



JIMMA UNIVERSITY

JIMMA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL ENGINEERING

**Extraction and Characterization of Nanocellulose for
Polyvinyl Alcohol Based Nano-composite Application**

By

Ebise Getacho

A Thesis Submitted to Jimma University, Jimma Institute of Technology, School of Chemical Engineering in Partial Fulfillment of the Requirement for the Degree of Masters in Process Engineering.

Jimma, Ethiopia

Dec 28, 2019 G.C

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Advisor: Hundessa Dessalegn (PhD)

Co-advisor: Mr. Ketema Beyecha (MSc)

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Jimma, Ethiopia

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Approval Page

This is to certify that the thesis prepared by **Ebise Getacho Bacha** entitled ‘**Extraction and characterization of nanocellulose for Poly vinyl alcohol based nano-composite application**’ and submitted as a partial fulfillment for the award of the Degree of Master of Science in Chemical Engineering (Process engineering) complies with the regulations of the university and meets the accepted standards with respect to originality, content and quality.

Approved and Signed by examining board

Kumsa Delessa (PhD)



16/01/2020

External Examiner

Signature

Date

Mr. Abraham Bekele (MSc)

Internal Examiner

Signature

Date

Ms. Meron Asteraye (MSc)

Chair Person

Signature

Date

Mr. Ermias Girma (MSc)

School Dean

Signature

Date

Declaration

I hereby declare that the thesis entitled “**Extraction and Characterization of Nanocellulose for Poly vinyl Alcohol Based Nano-composite Application**” was prepared by me, with guidance of my advisor. The work contained herein is the original work of my own except where explicitly cited otherwise in the text and that this work has not been submitted, in whole or in part, for any other degree or professional qualification.

Submitted by:

Ebise Getacho Bacha

Signature

Date

This thesis has been submitted for examination with approval of advisor and co-advisor

Hundessa Dessalegn (PhD)



Advisor

Signature

Date

Ketema Beyecha (MSc)

Co-advisor

Signature

Date

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Abstract

Nowadays, there are many polymeric materials that are used for different applications like packaging, constructions, medical and automotive devices. The majority of these materials are produced from fossil fuel-based resources which are non-renewable and affect the environment. Bio-composite materials which are composed of two or more different materials that have improved properties are the promising option to replace the non-renewable plastic materials. The bio composite materials can be produced by reinforcing cellulose, nanocellulose, nano clay, and others into the polymer matrix. The cellulose was extracted from teff straw by hot water treatment, acid-chlorite delignification, and alkaline hydrolysis process respectively. The process parameters of alkaline hydrolysis were optimized by response surface methodology (central composite design). The optimum values of temperature, time and sodium hydroxide concentration were 57.676°C, 1hour and 4(w/v) % respectively. The maximum cellulose yield was 78.748% and the nano cellulose yield was 42.87%. The nano cellulose particles were extracted from the cellulose by acid hydrolysis process (48%v/v) at 35°C for 30 min. The characterization of nano cellulose was done by using Fourier-transform infrared spectroscopy, dynamic light scattering, and x-ray diffraction to determine the functional group, particle size distribution and crystallinity respectively. The Fourier-transform infrared spectroscopy result shows that the reduction and total removal of lignin, hemicellulose and other amorphous parts found in teff straw. The average particle size was found to be 102.6 nm with a polydispersity index of 0.047. The crystallinity index of cellulose and nano cellulose was 60.80% and 77.18% respectively. The nanocellulose extracted was successfully reinforced into poly (vinyl) alcohol to illustrate the improvement in water absorption capacity, tensile strength, elongation at break and thermal stability of polyvinyl alcohol. Different ratios of nanocellulose loading were used to see the effects of nanocellulose loading on properties of poly (vinyl) alcohol. The equal amount of cellulose and untreated teff straw were also reinforced with poly (vinyl) alcohol to see the effect of reinforcement type.

Keywords: Teff Straw, Acid hydrolysis, Nanocellulose

Contents

Declaration	iv
Acknowledgment	v
Abstract	vi
List of Tables	xii
List of Figures	xiii
Acronyms	xiv
1 Introduction	1
1.1 Background	1
1.2 Problem Statement	3
1.3 Objectives	4
1.3.1 General Objective	4
1.3.2 Specific Objectives	4
1.4 Scope of the Study	4
1.5 Significance of the Study	5
2 Literature Review	6
2.1 Overview of Nanoparticles	6
2.2 Application Area of Nano-Celluloses	8
2.3 Challenges with the Production of Nano-cellulose	10
2.4 Components and Properties of Ligno-Cellulosic Material	11
2.4.1 Cellulose	11
2.4.2 Hemicellulose	12
2.4.3 Lignin	12
2.4.4 Extractives	13
2.5 Extraction of Cellulose from Ligno-cellulosic Materials	13

