 1140 is attributed to C−O stretching vibration for dimer citric acid. The strong peak at 3498 cm^{-1} is ascribed to O−H bond stretching vibration for the dimer. The other strong band at 3291 cm^{-1} is assigned to O−O bond stretching vibration for citric acid dimer.

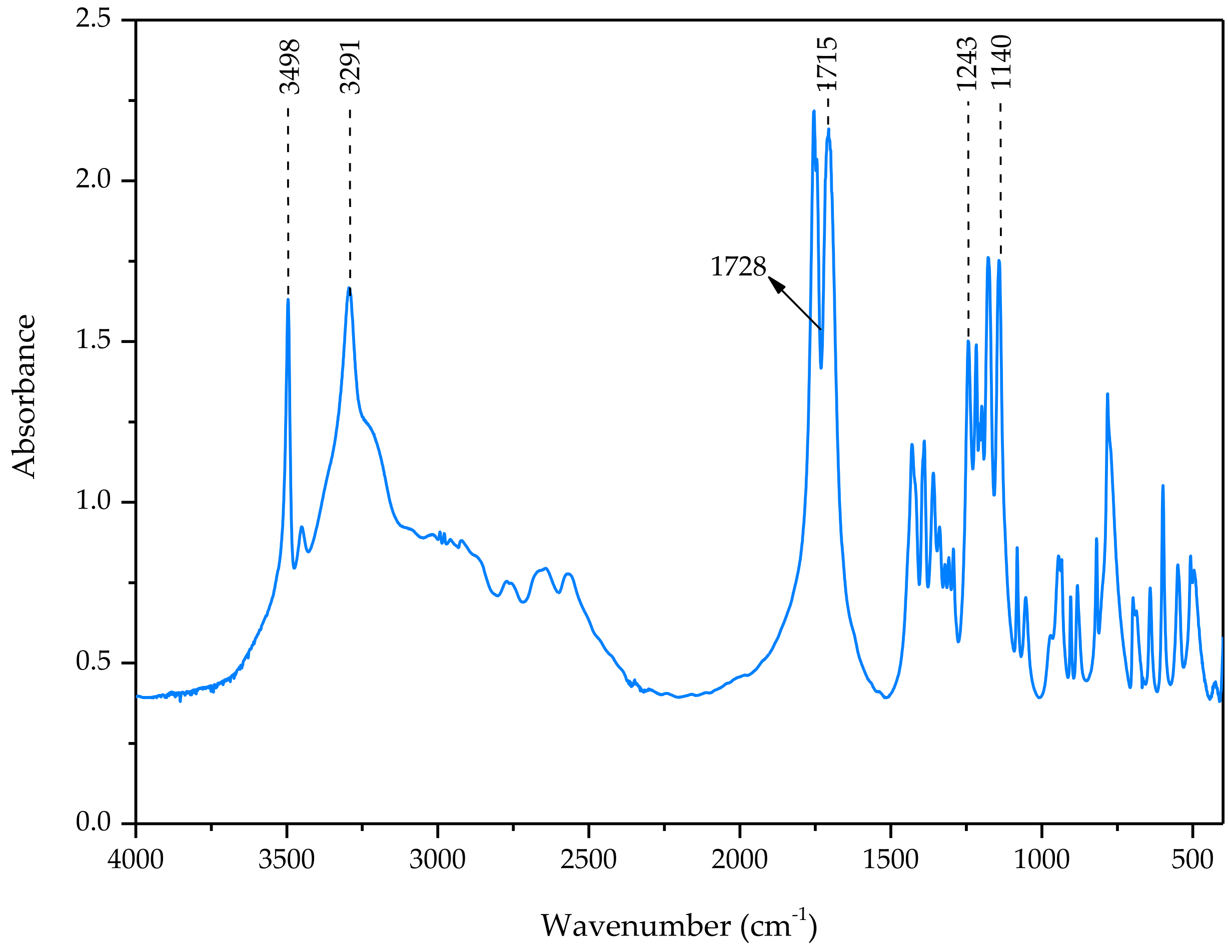

Figure 4.3 FTIR spectra of citric acid

As a whole, the FTIR spectra of the raw materials used depict the presence of important functional groups that are involved in the crosslinking reaction of the polymers. FTIR spectra of both polymers denote the existence of hydroxyl group and spectra of citric acid shows the presence of carboxylic acid functional group which are involved in the esterification reaction that results in the crosslinked network (Figure 2.3).

4.1.3. X-Ray Diffraction Analysis

X-ray diffraction (XRD) analysis is a special technique for estimating the degree of crystallinity in the polymer. Figure 4.4 shows the diffraction pattern of pure cellulose and NaCMC. The peaks correspond to the crystalline phase and the background corresponds to the amorphous phase. It is obvious that cellulose is semi-crystalline in nature hence the peaks are broad due to the small crystallites in cellulose granules, which confirm the theory of XRD. This theory states that very small imperfect crystals give broadened diffractions.

The diffraction patterns of NaCMC show a destruction of the crystalline structure of the original cellulose. All characteristic peaks for native cellulose have almost disappeared and transformed into an amorphous phase. Therefore, NaCMC has excellent solubility as lower crystallinity represents higher solubility(Mondal et al., 2015).

The main diffraction pattern of cellulose is displayed at diffraction angles 2θ around 15°, 23°, and 34.9° respectively. Diffraction planes of NaCMC overlap with each other and form one broad peak. This phenomenon was owed to the destruction of crystalline region. It also demonstrates that NaCMC has a relatively weaker band at $2\theta = 20°$ for the decrease of the ordered structure due to the presence of carboxylate group substituent on cellulose backbone.

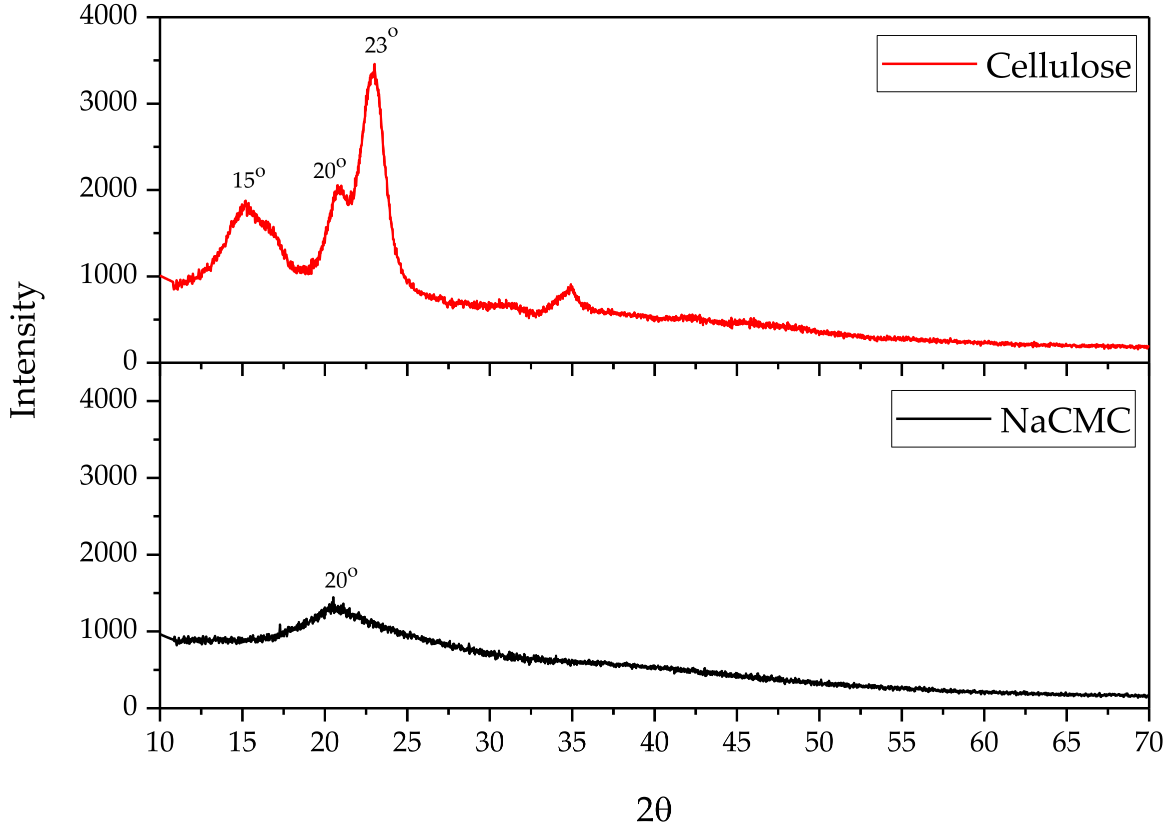

Figure 4.4 X-ray diffractogram of pure cellulose and sodium carboxymethylated cellulose (NaCMC)

4.2. Experimental Design Analysis

Typically, the classical method (one-at-a-time) provides for changing one independent variable while maintaining all others at a fixed level, which is extremely time-consuming and expensive for a large number of variables. The major disadvantage is the lack of inclusion of the interactive effects among variables. Consequently, it could not lead to real optima in many cases. Accordingly, procedures for optimization of factors by multivariate techniques have been encouraged, as they are faster, more economical, and effective and allow more than one variable to be optimized simultaneously.

Response surface methodology (RSM) is a system useful for modeling and process optimization using a collection of statistical and mathematical techniques. It is used when a relevant response is influenced by several variables and the objective is to optimize this response. Central composite design(CCD), common multilevel RSM design, is used extensively in building the second order response surface models. Moreover, it is easy to estimate the parameters in a second-order model using the method of least squares and this is used in the optimization process studies.

The experimental result was analyzed using Design Expert to develop a single model equation that can describe the synthesis variables significance. The suggested choice of model was a quadratic model that fits the data.

Table 4.1 Model summary

Model Summary Statistics						
Source	**Std. Dev.**	**Adjusted R-Squared**	**Predicted R-Squared**	**R-Squared**	**PRESS**	
Linear	4.555×10^{-4}	0.7985	0.7799	0.7384	1.454×10^{-5}	
2FI	3.634×10^{-4}	0.8931	0.8598	0.7825	1.209×10^{-5}	
Quadratic	1.151×10^{-4}	0.9900	0.9859	0.9802	1.098×10^{-6}	Suggested
Cubic	1.155×10^{-4}	0.9938	0.9858	0.9646	1.966×10^{-6}	Aliased

4.2.1. Model Equation

A model equation is a mathematical correlation that expresses the relation between the factors and the response. The model equation was developed to show the correlation between the synthesis parameters and swelling capability of the hydrogel. Swelling measurement is widely used as the extension of crosslinking of hydrogel networks.

The response that was obtained from the experiment ranges from 215 to 5595, hence ratio of maximum to minimum is 26.0233. A ratio greater than 10 usually indicates the transformation of data is required. Since Box-Cox plot shows λ should be −1, the inverse transform of the data was recommended (Appendix C). After the data transformation and analysis, the best-fitted regression equation in terms of coded factors for CCD is given by equation (4.1).

$$\begin{aligned}\frac{1}{swelling} = &+9.220 \times 10^{-4} + 8.698 \times 10^{-4} A + 5.873 \times 10^{-4} B \\ &+ 5.841 \times 10^{-4} C \ \times +3.401 \times 10^{-5}\ D[1] + 9.445 \times 10^{-5}\ D[2] \\ &+ 2.560 \times 10^{-4}\ AB\ + 3.305 \times 10^{-4} AC + 2.318 \times 10^{-5} AD[1] \\ &+ 5.257 \times 10^{-5} AD[2] + 1.814 \times 10^{-4} BC + 7.381 \times 10^{-7} BD[1] \\ &+ 1.408 \times 10^{-4} BD[2] + 3.765 \times 10^{-5} \times CD[1] + 3.088 \times 10^{-5} CD[2] \\ &+ 6.235 \times 10^{-4} A^2 + 2.223 \times 10^{-5} B^2 - 6.589 \times 10^{-5} C^2\end{aligned} \tag{4.1}$$

Where A: Temperature (℃), B: Time (hr.), C: Citric acid concentration (%),

D: Polymer composition or PEG content (wt.%)

4.2.2. Model Adequacy Checking

The model was tested for adequacy by analysis of variance. The regression model was found to be highly significant with the correlation coefficients of determination of R-Squared, adjusted R-Squared and predicted R-Squared having a value of 0.9802, 0.99 and 0.9859 respectively. It implies that 98.02% of the total variation in the percentage of the inverse of swelling is attributed to the experimental variables studied. The graph of the predicted values obtained using the developed correlation versus actual values is displayed in Figure 4.5. The result in Figure 4.5 demonstrates that the regression model equation provides a very accurate description of the experimental data, in which all the points are very close to the line of perfect fit. This result indicates that model is successful in capturing the correlation between the synthesis variables and the swelling equilibrium of the hydrogel.

The adequacy of the model was further checked with analysis of variance (ANOVA) as shown in Table 4.1, based on a 95% confidence level. F - value is a test for comparing model variance with residual (error) variance. If the variances are the same, the ratio will be close to one and it is likely that any of the factors have a significant effect on the response with the P – value less than 0.05. It is calculated by model mean square divided by residual mean square.

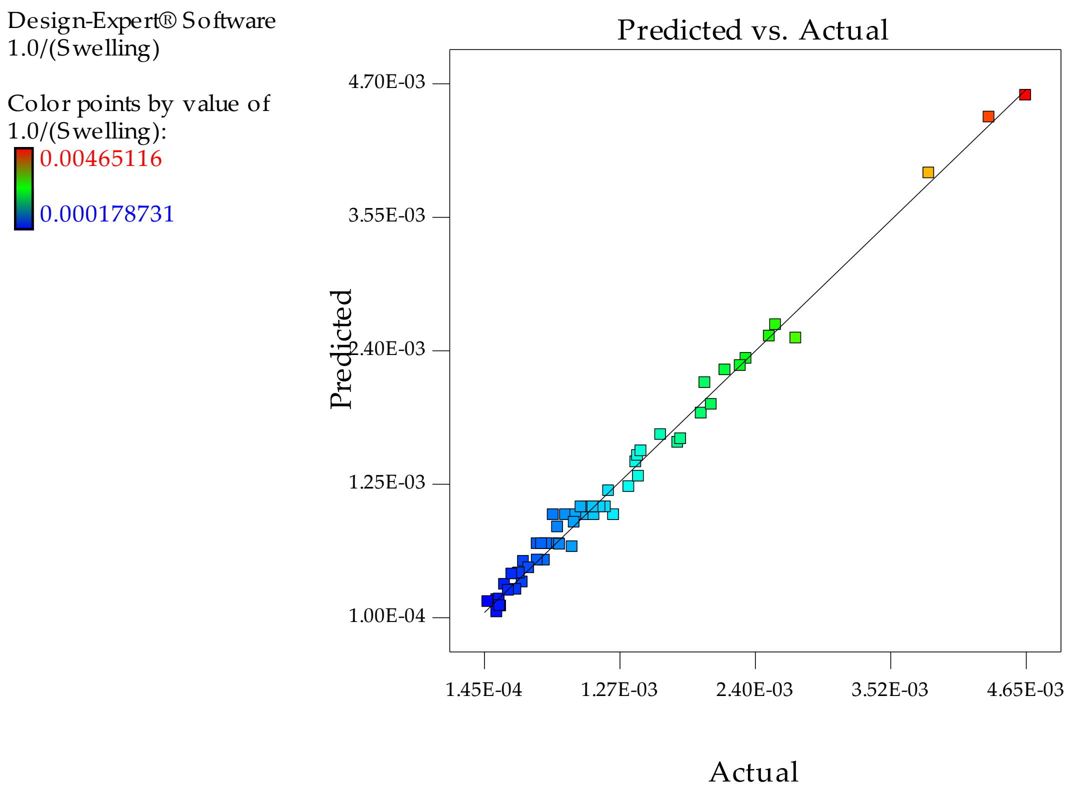

Figure 4.5 Plot of data predicted using the model versus the actual data

The Model F-value of 244.48 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Table 4.2 ANOVA for the regression model equation

Response 1 Swelling						
Transform: Inverse						
ANOVA for Response Surface Quadratic Model						
Analysis of variance table [Classical sum of squares - Type II]						
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	5.504×10^{-5}	17	3.238×10^{-6}	244.48	< 0.0001	significant
A-Temp.	2.270×10^{-5}	1	2.270×10^{-5}	1713.76	< 0.0001	
B-Time	1.035×10^{-5}	1	1.035×10^{-5}	781.27	< 0.0001	
C-Conc.	1.024×10^{-5}	1	1.024×10^{-5}	772.87	< 0.0001	
D-Comp.	1.117×10^{-6}	2	5.584×10^{-7}	42.17	< 0.0001	
AB	1.573×10^{-6}	1	1.573×10^{-6}	118.75	< 0.0001	
AC	2.622×10^{-6}	1	2.622×10^{-6}	197.97	< 0.0001	
AD	1.766×10^{-7}	2	8.829×10^{-8}	6.67	0.0031	
BC	7.898×10^{-7}	1	7.898×10^{-7}	59.64	< 0.0001	
BD	1.190×10^{-8}	2	5.952×10^{-9}	0.45	0.6410	
CD	8.555×10^{-8}	2	4.277×10^{-8}	3.23	0.0496	
A^2	3.207×10^{-6}	1	3.207×10^{-6}	242.20	< 0.0001	
B^2	4.078×10^{-9}	1	4.078×10^{-9}	0.31	0.5819	
C^2	3.581×10^{-8}	1	3.581×10^{-8}	2.70	0.1075	
Residual	5.562×10^{-7}	42	1.324×10^{-8}			
Lack of Fit	3.494×10^{-7}	27	1.294×10^{-8}	0.94	0.5721	not significant
Pure Error	2.068×10^{-7}	15	1.379×10^{-8}			
Cor Total	5.560×10^{-5}	59				

Values of "Prob > F" less than 0.05 indicate model terms are significant. In this case, A, B, C, D, AB, AC, AD, BC, CD, A^2 are significant model terms. Values greater than 0.05 indicate the model terms are not significant. This shows that temperature, time, citric acid concentration and PEG content (polymer composition), the interaction between temperature and time, temperature and citric acid concentration, temperature and PEG content, time and citric acid concentration, citric acid concentration and PEG content and tempertature^2 affect the hydrogel swelling. Insignificant model terms (not counting those required to support hierarchy) such as interaction effect of reaction time and polymer composition could be reduced to improve the model.

The "Lack of Fit F-value" of 0.94 implies the Lack of Fit is not significant relative to the pure error. There is a 57.21% chance that a "Lack of Fit F-value" this large could occur due to noise.

4.2.3. Effect of Individual Factor on Swelling

Figure 4.6 illustrates the percentage of swelling is significantly affected by reaction temperature. Lower temperature doesn't favor the formation of cyclic anhydride of citric acid which affects the crosslinking reaction resulting unstable hydrogel. Meanwhile higher temperature means tight crosslinking between the polymers due to sufficient amount of cyclic anhydride derivative of citric acid, yielding a hydrogel with low swelling percentage. Apparently, hydrogels synthesized around 80 ℃ exhibit maximum swelling capacity.

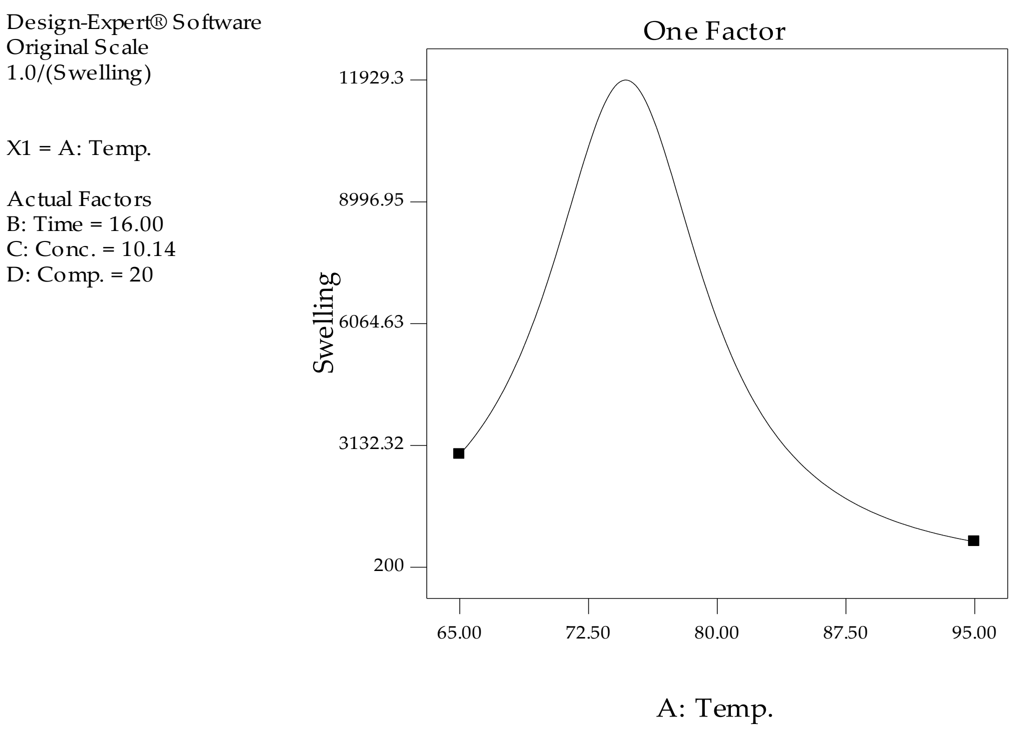

Figure 4.6 Swelling (%) versus reaction temperature

Figure 4.7 demonstrates the effect of reaction time on the degree of swelling. It can be clearly seen that longer acidification time reduces the electrostatic repulsion which decreases the swelling capability of the NaCMC Hydrogel. This is mainly due to the conversion of −COONa into −COOH, thus NaCMC polymer chains carrying more –COOH group are capable of forming hydrogen bonds which could result highly rigid network. Moreover, prolonging the acidification time from 8 h to 24 h creates not only hydrogen bond but also ester bond between citric acid and NaCMC, and citric acid and PEG producing rigid structure. On the contrary, with shorter acidification time, only a few −COONa groups convert into –COOH, leading to a NaCMC hydrogel with loosely cross-linked networks, which can absorb significant amount of water.