2.6	Factors Affect the Yield of Cellulose.....	14
2.7	Cellulose Nano-crystals.....	16
2.8	Extraction Methods of Nanocellulose	17
2.8.1	Acid Hydrolysis	17
2.8.2	Enzymatic Hydrolysis.....	18
2.8.3	Mechanical Treatment	18
2.9	Factors Affect the Nano Cellulose Yield in Acid Hydrolysis Process.....	20
2.10	Polyvinyl Alcohol	22
2.11	Preparation of Nanocellulose/PVA Composite.....	23
2.11.1	Fabrication of Nano-Cellulose Composites Using Solvent Casting.....	23
2.11.2	Fabrication of Nano-Cellulose Composites Using Melt Extrusion	24
2.11.3	Fabrication of Nano-Cellulose Composites Using <i>In situ</i> Polymerization.....	24
2.12	Production of Teff and its Straw in Ethiopia.....	25
2.13	Chemical Composition of Teff straw	26
3	Methodology.....	28
3.1	Chemicals and Equipment Used	28
3.2	Proximate Analysis of Teff Straw	30
3.2.1	Determination of Moisture Content	30
3.2.2	Determination of Ash Content	30
3.2.3	Determination of Volatile Matter Content.....	30
3.2.4	Determination of Fixed Carbon Content.....	31
3.3	Component Characterization of Teff straw	31
3.3.1	Determination of Extractive Content of the Straw	31
3.3.2	Determination of Hemicellulose Content	31
3.3.3	Determination of Lignin	32

3.3.4	Determination of Cellulose Content	32
3.4	Extraction of Nanocellulose from Teff Straw	33
3.4.1	Delignification Process	33
3.4.2	Isolation of Cellulose	33
3.4.3	Preparation of Nanocellulose	36
3.5	Characterization of Nanocellulose	38
3.5.1	Fourier Transform Infrared Spectroscopy (FTIR) Analysis	38
3.5.2	Particle Size Distribution	38
3.5.3	Crystallinity Analysis.....	39
3.6	Production of Nanocellulose/PVA Composite.....	40
3.7	Characterization of Nanocellulose/PVA Composite.....	42
3.7.1	Water Absorption Capacity.....	42
3.7.2	Mechanical Properties.....	42
3.7.3	Thermal Stability	43
4	Result and Discussion.....	44
4.1	Proximate Analysis of Raw Material (Teff straw)	44
4.1.1	Moisture Content	44
4.1.2	Ash Content	44
4.1.3	Volatile Matter	44
4.1.4	Fixed Carbon.....	44
4.2	Component Characterization of Teff Straw	45
4.2.1	Extractives.....	45
4.2.2	Hemicellulose	45
4.2.3	Lignin.....	46
4.2.4	Cellulose	46

4.3	Extraction of Nanocellulose from Teff Straw	46
4.4	Statistical Analysis of the Experimental Results	49
4.4.1	Experimental Data	49
4.4.2	Model Summary Statistics	50
4.4.3	Analysis of Variance.....	50
4.4.4	Model Adequacy.....	52
4.4.5	Development of Model Equation.....	54
4.4.6	Effects of Significant Individual Factors	54
4.4.7	The Interaction Effects of Factors.....	57
4.4.8	Optimization of Process Parameters for Alkaline Hydrolysis.....	60
4.4.9	Model Validation	62
4.5	Characterization of Nanocellulose suspension.....	63
4.5.1	Functional group Analysis	63
4.5.2	Particle Size	66
4.5.3	Crystallinity Index	68
4.6	PVA-Nanocellulose Composite Films	71
4.7	Characterization of PVA-Nanocellulose Composite Films	72
4.7.1	Water Absorption Test.....	72
4.7.2	Thermogravimetry Analysis	75
4.7.3	Mechanical Tests	76
4.8	Evaluation of Effectiveness of Reinforcing Nanocellulose	80
4.8.1	Improvement in Water Absorption Capacity	80
4.8.2	Improvement in Tensile Strength.....	81
4.8.3	Improvements in Elongation at Break	83
5	Conclusion and Recommendation.....	84

5.1	Conclusion.....	84
5.2	Recommendation.....	85
	Reference	86
	Appendix.....	99
	Appendix A: Results from Design Expert	99
	Appendix B: Some pictures from laboratory work.	101