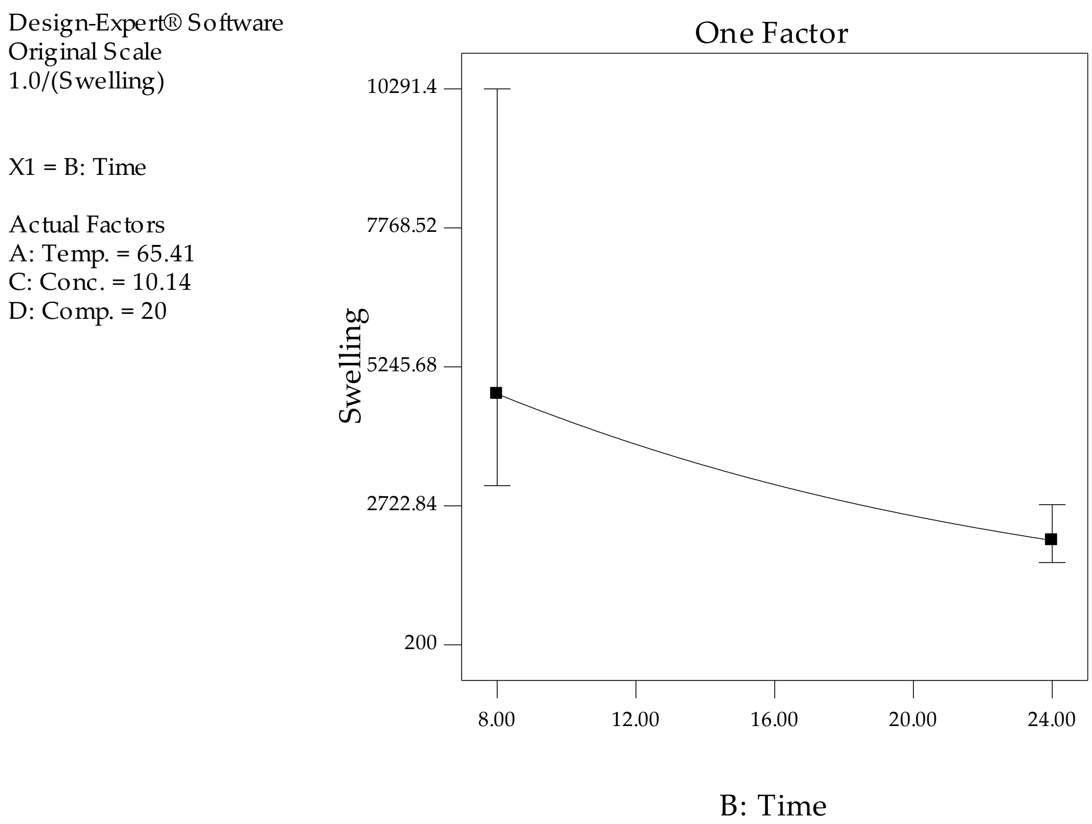

Figure 4.7 Swelling (%) versus reaction time

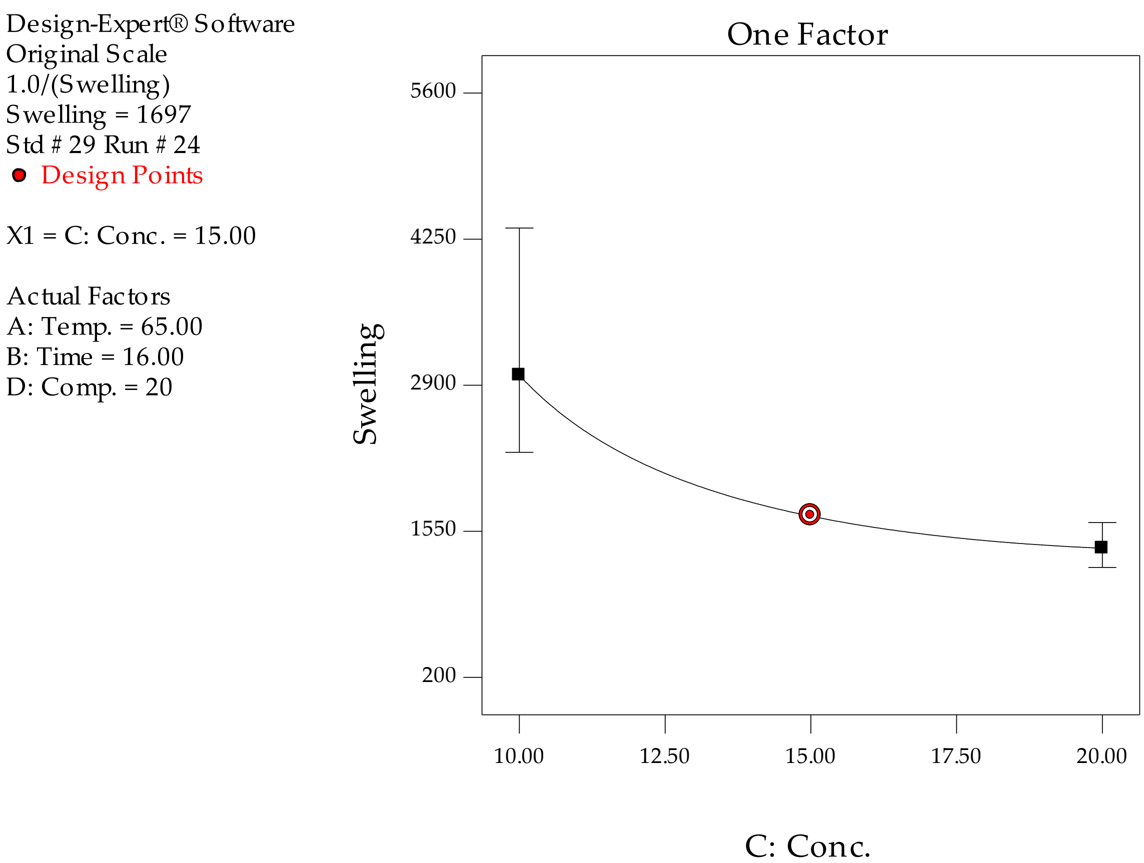

Figure 4.8 Swelling (%) versus citric acid concentration

Figure 4.8 shows the equilibrium-swelling (%) of the NaCMC and 20 wt.% PEG hydrogels with the gradual increase of citric acid concentration. It can be remarked that the concentration of citric acid used during preparation affects greatly the swelling behavior of the obtained NaCMC/PEG hydrogels. From the result (Table B-6) it can be observed that, for NaCMC and 20 wt.% PEG composite and lower concentrations of citric acid (i.e., 10%), superabsorbent hydrogel was produced with swelling potential of over 5000%. However, a drastic decrease of swelling percentage to approximately 260% was observed at higher concentration of 20% of crosslinker, which implied the formation of covalent bonds bridging the functional groups of the polymer chains and increasing the rigidity of the network.

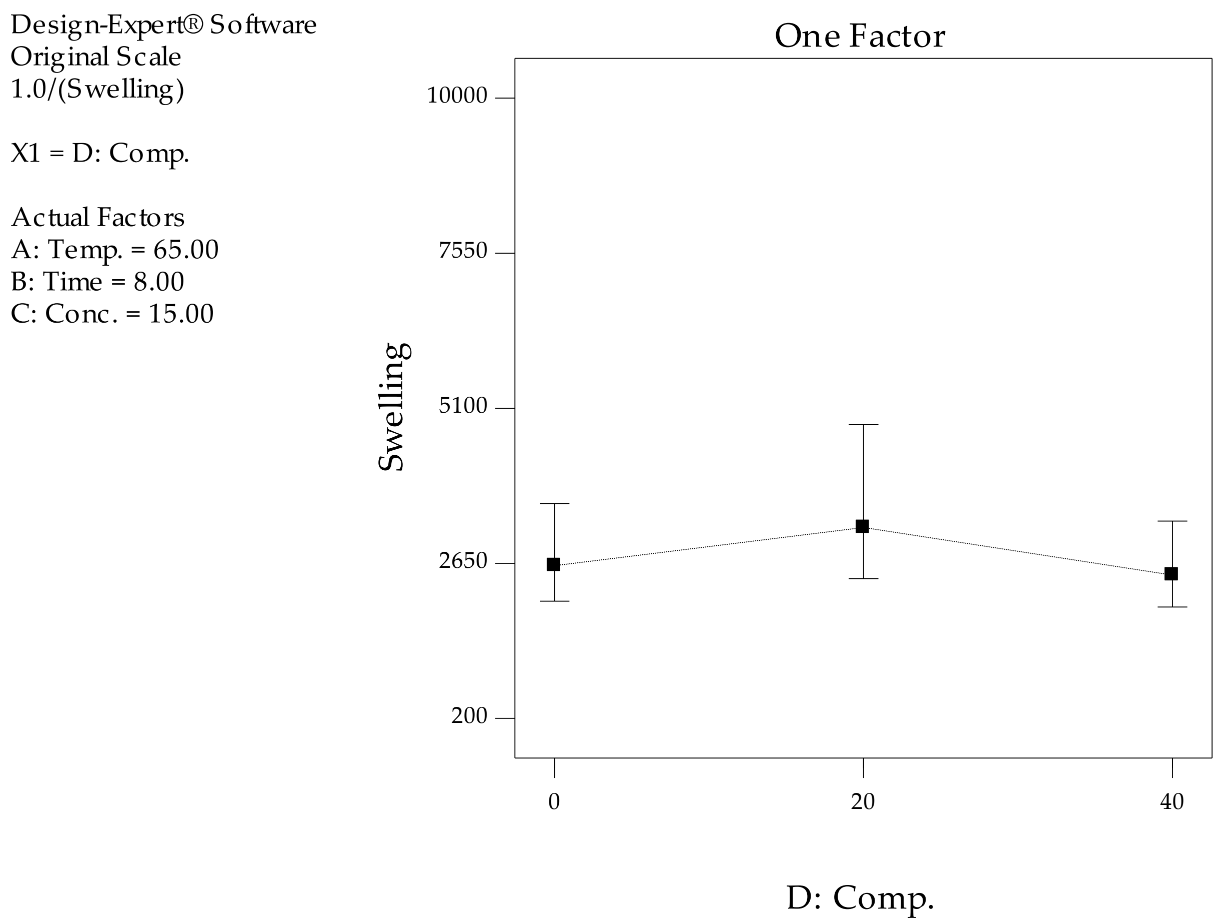

Figure 4.9 Swelling (%) versus polymer composition of hydrogel (PEG content)

Increasing the PEG content up to 20% increased the swelling property of the hydrogel working as a molecular spacer due to intercalation of PEG between the NaCMC chains. However, NaCMC alone promotes intramolecular rather than intermolecular cross-linking, resulting in a hydrogel with small swelling equilibrium relative to the NaCMC/PEG composite.

As the concentration of PEG increases to 40%, the degree of swelling value decreases indicating that PEG chains modified the network. This is connected to the fact that the addition of PEG increases the total amount of available hydroxyl groups for esterification. The effects of adding citric acid and PEG were summed up leading to higher crosslinked networks involving PEG and NaCMC functional groups producing more rigid hydrogels.

These results demonstrate that the NaCMC hydrogels can have their network structures and physicochemical properties tuned by the concentration of crosslinker, duration of the crosslinking reaction and PEG content for producing a superabsorbent hydrogel.

4.2.4. Interaction Effect of Factors on Swelling

The most common way to summarize the results of a central composite design experiment is in the form of a response surface plot. The ANOVA analysis depicts that except for interaction of acidification period (reaction time) and PEG content (polymer composition) all interaction effects are significant model terms. Evidently, the interaction of citric acid concentration and PEG content of the hydrogel has a relatively lower impact than the significant model terms.

Figure 4.10 and Figure 4.11 illustrate the effect of interaction between reaction temperature and time, and concentration of crosslinker (citric acid) and reaction temperature respectively. Although both figures exhibit a similar pattern, hydrogels synthesized at a lower temperature and lower crosslinker concentration have slightly higher degree of swelling than those prepared at a lower temperature and short reaction period.

The decrease in the reaction temperature and reaction time reduce the crosslinking of the NaCMC or NaCMC/PEG molecules. Such decrement in the degree of crosslinking increases the porosity available for swelling by increasing the flexible network structure that eases the mobility of the polymer chains subsequently it enhances the hydrogel swelling equilibrium.

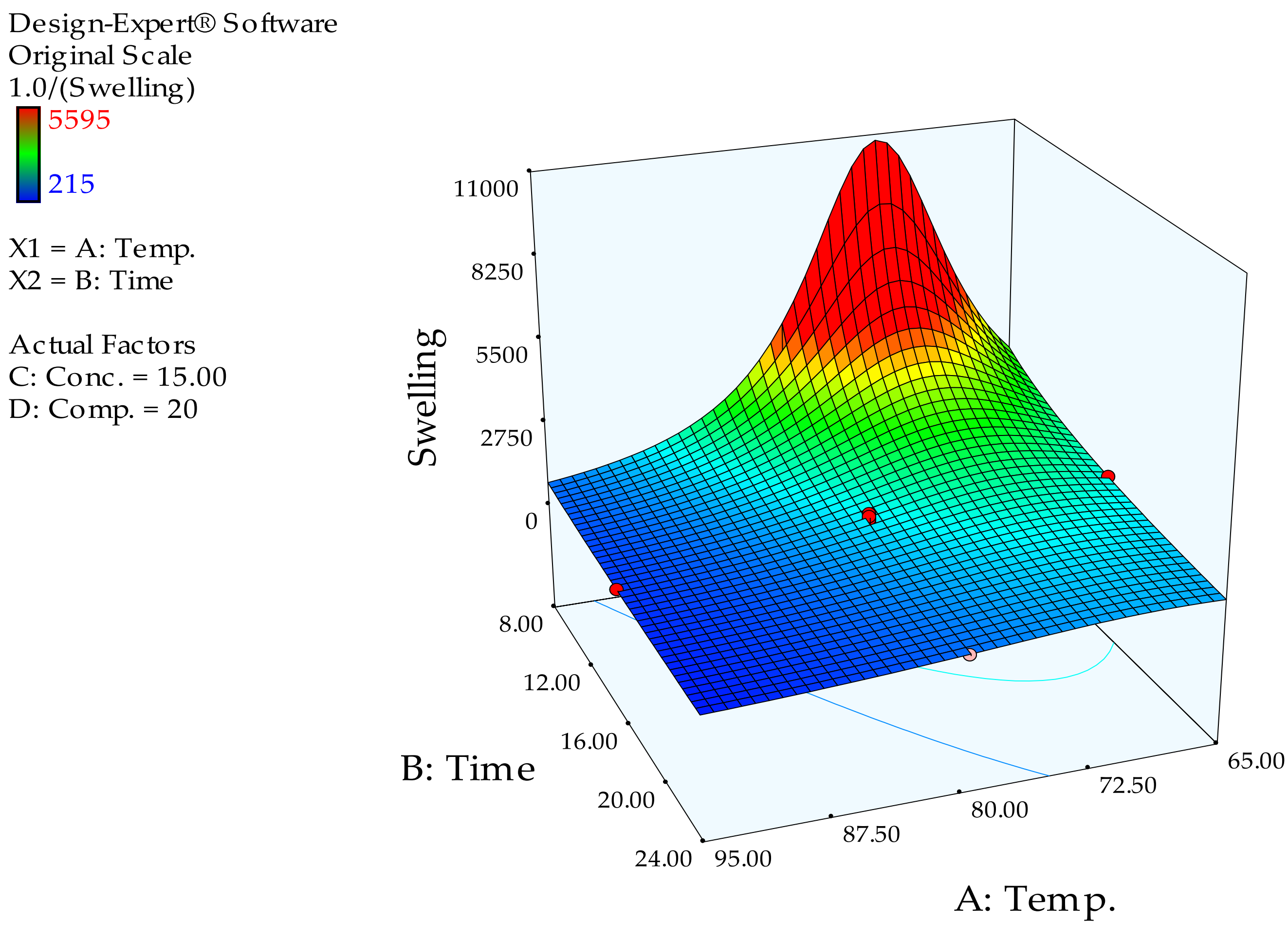

Figure 4.10 Surface plot of Time and Temperature interaction effect

It is worth noticing that the interaction of citric acid concentration and reaction temperature applied greatly affects the swelling behavior of the obtained NaCMC/PEG hydrogels. These results can be explained in terms of degree of crosslinking, which could also increase by raising the total citric acid concentration and the duration of the crosslinking reaction. The increase in the citric acid concentration and reaction time intensifies the crosslinking of the NaCMC or NaCMC/PEG molecules. Such rise in the degree of crosslinking reduces the free volume available for swelling by enhancing the tightness of the network structure that hinders the mobility of the polymer chains. Consequently, it lowers the hydrogel swelling.

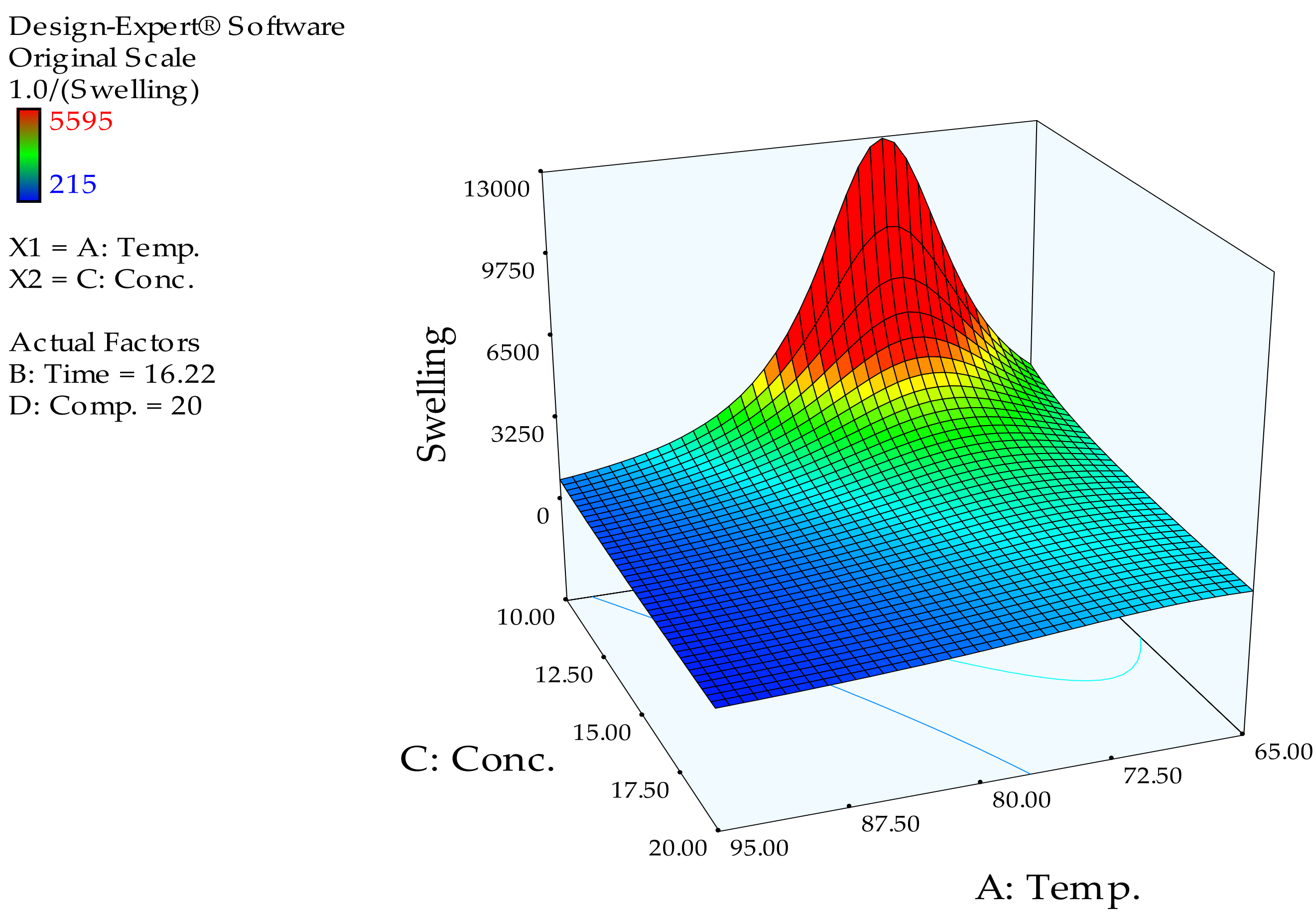

Figure 4.11: Surface plot of Citric acid concentration and Temperature interaction effect

Figure 4.12 illustrates that, for all the investigated compositions, the swelling degree of the NaCMC/PEG hydrogel diminishes when the temperature of the reaction is raised. Up to 60 wt.% NaCMC content, crosslinking is the predominant reaction which resulted in good and stable network structure able to absorb and retain a considerable amount of water. Such increase is attributed to the higher hydrophilic character of NaCMC molecules. This suggests that the electrostatic repulsions caused by the ionic character of the carboxylate anions (COO^-) in NaCMC had enlarged the space in the networks of hydrogels. Interestingly, the pore size of the hydrogels was very large and was enhanced with the increase of the NaCMC component. However, hydrogels prepared from NaCMC alone have a low degree of swelling indicating that NaCMC prefers intramolecular bonding rather than intermolecular bonding.

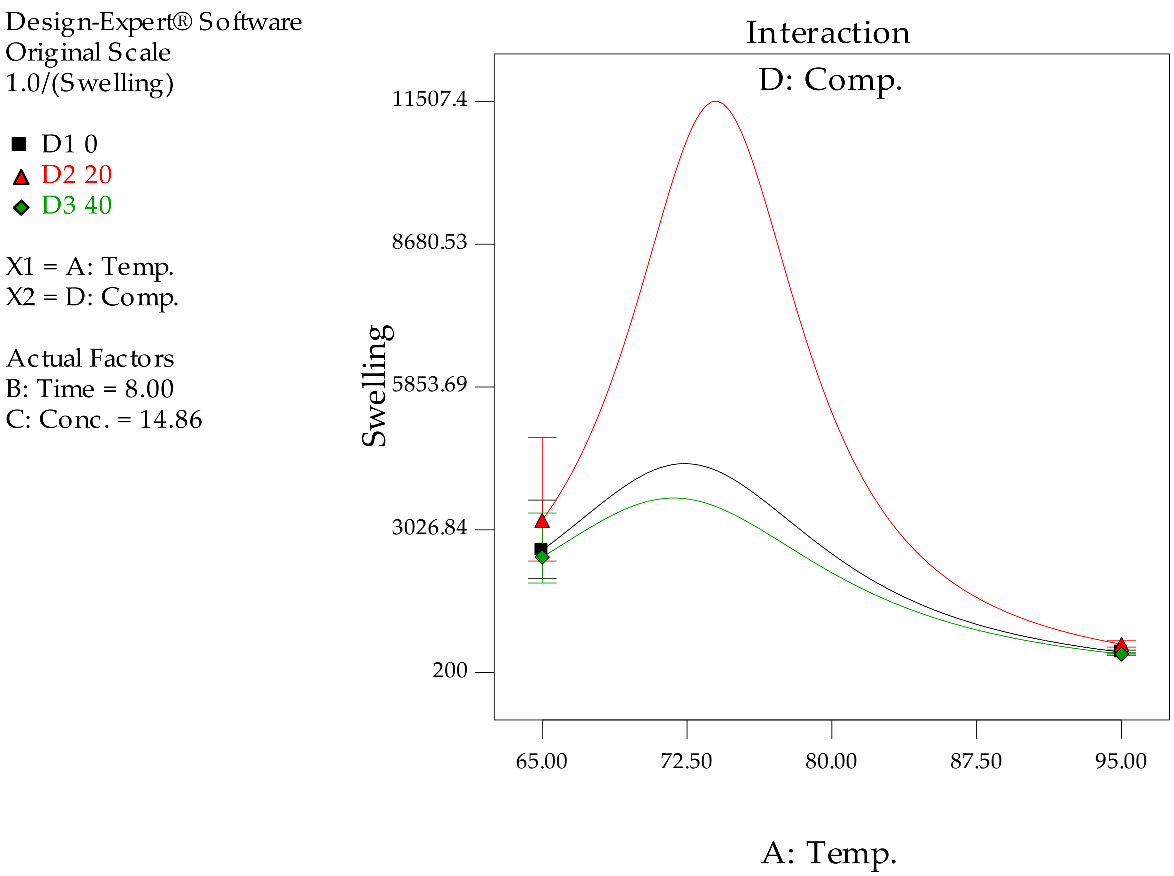

Figure 4.12 Interaction plot of Temperature and composition of the hydrogel

Generally, the abovementioned results revealed that the carboxymethyl group of NaCMC supplied the enlargement of pore due to the electrostatic repulsion, whereas cellulose acted as a backbone in the hydrogel to strengthen it. Meanwhile, PEG acted as a molecular spacer by intercalating between the cellulose backbone. Therefore, the numerous water molecules could easily diffuse into the hydrogel pores, leading to a higher swelling percentage.

4.2.5. Optimization of Synthesis Factors

Optimization is a method of analysis to identify the combination of variable settings that jointly optimize a single response or a set of responses. The aim of this work is to synthesize hydrogel with maximum swelling and stability. The central composite design, using the design space (defined limits of parameters) and maximum swelling optimization of the process was carried out. The Thermogravimetric Analysis of the hydrogel shows that NaCMC/PEG20 has higher stability. On the other hand, NaCMC/PEG40 hydrogels have low swelling. Thus, NaCMC/PEG20 is selected for the composition of the polymer.

Table 4.3 Constraints for the factors and responses in numerical optimization

Parameter	Ultimate goal	Experimental Region	
		Lower Limit	Upper limit
Reaction Temperature (℃)	In Range	65	95
Reaction Time(hr.)	Minimum	8	24
Citric acid Concentration (%)	In Range	10	20
Polymer Composition (wt.%)	80% NaCMC and 20% PEG	100 % NaCMC	60% NaCMC and 40% PEG
Swelling (%)	Maximum	215	5595

Under the optimum conditions selected, the model predicted swelling degree of 6853.54% with a desirability value of 1. To validate the optimum conditions predicted by the model using desirability ramp, triplicate experiments were conducted using the optimized hydrogel synthesis conditions. The mean swelling percentage gained is closely related to the data obtained from the optimization analysis using desirability functions.

Table 4.4 Result of optimization and model evaluation

Reaction Temperature (℃)	Reaction time (hr.)	Citric acid concentration (%)	Polymer composition (wt.%)	Swelling (%)	
				Predicted	Measured
72.38	8	16.54	80% NaCMC and 20% PEG	6853.54	6748

In summary, this study shows that NaCMC and PEG could be used to synthesize superabsorbent hydrogel and swelling capacity of the hydrogel could be optimized by tuning the synthesis parameters.

4.3. Characterization of the Hydrogel

As a general trend, it was observed that uniform and optically transparent membranes were produced before and after crosslinking with citric acid (Appendix D). For NaCMC and NaCMC/PEG blend without any citric acid stable hydrogels were not formed and the systems fully dissolved in water. While hydrogels synthesized using citric acid swell when placed in water for 24 hrs. without dissolving.

4.3.1. Swelling Kinetics

The kinetic swelling measurements in distilled water showed a fast uptake for NaCMC/PEG20 hydrogel formulation. After 30 minutes, all the samples almost reached above 85% of the equilibrium values of the maximum swelling. Indeed, a stable “plateau” region could be observed in the time frame between 60 and 300 minutes. A time length of 30 minutes was thus considered as a reasonable and acceptable duration for almost complete hydrogel swelling when applying the hydrogel in agriculture.

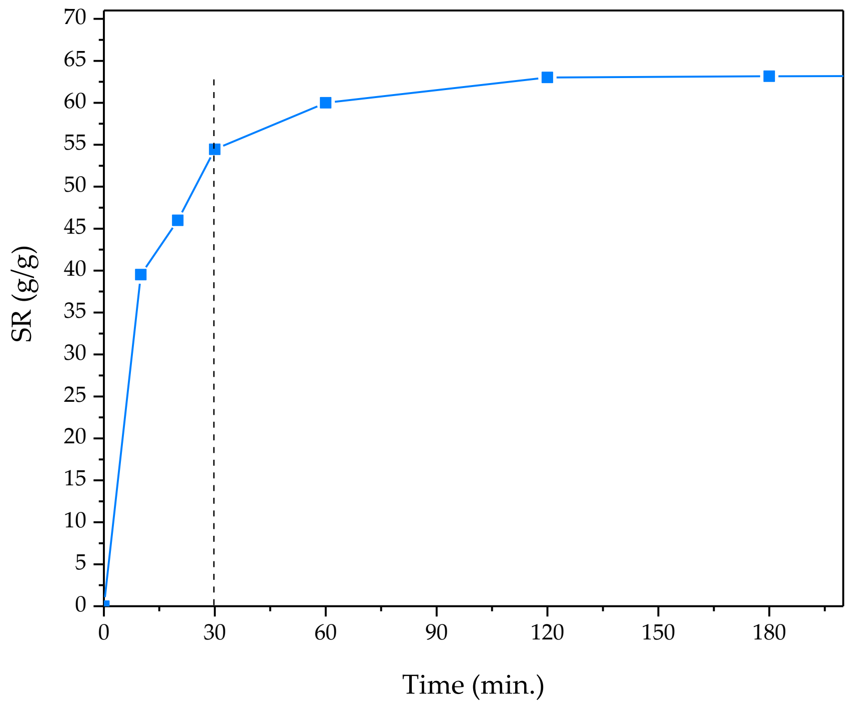

Figure 4.13 Swelling kinetics of the hydrogel

4.3.2. Moisture Retention Capability

Being one of the most important criteria for the superabsorbent hydrogels, the moisture retention capability of NaCMC based hydrogel was investigated. Figure 4.14 displays the moisture retention capacity of the optimized NaCMC/PEG20 superabsorbent hydrogel placed at room temperature.