List of Tables

Table 2.1: Chemical properties of cellulose	12
Table 2.2: Different works on the extraction of cellulose	15
Table 2.3: Different works on the extraction of nanocellulose.....	21
Table 2.4: Chemical properties of Polyvinyl Alcohol	23
Table 2.5: Different uses of some agricultural residues	26
Table 2.6: Chemical composition of lignocellulosic materials.....	27
Table 3.1: List and description of equipment used for laboratory work.....	29
Table 3.2: Levels of three independent variables studied.....	33
Table 3.3: Selected and screened design parameters for the alkaline process by CCD.....	35
Table 3.4: Formulation ratio for the preparation of composite films	41
Table 4.1: Results of proximate analysis for Teff straw with literature values	45
Table 4.2: Value of component analysis with literature values	46
Table 4.3: The value of experimental data and predicted data at selected parameter values.	49
Table 4.4: Suggested model for the design.....	50
Table 4.5: Analysis of variance (ANOVA) for Response Surface Quadratic Model.....	51
Table 4.6: Model statics of the design	52
Table 4.7: Adjusted process parameters in range to maximize the yield.....	60
Table 4.8: Optimal possible solutions.....	61
Table 4.9: FTIR characteristic peaks of Teff straw, cellulose, and nanocellulose	64
Table 4.10: Z-Average particle size from DLS instrument	66
Table 4.11: Comparison of average particle size with literature	67
Table 4.12: Crystallinity index values for Teff straw, cellulose, and nanocellulose	70
Table 4.13: Comparison of Crystallinity Index obtained in this work with previous works.....	70
Table 4.14: Water absorption capacity as a function of nanocellulose loading.....	72
Table 4.15: Comparison of a result of the WAC of composite materials with literatures.....	74
Table 4.16: Tensile strength and elongation at break of different composites	77
Table 4.17: Comparison of mechanical properties of PVA composite films with literature.....	79
Table A.1: Lack of fit test from ANOVA.....	99
Table A.2: Peak analysis from Origin Pro 8.5.....	100

List of Figures

Figure 2.1: Different application area of nanocellulose.....	9
Figure 2.2: Schematic diagram of nanocrystalline cellulose	17
Figure 2.3: Teff straw	25
Figure 3.1: Collected and grinded Teff straw	28
Figure 3.2: Overall flow diagram of the production process of composite from Teff straw.....	37
Figure 4.1: Produced cellulose after delignification and alkali treatment.	47
Figure 4.2: Produced nanocellulose suspension	48
Figure 4.3: Normal plots of residuals for cellulose yield.....	53
Figure 4.4: Plot of predicted versus residuals for the yield.	53
Figure 4.5: Plot of actual yield versus the predicted yield of cellulose	54
Figure 4.6: Plot of the effect of temperature (a) and time (b) on a yield of cellulose	55
Figure 4.7: Effect of NaOH concentration on the yield of Cellulose	56
Figure 4.8: The 3D graph of time and temperature interaction effects on yield.....	58
Figure 4.9: The contour plot of time and temperature interaction effects on yield.	58
Figure 4.10: The contour plot of time and NaOH concentration effects on yield.	59
Figure 4.11: The 3D graph of interaction effects of time and NaOH concentration on yield.	59
Figure 4.12: FTIR spectra for Teff straw, Cellulose and Nanocellulose suspension	65
Figure 4.13: Particle size distribution obtained by Dynamic Light Scattering.....	67
Figure 4.14: X-ray Diffraction patterns for nanocellulose (a), cellulose (b) and teff straw (c)....	69
Figure 4.15: Prepared composite films.	71
Figure 4.16: The plot of Nanocellulose loading versus Water Absorption capacity	73
Figure 4.17: TGA and DTG curves of neat PVA and NC/PVA films.....	76
Figure 4.18: Tensile strength and elongation at break of composite versus nanocellulose	78
Figure 4.19: Plot of WAC for Neat PVA and Reinforced PVA composite films	81
Figure 4.20: Plot of the tensile strength of neat PVA and reinforced PVA composite films.	82
Figure 4.21: Plot of elongation at the break of neat PVA and reinforced PVA composites.	83
Figure A.1: Plot of residual versus run	99
Figure B.1: Raw material and major products after each procedure	101
Figure B-2: Main Processes in nanocellulose production.....	102
Figure B-3: Production process of PVA composite.....	103