It is clear that, as time increases water retention capability of the hydrogel decreases significantly. The hydrogel retained about 60 wt.% of the absorbed water for investigated composition after 24 hrs. at 20°C. After 72 hrs. about 5% of the initial moisture was kept by the hydrogel. Also, it can be noticed that, the moisture retention capacity of the investigated sample with 20 wt.% PEG is high. This is due to the well-built network structure that retains significant amount the water inside it. From this point of view, NaCMC/PEG20 hydrogels have good prospect to be used as a superabsorbent for agriculture applications because of their good moisture retention capability and considerable swelling ability.

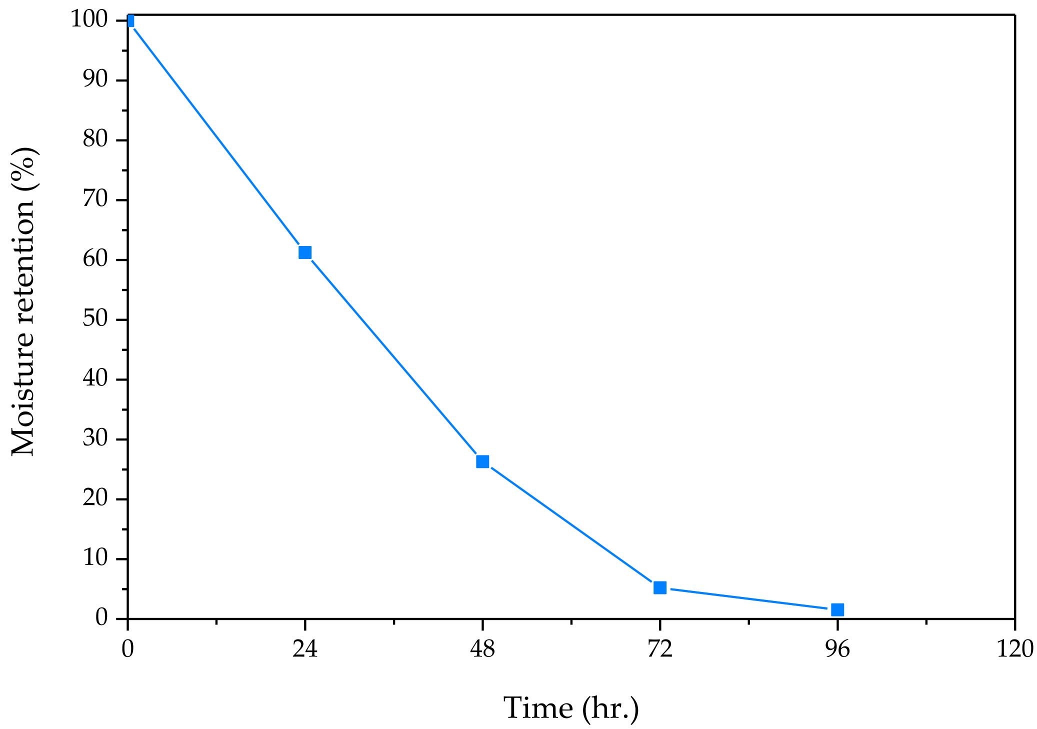

Figure 4.14 Moisture retention percentage of the hydrogel

4.3.3. Swelling in Salt Solution

The effect of the ionic strength of the external solution on the equilibrium sorption properties of the hydrogels is shown in Figure 4.15. Distinctly, all of the samples tested were found to be particularly sensitive to ionic strength variations, due to the presence of the polyelectrolyte NaCMC in the polymer network, which is known to lead to the establishment of "Donnan type" equilibrium between the gel and the surrounding solution. Obviously, for each sample, increasing the ionic strength of the external solution decreased the difference between the concentration of ion species in the gel and in the external solution and, as a result, the water uptake.

According to the Donnan equilibrium theory, with rising of the ionic strength, the distribution in the concentration of mobile ions between the gel and solution is reduced, consequently the osmotic swelling pressure of the mobile ions inside the gel decreases and the hydrogel collapse. The obtained data showed in Figure 5.15 revealed that the swelling degree decreases significantly with the increase of the ionic strength of the solution. This well-known phenomenon, commonly observed in the swelling of ionic hydrogels often results from a charge screening effect of the additional cations causing a non-perfect anion–anion electrostatic repulsion, led to a decrease in the osmotic pressure (ionic pressure) difference between the hydrogel network and the external solution and the hydrogel collapse.

Furthermore, it can be noticed that the swelling degree of NaCMC/PEG20 hydrogel decreases with the high charge of the cation (multivalent < monovalent). It may be explained by complexing ability arising from the coordination of the multivalent cations with carboxylate groups on the NaCMC. This ionic crosslinking mainly occurs at the surface of the hydrogel. It is found that NaCMC/PEG20 hydrogels are rubbery and very hard when they swell in $CaCl_2$ solution. In contrast, the hydrogels swollen in univalent cation solutions exhibit lower strength. It is also clear that Na^+ has less atomic radius than Ca^{2+} consequently with an increase in the size of the ions present in the swelling medium decreases the swelling capacity of the hydrogel due to the difficulty in the penetration of the ions into the hydrogel. Hence according to the above aspects, the swelling trend is higher for NaCl salt solution than $CaCl_2$.

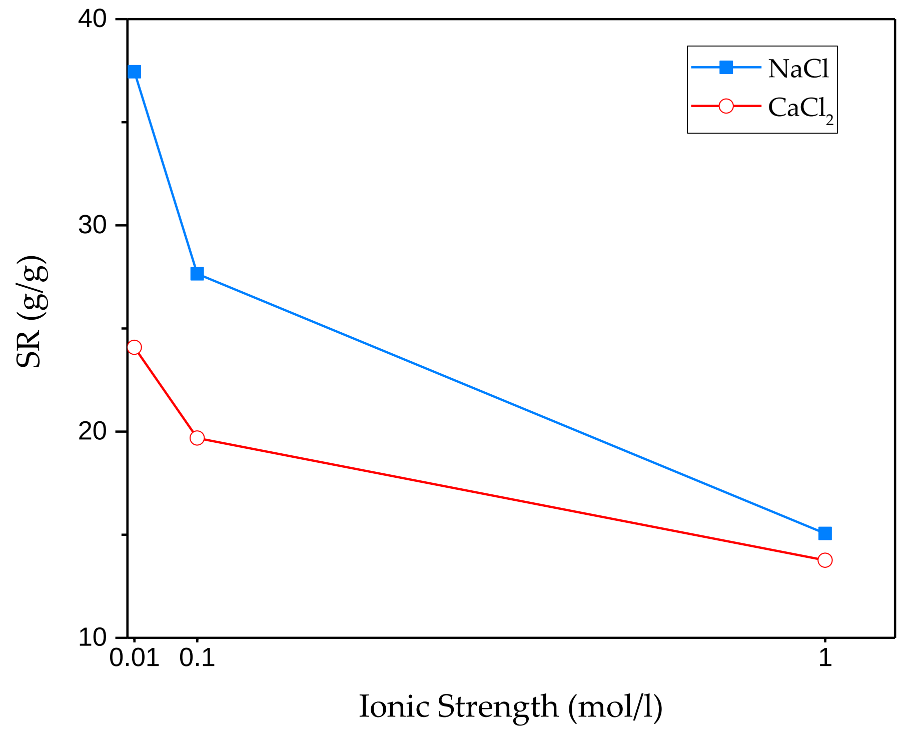

Figure 4.15 Hydrogels equilibrium swelling properties in water solution at different ionic strength

4.3.4. pH Effect on Swelling

With regard to the hydrogel sensitivity to pH variations, an increase of the swelling ratio could be observed when increasing the pH of the external solution (Figure 4.16). This was related to the dissociation of the carboxylic groups present on NaCMC chains, which clearly depends upon the pH of the surrounding environment. As the pH of the external solution decreases, the number of negative charges tethered to the polymer backbone diminishes, since H^+ ions will be associated with the carboxylic groups brought by NaCMC. This reduces the ionic "Donnan type" contribution to the hydrogel equilibrium swelling capacity, thus resulting in lower swelling ratios. The supply of H^+ ions from the dissociated groups on the backbone is, however, limited. This suggests that, at a certain high value of the pH, all the carboxylic groups will be dissociated, giving rise to a fully charged network and thus leading to a maximum value of swelling capability.

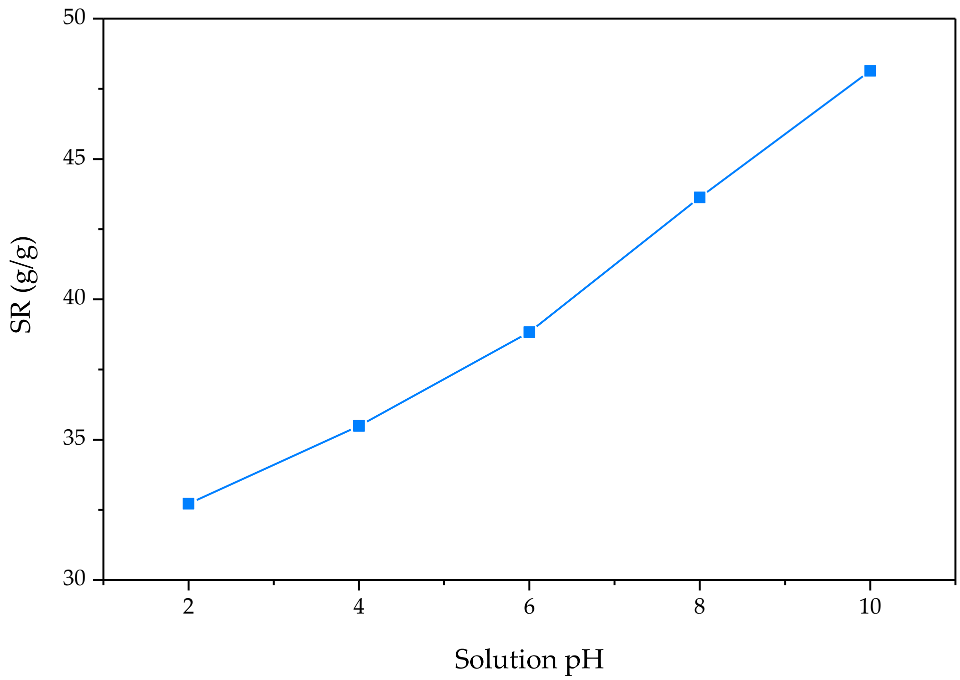

Figure 4.16 Effect of pH of the solution on swelling of the hydrogel

4.4. Spectroscopic and Thermal Analysis of the Hydrogel

4.4.1. Fourier Transform Infrared Spectroscopy

FTIR spectroscopy was used to monitor the crosslinking of NaCMC/PEG20 by citric acid.

The FTIR spectra of NaCMC/PEG20 crosslinked hydrogel demonstrates that carboxylates (–COO^- bands at 1592 cm^{-1}, 1416 $cm^{-1,}$ and 1324 cm^{-1}) and carboxylic acid (–COOH bands at 1730 cm^{-1} and 1243 cm^{-1}) co-existed in the NaCMC/PEG20 hydrogel due to the substitution of Na^+ by H^+ in the NaCMC polymer chains during the acidification promoted by citric acid. Crosslinked cellulose hydrogels showed a relative decrease of intensity of -OH peak at approximately 3400-3200 cm^{-1}.

In addition, the increased vibration at 1230-1205 cm^{-1} in the crosslinked hydrogels is ascribed to C−O of ester bonds formed. Moreover, the relative increase of the stretching vibration band of C=O at approximately 1730-1715 cm^{-1} indicates changes of ester bonds as a result of the crosslinking reaction. However, these changes in the FTIR spectra are more difficult to quantify as the reaction progressed due to overlapping with carboxylic bands of NaCMC.

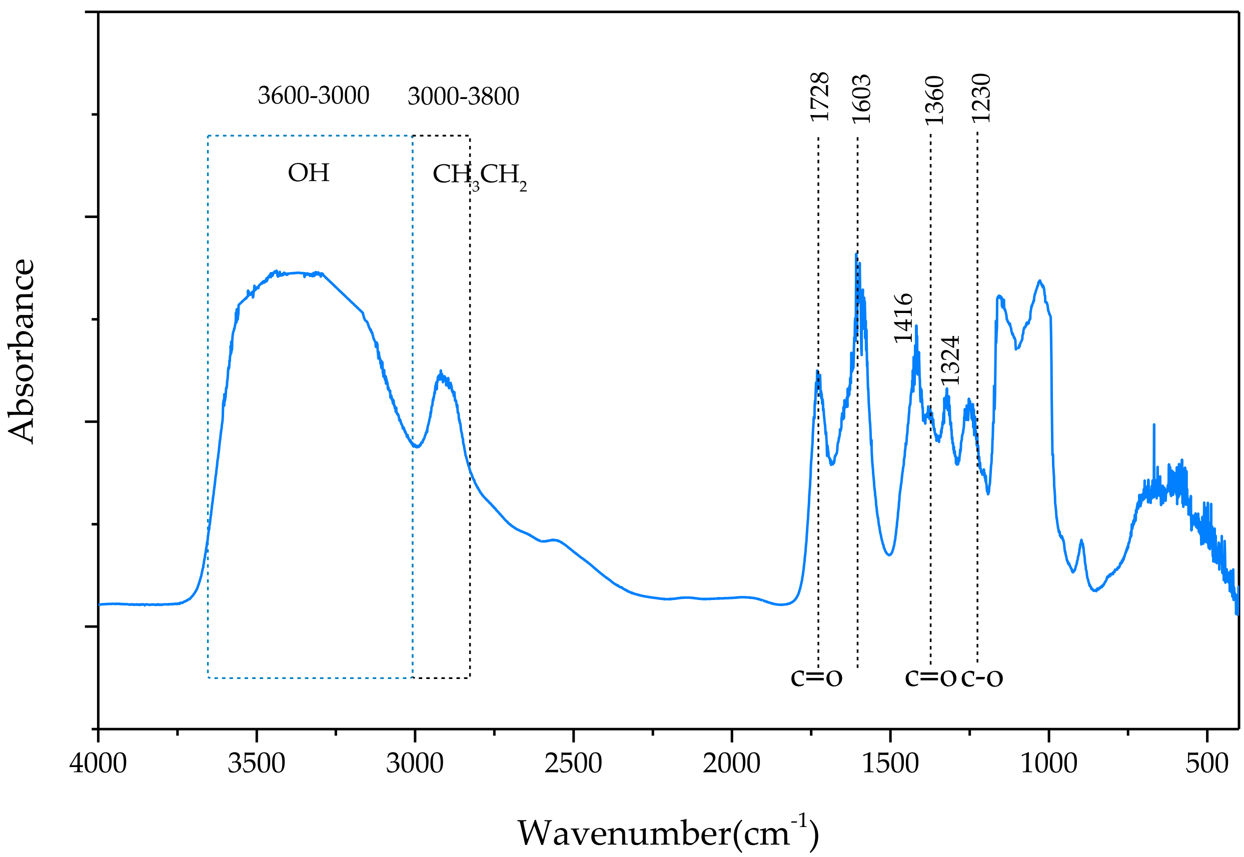

Figure 4.17 FTIR spectra of NaCMC/PEG20 Hydrogel

The addition of PEG to NaCMC promotes the formation of hydrogels predominantly stabilized via hydrogen bonds between functional groups of both polymers (i.e., PEG: C−O−C and −OH; and NaCMC: −OH and C=O), which is verified by the significant increase of the vibrational signals of hydroxyl groups from 3000 to 3600 cm^{-1}. Therefore, the FTIR spectra indicate the formation of hydrogels with hybrid structures composed of an amorphous phase mostly assigned to NaCMC polymer chains and intercalated with semi-crystalline domains of PEG stabilized by hydrogen bonding. This effect is more noticeable by the significant reduction of the peaks as 1360 cm^{-1} and 1343 cm^{-1} related with PEG crystallinity implying its higher miscibility in the NaCMC.

Considering the esterification reaction between alcohols and carboxylic acids, it is expected that the crosslinking reactions between citric acid with NaCMC/PEG20 would reduce the hydroxyl groups and increase the ester signal. Therefore, crosslinked NaCMC/PEG20 hydrogel shows a significant decrease of the hydroxyl band at 3200-3600 cm^{-1} with increasing citric acid content. Moreover, bands at 1230-1205 cm^{-1} (C−O) and 1730-1715 cm^{-1} (C=O) increased due to the formation of ester groups. Nevertheless, it should be noted that the analysis at this region of the FTIR spectra is very complex because different groups are simultaneously formed and consumed in the reaction. In addition, it is also affected by pH such as the protonation of carboxymethyl groups of NaCMC by adding citric acid. Therefore, the intensities of these bands are not a direct indication of the extension of crosslinking because other interactions can be overlapped in the same region of IR spectrum. It is clear that miscibility of PEG increases as the crosslinking reaction progresses, the peaks associated with its crystallinity (1360 cm^{-1} and 1343 cm^{-1}) disappears for the crosslinked blends and the intensity of the other bands of PEG diminishes. Hence, comparing with NaCMC, the addition of PEG enhances the crosslinking most likely due to the presence of its hydroxyl groups stabilizing the polymeric network.

4.4.2. Thermogravimetric Analysis

For NaCMC and NaCMC/PEG20 crosslinked with 10% (w/w) citric acid hydrogel structures, two stages were observed. The first stage is related to water loss and it can be separated in two steps: removal of free water (below 110℃) and vaporization of bound water tightly attached to polymer matrix (below 240℃).

The second stage is the exothermic degradation of the polymeric chains. For NaCMC hydrogel crosslinked with 10% citric acid, carboxymethyl functional group disrupts the higher order of cellulose polymeric packing by both steric hindrance and electrostatic repulsion lowering the thermal stability. Moreover, the esterification reaction associated with crosslinking can reduce the number of remaining hydrogen bonds of NaCMC leading to an even lower degradation temperature of crosslinked hydrogels.

Regarding the addition of 20 wt.% polyethylene glycol (PEG) to produce hydrogel blends (NaCMC/PEG), it was observed that PEG improved the thermal stability of the hydrogels as the degradability was reduced for temperature above 240℃. This was attributed to the strong interactions of several functional groups of both molecules. The incorporation of PEG increases the total amount of −OH groups available for esterification reaction hence forming thermally stable structure.

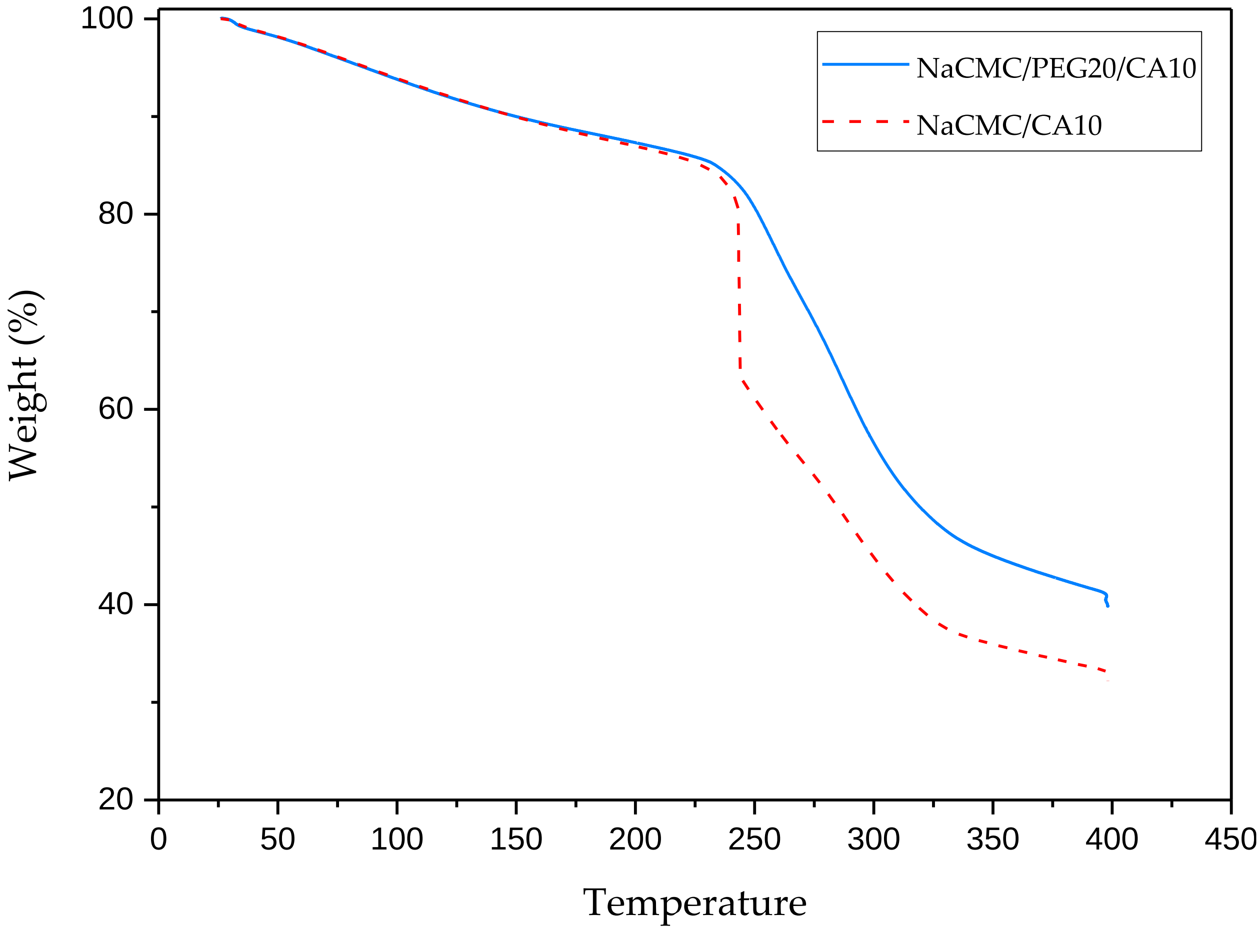

Figure 4.18 Thermo-gravimetric analysis (TGA) of sodium carboxymethyl cellulose (NaCMC/CA10) hydrogel, and carboxymethyl cellulose and 20 wt.% polyethylene glycol (NaCMC/PEG20/CA10) hydrogel crosslinked with 10% citric acid

The remaining residue after the rapid decomposition of NaCMC hydrogel crosslinked with 10% weight of the polymer citric acid(NaCMC/CA10) was about 33-35% attributed to the formation of sodium containing species (Na_2CO_3 and Na_2O). On the contrary, the NaCMC and 20 wt.% PEG composite crosslinked with 10% weight of the polymer citric acid (NaCMC/PEG/CA10) after decomposition about 40-45% remaining mass was obtained credited to both sodium containing species and PEG.

4.5. Agricultural Application

4.5.1. Urea Loading and Release

The loading of hydrogels could be affected by different factors such as soaking time, hydrogel size and active material concentration. The effect of urea concentration on the hydrogel loading is shown in Figure 4.19.

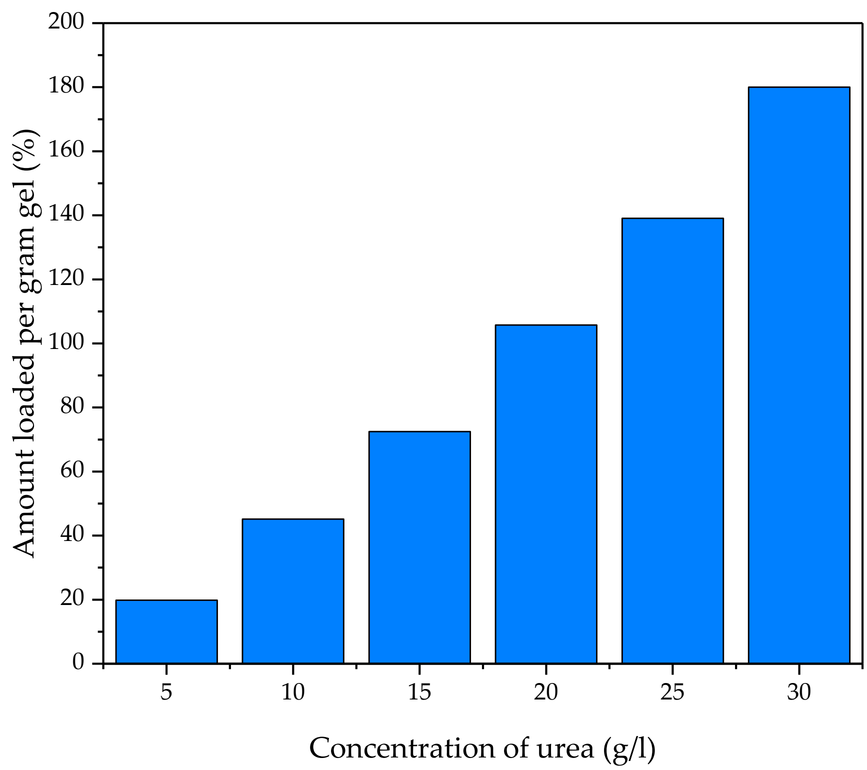

Figure 4.19 Urea solution concentration effect on the loading (%) of NaCMC/PEG20 Hydrogel

It can be seen that the loading percent is enhanced by increasing urea concentration of the loading solution. These results may be due to the increase of urea diffusion inside the hydrogel matrix upon raise of urea concentration. The dependence of urea loading percentage on urea concentration may be due to the fact that urea is neutral molecule, which doesn't affect the electrostatic repulsion force of the carboxylate groups on the hydrogel chains. The addition of urea in water doesn’t change the hydrogel-solvent interaction. Therefore, aqueous solutions of urea with different concentrations can hardly change the swelling process of NaCMC/PEG20 hydrogel.

It is well known that most fertilizers are water-soluble and prone to evaporate at room temperature. Due to surface runoff, leaching, and vaporization, the utilization efficiency or plant uptake of urea is generally low and most of the urea escapes to the environment, resulting in not only huge economic and resource losses but also very serious environmental pollution. So, it is important to study release behavior of the loaded active material from the hydrogel.

The release behavior of the hydrogel occurs as a result of water penetration into the hydrogel matrix. The interaction between water, hydrogel and active agent is the primary factor in the slow release process. The release of active material from the loaded hydrogel closely relates to its water sorption as it has been already established that a highly swelling hydrogel should release a greater amount of solute entrapped within the gel. The release behavior of the loaded CMC/PEG20 hydrogel with 180% urea loading was investigated and shown in Figure 4.20.