Acronyms

AGU	An hydro-glucopyranose units
ANOVA	Analysis of Variance
ASTM	American Standard of Testing Material
BC	Bacterial Cellulose
CCD	Central Composite Design
CMC	Commercial Micro-Cellulose Crystalline
CNC	Cellulose Nano Crystals
CI	Crystallinity Index
DLS	Dynamic Light Scattering
DOE	Design of Experiment
DP	Degree of polymerization
EB	Elongation at break
FTIR	Fourier Transform Infrared Spectroscopy
IBG	Imperata Brasiliensis grass
MFC	Micro-fibrillated cellulose
MWCO	Molecular Weight Cut Off
NC	Nano-Cellulose
OPEFB	Oil Palm Empty Fruit Bunches
PCL	Poly caprolactone
PDI	Poly-dispersity Index
PEG	Polyethylene glycol
PLA	Poly Lactic Acid
PVA	Polyvinyl Alcohol
SCB	Sugar Cane Bagasse
TeS	Teff Straw

RSM	Response Surface Methodology
TS	Tensile Strength
WAC	Water Absorption Capacity
XRD	X-ray diffractometry

1 Introduction

1.1 Background

There have been increased challenges in society when it comes to needs such as food, fuel, energy, and materials. These needs largely depend on diminishing fossil resources, which are caused by more advancement in science and technology enabling mankind to consume more of the fossil resources(Othman, 2014). There are many materials that are based on petroleum products that have caused serious environmental impacts such as the depletion of natural non-renewable resources, energy crisis and global warming (Mohanty and Swain ,2017). Due to its uses in different applications, plastic materials are one of the segments that are growing fast in the waste stream. As the petroleum-based synthetic polymer products like plastics do not decompose upon disposal, the ecological concerns have resulted in interest in a new natural and compostable material to improve the biodegradability and environmental safety(Roy *et al.*, 2014). To meet the rapid demand for environmental safety and sustainability many researchers have been developed different packaging materials that can be easily degraded. Nowadays, the production of bio-composite from a renewable source is attracting the attention of industrialists and researchers instead of using petrochemical resources. Bio composites are a promising option to further improve material properties while maintaining their biodegradability. They are materials composed of two or more different materials with the properties of the resultant material being superior to the properties of individual material that made them (Fowler *et al.*, 2006). They have improved properties such as low density, biodegradable, and good mechanical properties due to high aspect ratio and high surface area of nano-particles (Othman, 2014) (Mohanty and Swain, 2017). Due to their lack of sufficient strength, dimensional stability, and stiffness, most of the plastics by themselves are not suitable for load-bearing applications. However, fibers possess high strength and stiffness but are difficult to use in load-bearing applications by themselves because of their fibrous structure(Roy *et al.*, 2014). In fiber-reinforced composites, the fibers serve as reinforcement by giving stiffness and strength to the structure and the plastic matrix serves as the adhesive to hold the fibers in place so that suitable structural components can be made(Sanjib *et al.*,2017).

Cellulose is the most abundant, natural, renewable and biodegradable polymer. It can be found in hardwood, softwood, cotton, bacteria, algae and etc (Wang *et al.*, 2019 ; Mandal and

Chakrabarty, 2011). It can be obtained from these materials by mechanical, steam explosion, high-pressure homogenization, cyro-crushing, and chemical methods (Chakraborty *et al.*, 2005; Ibrahim 2010; Mzimela *et al.*, 2018). The chemical method is an effective way to obtain high purity cellulose. A combination of chlorite bleaching and alkali treatment are the most commonly used methods for extracting cellulose from plants (Ching and Ng, 2014). This method was used in this work for its simplicity. There are different methods that can be used to obtain nanocellulose from different lignocellulosic materials. These are acid hydrolysis, mechanical treatment and enzymatic hydrolysis (Bondeson *et al.*, 2006 ; Brinchi *et al.*, 2013). The widely used method by different researchers is the acid hydrolysis method. It is an easy and fast method to produce nanocellulose with better properties and small particle size. Because of its benefits of being non-toxic and highly durable, PVA is considered a suitable source of materials for composite production (Hallensleben, 2000). Besides that, PVA is a synthetic polymer that is biodegradable in the environment, water-soluble, semi-crystalline with excellent chemical resistance (Lani *et al.*, 2014). However, due to their high cost, brittleness, high water absorption capacity, and low mechanical properties make the applications of PVA materials limited (Takasu *et al.*, 2004 ; Wu *et al.*, 2013). To solve these limitations, PVA is often blended with other cheap and biodegradable polymers like cellulose, nanocellulose, nano clay and etc.

Ethiopia is currently producing a large amount of teff annually in different areas. It is one of the main cereal crops mostly cultivated in Ethiopia and Eritrea for food (Bachewe *et al.*, 2015). In recent years, as the report from the central statistical agency implies that an average of 3.7 million tons of teff cereal has been produced per annum and around more than 2 million tons of straw has also been reported as waste every year (Ethiopian Central Statistical agency, 2013). A very few Ethiopian scholars try to investigate the use of teff straw for biosilica synthesis (Bageru and Srivastava, 2017), for the removal of heavy metals (Tadesse *et al.*, 2015) and bio-methane production (Chufu *et al.*, 2015). Up to our knowledge, there is no studies have been performed and reported on the preparation of nano-cellulose from teff straw.

This study attempt was made to investigate the possibility of using teff straw as the source of nanocellulose, used for producing nanocomposite, with an acid hydrolysis method and the improvement of polyvinyl alcohol properties with incorporating nanocellulose.

1.2 Problem Statement

Currently, there are many different polymeric materials that are used for different applications like packaging, constructions, aeronautics, medical and automotive devices. The majority of these materials are produced from petroleum and fossil fuel-based resources which are non-renewable, not environmentally friendly, non-biodegradable and cause the depletion of these resources. Moreover, all these polymer products are mainly discarded into landfills and cause pollution as well. The high usages of plastics are leading to serious environmental pollution, a problem that has to be faced by all societies. Nevertheless, there is an alternative to reduce the environmental problems caused by plastics. One of these alternatives is the production and application of biodegradable plastics based on resources such as natural fiber and starches can be pursued to provide benefits to the environment with respect to the degradability. However, the applications of biodegradable plastics like polyvinyl alcohol and Polylactic acids were limited due to their mechanical and water absorption properties. So, the improvement of the properties of those degradable materials by incorporating nanofillers is attracting the attention. Different works were done on the area to develop different composite materials by extracting nanocellulose and nano fibrillated cellulose from different materials like bagasse, rice husk, wheat straw, flax, hemp, sisal, jute, corn straw, cotton and pineapple (Wu *et al.*, 2013 ; Nuruddin *et al.*, 2013 ; Morán *et al.*, 2008 ; Hayati *et al.*, 2017). Teff straw, the abundant and indigenous lignocellulosic material in Ethiopia and produced on large scale and used for other local uses like bedding, construction, and others but it is recognition in further scientific studies do not get attention when compared to other lignocellulosic materials. Nowadays, as the industry attempts to reduce its dependence on petroleum-based products there is an increasing need to investigate more environmentally friendly with improved properties and sustainable materials to replace the existing ones. So, this study was done to evaluate the effectiveness of teff straw as a cellulose source to improve the properties of the polymer by extracting nanocellulose fiber and reinforce it with polyvinyl alcohol.

1.3 Objectives

1.3.1 General Objective

- ❖ The main objective of this work is to extract and characterize nanocellulose from Teff straw for bio composite application.

1.3.2 Specific Objectives

- ❖ To determine proximate analysis and chemical composition of raw material.
- ❖ To study the optimum conditions of alkaline hydrolysis parameters (temperature, time and alkali concentration) on the yield of cellulose.
- ❖ To extract nanocellulose from Teff straw and characterize its functional group, crystallinity and particle size and distribution.
- ❖ To produce composite material and characterize it (water absorption capacity, mechanical properties, and thermal stability).
- ❖ To compare and evaluate the properties of neat PVA with that PVA reinforced with cellulose, untreated teff straw, and nano cellulose composites.

1.4 Scope of the Study

This study was mainly focused on the extraction and characterization of nanocellulose from Teff straw. The cellulose was extracted from Teff straw and the process parameters (temperature, time and alkali concentration) of the alkaline process were optimized by using response surface methodology (central composite design). The nanocellulose was extracted by three main stages using chlorite delignification, alkaline hydrolysis, and acid hydrolysis process. Then, the product was characterized by fourier transform infrared spectroscopy, x-ray diffractometer, and dynamic light scattering to observe the functional group analysis, crystallinity, particle size distribution and average particle size respectively. After that, the composite films were prepared by using a solvent casting method to observe the effectiveness of nanocellulose on the improvement of polyvinyl alcohol properties. The characterizations done for composite films were thermal stability, water absorption test, tensile strength, and elongation at break.