The release profile indicates that the amount of emitted urea increases with time. The results are as expected when the initial load is larger, the movement of solute into the solvent front penetrating the surface of the loaded hydrogel is faster. Almost 20% of the urea was liberated within the first 3 hrs. after placing the hydrogel in water. This is mainly because of the release of the loosely attached urea on the surface of the hydrogel. Then after some time of soaking the slow release of the urea from the loaded hydrogel begins.

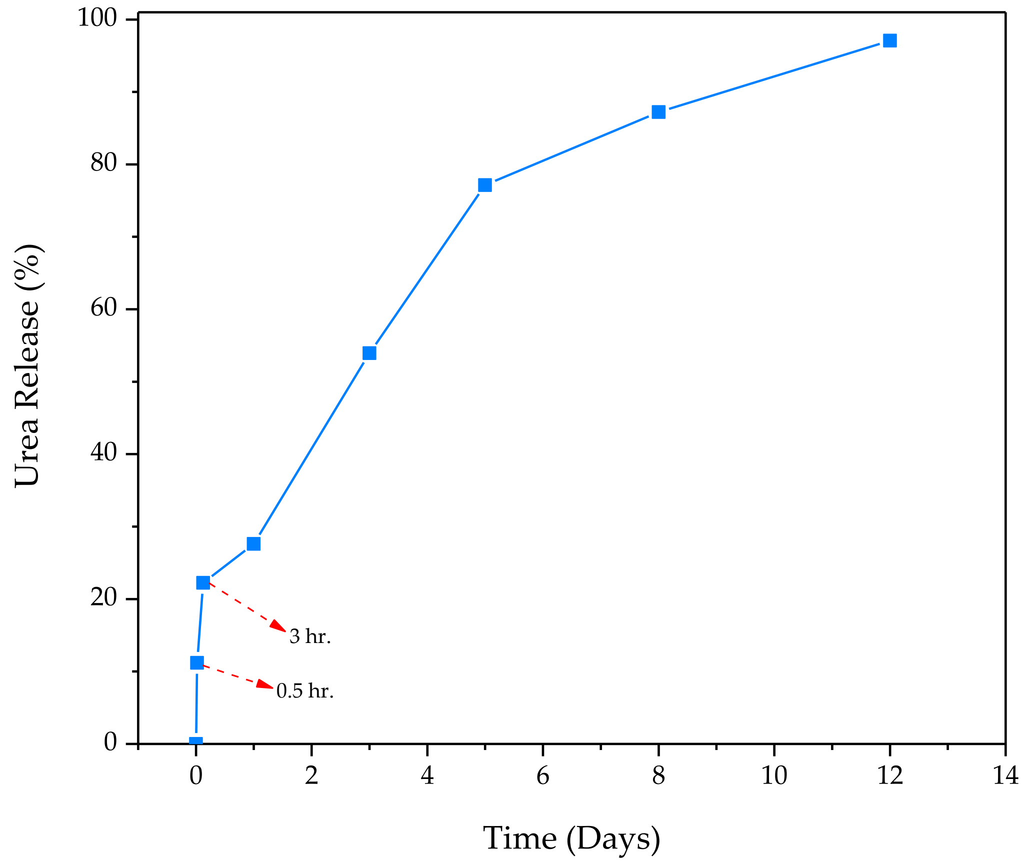

Figure 4.20 Urea release plot of hydrogel with 180% loading percentage

4.5.2. Hydrogel Water Retention in Soil

Although It has been already established that the hydrogel has the capacity to retain water after swelling, water retention of the hydrogel placed in soil was also studied. First, pH and electrical conductivity of the soil was determined. The soil used has pH of 6.75 and electrical conductivity of 0.4 ms/cm. This result is in agreement with soil found in most highlands of Ethiopia.

As expected, the hydrogel-amended soil displayed a higher water retention capability compared to the hydrogel- free control. Moreover, a similar response is observed when hydrogel loaded with urea was used in the soil. After 24 hrs. the soil amended with hydrogel has indicated a small amount of water evaporation in comparison to the soil containing hydrogel loaded with urea. The soil containing hydrogel loaded with urea carries out absorbance of water and release of urea simultaneously. Since most of the space was occupied by the fertilizer, in the first 24 hrs. some of the water that wasn't absorbed by the hydrogel was evaporated. However, after 48 hrs. both hydrogel amended soil display almost similar pattern of water evaporation. The analysis was performed in triplicate. Each point found in the curve is the average of the measured values. The temperature at 40°C was used to favor soil microbial activity and chemical reactions.

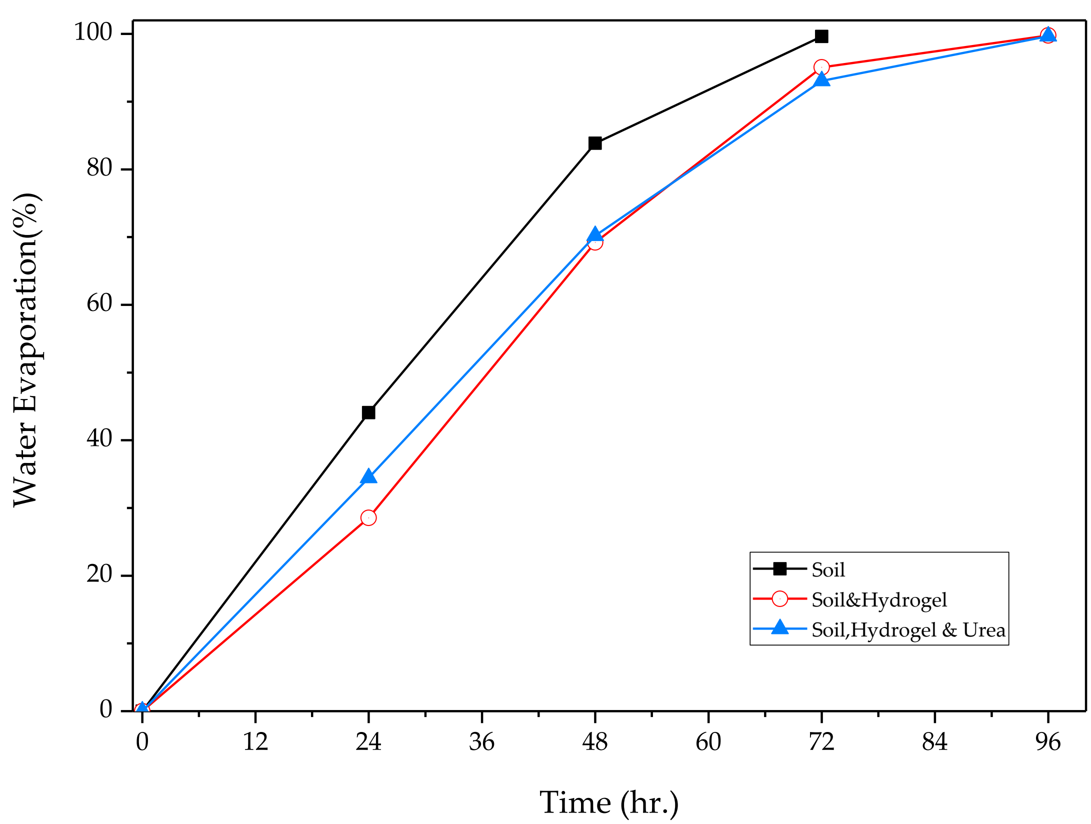

Figure 4.21 Water retention behaviors of soil, soil with Hydrogel, and soil with Hydrogel loaded with urea

Chapter 5

Conclusions and Recommendations

5.1. Conclusions

Application of natural polymers along with synthetic polymers as a matrix for preparing hydrogels can improve the performance of these materials and make them environmentally friendly. In this work, superabsorbent NaCMC and NaCMC/PEG hydrogels of different compositions were prepared using citric acid as a crosslinking agent.

The FTIR spectra of raw materials used indicated the presence of main functional groups (O−H and $-COO^-$) that are involved in the crosslinking reaction. While the XRD result showed that the crystallinity of the sodium carboxymethyl cellulose used was destroyed due to the carboxymethyl functionalization of the cellulose backbone making it ideal for hydrogel preparation.

These results showed that sodium carboxymethyl cellulose-based hydrogels produced with a broad range of hydrophilicity (typically from 215 - 5595%) for water incorporation. These hydrogels also retained about 60 wt.% of their water content after 24 hrs. at 20 °C. Maximum swelling and stability was observed for hydrogels synthesized using NaCMC and 20 wt.% PEG (polymer composition). FTIR spectra of these hydrogels confirmed the formation of an ester bond between the crosslinker and the polymers.

Response surface methodology was applied to optimize the synthesis variables of the hydrogel. Analysis of experimental results shows that the two process variables interaction effect except for interaction between time and polymer composition exhibited a significant impact on the percentage of swelling. The optimum hydrogel with swelling degree of 6748% was synthesized at 72.38 °C temperature, 8 hrs. of reaction time, 16.54% citric acid concentration, and 80% NaCMC and 20% PEG composition.

To evaluate the suitability of the NaCMC/PEG hydrogels as biomaterials, their swelling ratios were studied in different simulated biological solutions. The effects of physical saline solutions and pH of the solution on the swelling phenomena of the different hydrogels were investigated. The result shows that the synthesized hydrogels were sensitive to anionic and cationic solutions and to solutions of different ionic strength.

These hydrogels were also tested for urea loading and release application and water retention in the soil. The amount of released urea from NaCMC/PEG loaded hydrogels increased with time establishing their slow release potential. The amount of water evaporated from the hydrogel mended soil was also small proving their moisture holding capability in the soil. Thus, they can be evidently suitable for agrochemicals slow release and moisture retention application where the swelling behavior is of paramount importance. Furthermore, their slow release capacity can prevent leaching or evaporation of the loaded agrochemicals.

In conclusion, NaCMC/PEG superabsorbent hydrogels may be used as potential eco-friendly water saving materials for agriculture applications in sandy soil as a soil conditioner in view of increasing their water-holding capacity and/or nutrient retention.

5.2. Recommendations

Therefore, based on the outcomes of this research work and overall understanding of the synthesis of cellulose-based hydrogels and their agricultural application, the following recommendations are stated.

- The sodium carboxymethyl cellulose (NaCMC) used in this study has a lower degree of substitution (0.55) which significantly affect swelling of the hydrogel. Hence to further improve the swelling equilibrium of the hydrogel, the degree of substitution of the NaCMC should be considered as a variable that needs optimization.
- Further study of agricultural application of this hydrogel in pilot scale plantation is required to determine feasibility of the technology
- Additional investigation is necessary to understand the urea release kinetics of the loaded hydrogel
- Further investigation of slow release potential of other phytopharmaceutical (liquid fertilizers, pesticide, herbicides) of the hydrogel is recommended
- The hydrogel potential as a superabsorbent in the hygiene industry (diaper, hospital bed sheet) should also be studied.
- Other crosslinking methods of the polymers should also be explored to obtain hydrogel with desirable swelling percentage and stability.

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Appendices

Appendix A: Infrared Spectroscopy Correlation Table

Functional group names	Absorption ranges (cm^{-1})	Type of vibration causing IR absorption
Alkanes	3000-2800	H−C−H asymmetric and symmetric stretching
	1500-1440	H−C−H bend
Alkenes	3100-3000	C=C−H asymmetric stretching
	1675-1600	C−C=C symmetric stretch
Alkynes	3300-3200	C−H stretch
	2200-2100	C≡C
Alcohols, Phenols	3600-3100	Hydrogen-bonded O−H stretch
Carboxylic Acids	3400-2400	Hydrogen-bonded O−H Stretch
	1730-1650	C=O stretch
Esters	1755-1650	C=O stretch
	1300-1000	C−O stretch

Appendix B: Experimental Result

Table B-1 Moisture content of NaCMC

Run	Sample weight(g) W_0	W_f	W_0-W_f	Moisture Content (%)	Average Moisture Content (%)
1	3.0001	2.705	0.2951	9.836	
2	3.0001	2.7102	0.2899	9.96	9.802
3	3.0001	2.7118	0.2883	9.61	

$$\text{Moisture content}(\%) = \frac{w_0 - w_f}{w_0} \times 100$$

Table B-2 Purity of NaCMC

Run	Sample weight(g) B (mass of specimen used)	A (mass of dried residue)	Moisture content (%)	Purity (%)	Average Purity (%)
1	3.0001	2.5707	9.802	95	
2	3.0001	2.5829	9.802	95.45	95.26
3	3.0001	2.5802	9.802	95.35	

$$Purity(\%) = \frac{A \times 10000}{B \times (100 - C)}$$

Table B-3 Ash Content Determination

Run	Weight(g) Crucible	Crucible + Sample	Crucible +Ash	W_1 (sample)	W_2 (Ash)	W_2/W_1	Ash Content (%)	Average Ash Content (%)
1	24.8719	27.8793	25.3633	3.0074	0.4914	0.1634	16.34	
2	23.6050	26.6092	24.0823	3.0042	0.4773	0.1589	15.89	16.15
3	23.5867	26.5938	24.0745	3.0071	0.4878	0.1622	16.22	

$$Ash\ Content(\%) = \frac{W_2}{W_1} \times 100$$

Where $W_1 = W_{Crucible+Sample} - W_{Crucible}$

$W_2 = W_{Crucible+Ash} - W_{Crucible}$

Table B-4 Titration of Carboxymethyl cellulose (NaCMC) Ash for the determination of Degree of substitution