1.5 Significance of the Study

The finding of this research is to discover the performance of nano cellulose from agro-waste (Teff straw) fiber as reinforcing materials in polymer composites. These composite materials have good properties such as mechanical, degradability, and compatibility. This provides composite materials that can be degraded and improved properties that play a vital role in the variety of applications for their outstanding performance. The demands of polymeric materials are increasing rapidly for different applications such as packaging, building, and construction, aeronautics, medical and automotive devices. But, most of these products are not environmentally friendly and not easily biodegradable upon discard to the environment causing serious environmental problems. However, there is an alternative option such as the production and application of biodegradable composites based on natural resources derived from agro-wastes that provide environmental benefits. The reduction of petroleum resources and rising its cost results in the finding of cost-effective ways to produce different materials from renewable and abundant natural resources. By using renewable and abundant natural resources such as agricultural wastes for the production of composite materials, nanocellulose can provide a viable solution to overcome the issues concerning diminishing petroleum resources coupled with global environmental problems.

The other advantage of this research is to provide a way of converting agricultural wastes into valuable products. Teff is the main cereal crop mainly used in Ethiopia for food and has been growing in popularity across the world in recent years. The production of teff is increasing dramatically every year. The Ethiopian government is planning to export teff to other countries like Europe and the US. Teff is in demand because of its various health benefits and unique nutritional content. So, as the production of teff increases, the amount of teff straw also increases. As different sources imply around 10.1% of teff straw was left on the field and converting this waste to a valuable product like nanocellulose is another benefit for the environment. Apart from these, the investigation of this research was important to provide the opportunity for Nano engineered biomaterials in composite processing that opens a new area of research in Ethiopia for converting unused teff straw into nanocellulose.

2 Literature Review

2.1 Overview of Nanoparticles

Nano-scale materials are defined as a set of substances where at least one dimension is approximately in a nanometer range. A nanometer is one-millionth of a millimeter. Nano materials are cornerstones of Nano science and nanotechnology. Nanostructure science and technology is a broad and interdisciplinary area of research that has been growing explosively worldwide in the past few years (Alagarasi, 2016). Nano-materials are of interest because of their unique optical, magnetic, electrical, and other properties. The best properties of nanoparticles make them the potential for great applications in packaging, electronics, medicine, and other fields. Nanoparticles are entrapped into the biopolymer matrix with the intention, first and foremost, to reinforce the material, but there is an influence also on other physical properties. One can find a change in the color, optical, rheological, thermal, electrical, and magnetic properties and improvement of the dimensional stability, surface characteristics, and durability. The chemical reactivity, biodegradability, and processability are affected as well. These numerous modifications are determined by the interactions between nanoparticles and biomolecules. Nano-sized particulates differ by their dimensions and shape. Both these factors hold much significance for the formation and properties of bio-nano composites (Alexandre and Dubois, 2000). The nanoparticles have a highly extended surface area that is increased with a decrease of dimensions. The surface area provides an abundance of contacts and the effectiveness of interactions with biomolecules in the bio-nano composite matrix (Sotiriou *et al.*, 2011). Consequently, a significant effect of nano-particulate additives to the composite materials occurs at a small amount of a few percentage points (Shchipunov, 2012).

Nano-composites are composite materials comprising one or more phase(s) derived from a biological origin (Fowler *et al.*, 2006). The reinforcing phase in most cases is derived from plant fibers in crops such as cotton, flax or hemp, or from recycled wood, waste paper, crop processing by-products, and agro-wastes. The matrix phase within a bio-composite may take the form of a natural polymer, possibly derived from vegetable oils or starches. Bio composite materials are the promising option to further improve material properties while maintaining their biodegradability and they have received significant interest in recent years, due to the increased awareness of and drive towards more environmentally sustainable technologies. In a broad sense,

the word ‘composite’ defined as ‘made of two or more different parts’ or ‘a composite is a combination of two or more different materials that are mixed in an effort to blend the best properties of both’ (Abba *et al.*, 2013).

The most composite material consists of one or more discontinuous phases of distributed in one continuous phase. The discontinuous phase is usually harder and with superior mechanical properties than the continuous phase. The continuous phase is called the “*matrix*” while the discontinuous phase is called “*reinforcement, or reinforcing material*” (Ariadurai, 2014). The bio-nano composites consist of a biopolymer matrix reinforced with particles (nano-particles) having at least one dimension in the nanometer range (1-350 nm) (Plermjai *et al.*, 2018) and exhibit much-improved properties due to high aspect ratio and high surface area of nano-particles (Nasir *et al.*, 2017 ; Mtibe *et al.*, 2015). It has also unique properties such as low density, biodegradable, stiffness, and good mechanical properties. In addition, it is also easily modified and has a high surface area and typical morphology (Mohanty and Swain, 2017).

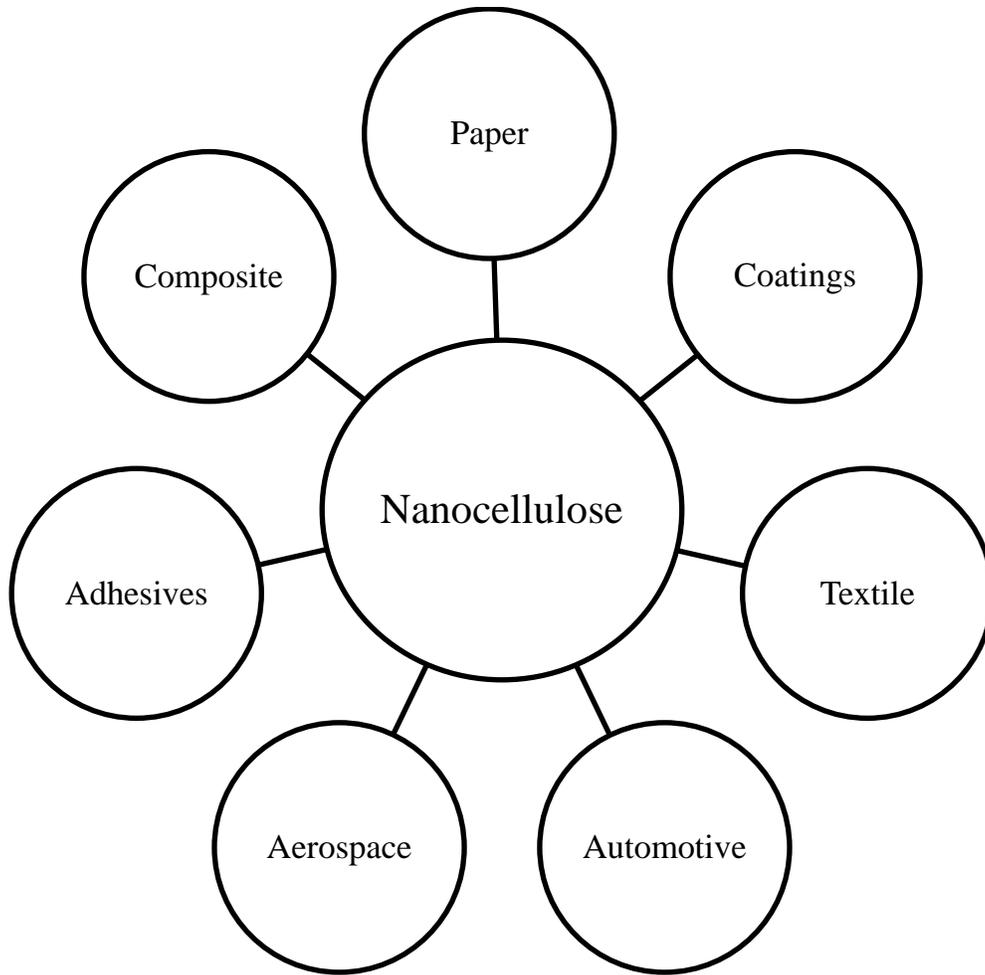
The reinforcement gives the composite material the best mechanical performance, whereas the role of the matrix is to transmit to the fiber to the external mechanical load and protect the fibers against external attack. In many cases, bio-based materials have reduced weight, occupational health benefits, and added functionality. The environmental benefits of bio-based material sources include low embodied energy, CO₂ sequestration, reduced depletion of fossil-based resources and a positive impact on agriculture (Balaji *et al.*, 2015).

Many biopolymers are used as the reinforcement material for nano-bio composites such as poly (vinyl) alcohol (PVA), poly (ethylene glycol) (PEG), poly (caprolactone) (PCL), Polylactic acid (PLA) and etc. (Santos *et al.*, 2016). Nano-composites have improved properties like mechanical properties including strength, modulus and elongation at break, dimensional stability, electrical conductivity, thermal stability and chemical resistance (Jayaramudu *et al.*, 2013). It becomes attractive due to the tremendous interaction between nano-metric particles and the polymeric matrix within the structure. The great surface area (interfaces) within the nano-composites promotes adhesion energy, increasing molecular bonding, and this increase in chemical bonding enhances the polymer cross-linking resulting in improvements in mechanical properties (Darder *et al.*, 2007).