Run	Volume of 0.1 N H_2SO_4 (ml)	Color Change
1	81	from yellow to reddish
2	79	from yellow to reddish
3	80	from yellow to reddish
Average Value	80	

Table B-5 Degree of substitution Carboxymethyl cellulose (NaCMC)

Run	m (mass of NaCMC)	A (Volume of 0.1 N H_2SO_4)	$\frac{0.1 \times A}{m}$	DS	Average DS
1	3.0074	81	2.69	0.556	
2	3.0042	79	2.63	0.540	0.55
3	3.0071	80	2.661	0.546	

$$DS = \frac{0.162 \times \frac{0.1 \times A}{m}}{1 - 0.08 \times \frac{0.1 \times A}{m}}$$

Table B-6 Experimental design and result

No.	Run	Block	Temp (℃)	Time(h.)	Conc. (%)	Comp. (% of PEG)	Response (swelling)
1	50	Block 1	65.00	8.00	10.00	0	3954
2	36	Block 1	95.00	8.00	10.00	0	1318
3	8	Block 1	65.00	24.00	10.00	0	2111
4	38	Block 1	95.00	24.00	10.00	0	465
5	48	Block 1	65.00	8.00	20.00	0	3163
6	39	Block 1	95.00	8.00	20.00	0	430
7	33	Block 1	65.00	24.00	20.00	0	710
8	6	Block 1	95.00	24.00	20.00	0	230
9	1	Block 1	65.00	16.00	15.00	0	1137
10	55	Block 1	95.00	16.00	15.00	0	365
11	45	Block 1	80.00	8.00	15.00	0	2156
12	20	Block 1	80.00	24.00	15.00	0	569
13	26	Block 1	80.00	16.00	10.00	0	2431
14	7	Block 1	80.00	16.00	20.00	0	703
15	59	Block 1	80.00	16.00	15.00	0	1213
16	17	Block 1	80.00	16.00	15.00	0	1000
17	29	Block 1	80.00	16.00	15.00	0	1100
18	25	Block 1	80.00	16.00	15.00	0	817
19	34	Block 1	80.00	16.00	15.00	0	943
20	37	Block 1	80.00	16.00	15.00	0	1385
21	41	Block 1	65.00	8.00	10.00	20	5595
22	3	Block 1	95.00	8.00	10.00	20	1541
23	4	Block 1	65.00	24.00	10.00	20	2319
24	43	Block 1	95.00	24.00	10.00	20	512
25	18	Block 1	65.00	8.00	20.00	20	3675
26	51	Block 1	95.00	8.00	20.00	20	491
27	35	Block 1	65.00	24.00	20.00	20	740
28	5	Block 1	95.00	24.00	20.00	20	260
29	47	Block 1	65.00	16.00	15.00	20	1697
30	40	Block 1	95.00	16.00	15.00	20	504

31	16	Block 1	80.00	8.00	15.00	20	3509
32	12	Block 1	80.00	24.00	15.00	20	699
33	49	Block 1	80.00	16.00	10.00	20	3955
34	9	Block 1	80.00	16.00	20.00	20	846
35	32	Block 1	80.00	16.00	15.00	20	1525
36	14	Block 1	80.00	16.00	15.00	20	1700
37	28	Block 1	80.00	16.00	15.00	20	1300
38	24	Block 1	80.00	16.00	15.00	20	1400
39	10	Block 1	80.00	16.00	15.00	20	1500
40	46	Block 1	80.00	16.00	15.00	20	1600
41	23	Block 1	65.00	8.00	10.00	40	3624
42	52	Block 1	95.00	8.00	10.00	40	1116
43	19	Block 1	65.00	24.00	10.00	40	1930
44	11	Block 1	95.00	24.00	10.00	40	439
45	56	Block 1	65.00	8.00	20.00	40	2273
46	31	Block 1	95.00	8.00	20.00	40	397
47	42	Block 1	65.00	24.00	20.00	40	689
48	54	Block 1	95.00	24.00	20.00	40	215
49	44	Block 1	65.00	16.00	15.00	40	1292
50	53	Block 1	95.00	16.00	15.00	40	389
51	22	Block 1	80.00	3.00	15.00	40	2651
52	27	Block 1	80.00	24.00	15.00	40	619
53	13	Block 1	80.00	16.00	10.00	40	2860
54	15	Block 1	80.00	16.00	20.00	40	561
55	58	Block 1	80.00	16.00	15.00	40	964
56	21	Block 1	80.00	16.00	15.00	40	1000
57	60	Block 1	80.00	16.00	15.00	40	865
58	57	Block 1	80.00	16.00	15.00	40	900
59	30	Block 1	80.00	16.00	15.00	40	950
60	2	Block 1	80.00	16.00	15.00	40	1050

Table B-7 Swelling kinetics study result

Time(min)	W_s(g)	Swelling Ratio (g/g)
0	0.6	1
10	23.709	39.515
20	27.59	44.31667
30	32.67	54.45
60	35.81	59.683
120	37.81	63.01667
180	37.9	63.16667
300	37.98	63.3

Where $W_0 = initial\ weight\ before\ swelling (0.6\ gram)$

Table B-8 Swelling ratio of hydrogel in salt solution

	Swelling Ratio in different salt solutions(g/g)	
Ionic strength	NaCl	$CaCl_2$
0.01 M	37.44076	24.08333
0.1 M	27.65	19.68533
1 M	15.05667	13.7605

Table B-9 Swelling ratio of the hydrogel in different pH solutions

pH of Buffer solution (0.04 M NaCl)	Swelling Ratio (%)
2	32.72
4	35.49
6	38.83
8	43.63
10	48.14

Table B-10 Moisture retention capability

Time(hr.)	Moisture retained (%)
0	100
24	61.24537
48	26.29914
72	5.22203
96	1.53193

Table B-11 Urea loading

Urea Conc. (g/L)	M_l	Urea loading (%)
5	1.1985	19.85
10	1.4515	45.15
15	1.7246	72.46
20	2.0576	105.76
25	2.3907	139.07
30	2.80	180
50		hydrogel collapsed

Table B-12 Urea release

Time (day)	Amount of urea released	Urea released (%)
0.0208	0.0005	11.2
0.125	0.0008	22.24
1	0.001	27.62
3	0.002	53.95
5	0.0029	77.14
8	0.0033	87.23
12	0.0037	97.09

Appendix C: Response Transformation and Box-Cox Plot

Transformations apply a mathematical function to all the response data. By default, the transformation option is set to "none", meaning that the response data will be analyzed as is. Transformations may be needed to meet the assumptions that make the ANOVA valid. Residuals must be normally distributed with a constant variance. Check the diagnostic plots to validate these assumptions. If the plots don't look right try some transformations. Here is a list of the transformations and some data types that may benefit from using that transformation:

- **Square Root** Count or Frequency data
- **Natural Log** Variance (std dev) or Growth data
- **Base 10 Log** Variance (std dev) or Growth data
- **Inverse** Rate data, Decay data
- **Logit** Bounded data, Yield data
- **Arcsin Sqr Root** Probability, Fraction defective

The Box-Cox plot is a tool to determine the most appropriate power transformation to apply to response data. Most data transformations can be described by the power function, $\sigma = fn(\mu^{\alpha})$, where sigma ($\sigma$) is the standard deviation, mu (μ) is the mean and alpha (α) is the power. Lambda (λ) is $1-\alpha$ in all cases. If the standard deviation associated with an observation is proportional to the mean raised to the á power, then transforming the observation by the $1 - \alpha$ (or λ) power gives a scale satisfying the equal variance requirement of the statistical model. As a reminder, here are the commonly used transformations are:

- $\lambda = -1$ inverse
- $\lambda = 0$ natural log

- λ = 0.5 square root
- λ = 1 no transformation

The lowest point on the Box-Cox plot represents the value of lambda (l) that results in the minimum residual sum of squares in the transformed model. The potential for improvement is greatest when the range of the maximum to minimum response value is greater than 3. If a different transformation is recommended (say a change from log to square root) then the new recommendation should be tried. This may happen when the effects/model chosen changes as a result of implementing the transformation. In all cases, the transformations should be improving the statistical analysis and/or the diagnostic plots.

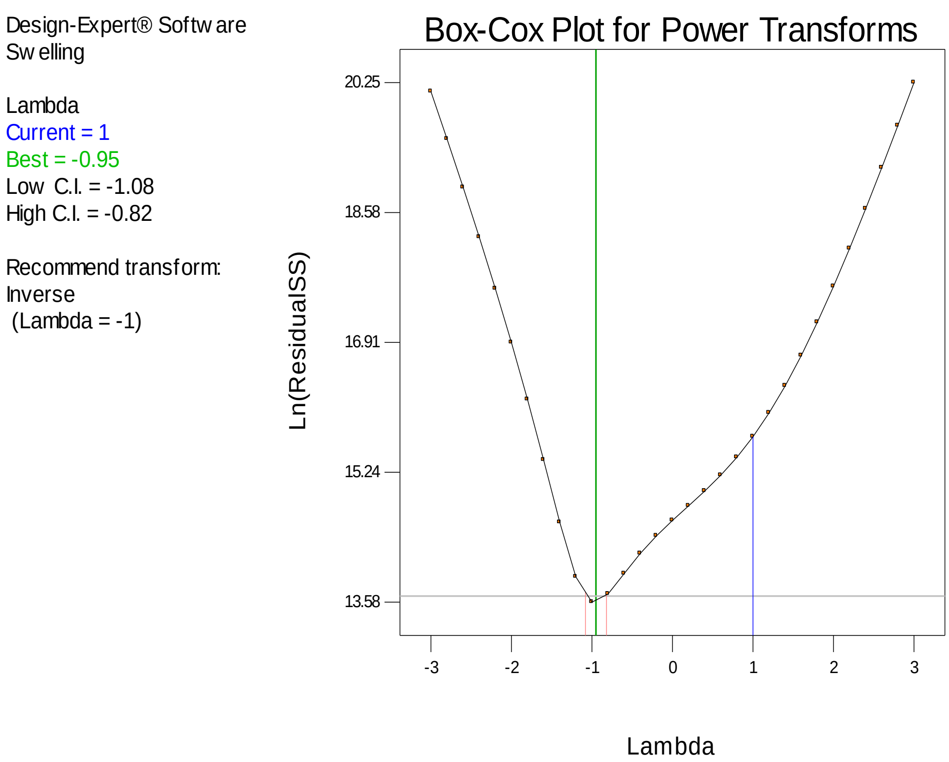

Figure C-1 plot of Box-Cox for power transform and Studentized Residuals

Appendix D: Images of Synthesized Hydrogels

Figure D-1 Colorless Carboxymethyl cellulose(NaCMC) solution

Figure D-2 Crosslinking reaction of Polymer solution inside the oven

Figure D-3 Synthesized Hydrogel disk

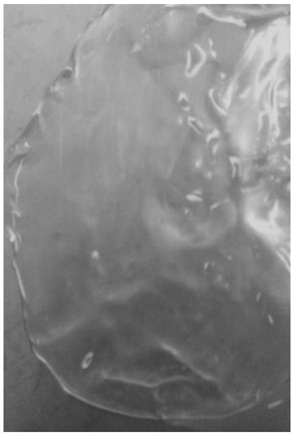

Figure D-4 Hydrogel swelling

Figure D-5 Hydrogel soaked in 1 mol/L NaCl solution

Figure D-6 Hydrogel soaked in 1 mol/L $CaCl_2$ solution

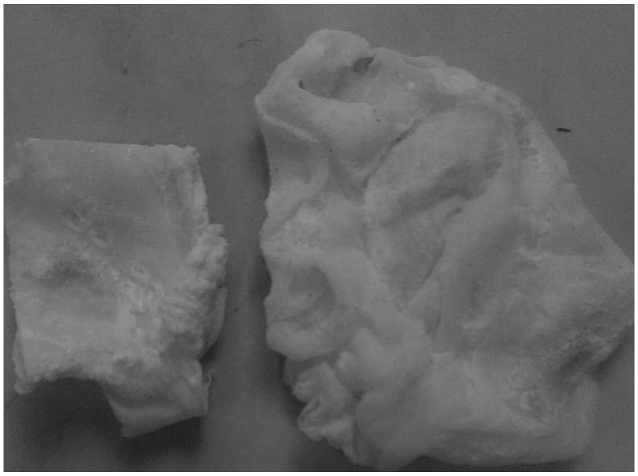

Figure D-7 Urea loaded Hydrogel

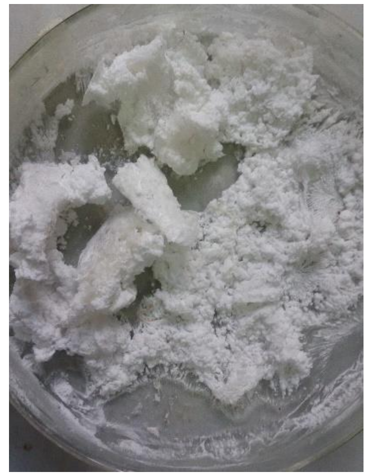

Figure D-8 Collapsed Hydrogel after swelling in 50 g/L urea solution

Figure D-9 Red soil used for water retention test