2.2 Application Area of Nano-Celluloses

Nanocellulose is a term referring to nano-structured cellulose. This may be either cellulose Nano crystal (CNC or NCC) or bacterial nanocellulose, which refers to nano-structured cellulose produced by bacteria (Islam *et al.*, 2014). The properties of nanocellulose make it an interesting material for many applications. In paper and paperboard production, nano celluloses are used to enhance the fiber-fiber bond strength and, have a strong reinforcement effect on paper materials. It also used as a barrier in grease-proof type of papers and as a wet-end additive to enhance retention, dry and wet strength in commodity type of paper and board products (Shak *et al.*, 2018). It can be used for carbohydrate additives used as thickeners, flavor carriers, and suspension stabilizers in a wide variety of food products (Gómez *et al.*, 2016).

The integration of CNC appears to alter the structure of the biofilms and enable a more controlled release of the antimicrobial agent. Such property increased the lifetime of the bioactive films that remained active over a prolonged period. The food applications arise from the rheological behavior of the nanocellulose gel (Criado *et al.*, 2018). The dried nanocellulose aerogels used in sanitary napkins, tampons, diapers or as a wound dressing. The use of nanocellulose as a composite coating agent in cosmetics such as hair, eyelashes, eyebrows or nails is also increasing (Lam *et al.*, 2012). Due to its good biocompatibility, and excellent physical properties, nanocellulose is also widely applied in the medical field. Nanocellulose dressing can be well adhered to wound and easily detached by itself after skin recovery. Other applications of nanocellulose in the medical field such as drug delivery into target cells, the implant of soft tissue, blood vessel replacements and so on are also investigated in recent years (Phanthong *et al.*, 2018).



Source: (Lam *et al.*, 2012)

Figure 2.1: Different application area of nanocellulose

The composites produced from nanocellulose by reinforcing with polymer matrix are also widely used for different applications as the packaging industry, automotive industry, aerospace industry, building industry, furniture industry, biomedical industry and etc. The need for lightweight materials for automotive and aerospace applications opened new frontiers of advanced materials. Natural fiber composites are being used for the manufacturing of many components in the automotive sector. The use of plant fiber-based automotive parts is attractive for automotive industries worldwide because of its reduction in weight about 10%, energy production of 80% and cost reduction of 5% (Balaji *et al.*, 2015). Among the usage of the total plastic, packaging occupies the top position with 41%, of which about 20% is used in the food industry. But, most of the packaging materials are made up of nonrenewable and non-degradable

synthetic plastics, packaging waste also occupies the top position in landfills (Soulestin *et al.*, 2011). Building and construction materials utilize about 23% of the world's total plastic usage and they are energy-intensive materials.

Bio-composites play a vital role since they are biodegradable and importantly biocompatible, which is the most critical aspect for bio-medical applications. In fact, the bio-materials that are used in the human body must be compatible with the tissue and other related organs that they are found or fitted into. Also, the prime reason for the biomaterials to biodegrade inside the body is to eliminate any further surgical or medical intervention for the removal of the part that was made from the biomaterial. One of the main applications of bio nano-composites in the bio-medical field is in the regeneration of damaged tissues and in implants (Darder *et al.*, 2007).

2.3 Challenges with the Production of Nano-cellulose

Although nanocellulose appears as a promising material for environmental remediation, there are still many challenges and drawbacks affecting the application of this nanomaterial. To promote the commercialization and marketability of nanocellulose for environmental remediation, the application must be easily scalable, low cost, and produce valuable end-products (Carpenter *et al.*, 2015). So far, most investigations on nanocellulose production are only on a laboratory scale. The challenges lie in the scalability, environmental impact, and cost that come with the selection of treatment routes to produce nanocellulose. Several commonly used techniques related to mechanical disintegration are suitable for up-scaling. However, these techniques are inclined toward high energy consumption (Alexandrescu *et al.*, 2013). Although other mechanical techniques are being studied to overcome this issue, most are still in its infancy and considered not suitable for up scaling. The biological and chemical pretreatment techniques were developed to improve this issue. The chemical pretreatment of nanocellulose could actually result in a higher environmental impact due to the presence of solvent waste and acidic waste although lower electricity usage is required. Another challenge would be the questionable large-scale production of bacterial cellulose and cellulose nano fibrillated, which is difficult due to the nature of their production (low yield). The production strategies of nanocellulose still require a continuous examination to construct environmentally responsible and economically feasible nanocellulose (Nechyporchuk *et al.*, 2016 ; Shak *et al.*, 2018).

2.4 Components and Properties of Ligno-Cellulosic Material

2.4.1 Cellulose

Cellulose is one of the most abundant, major constituent of all plant materials, renewable and biodegradable natural polymers. It forms about half to one-third of plant tissues and is constantly replenished by photosynthesis (Gea *et al.*, 2018). In particular, cellulose is the main constituent of higher plants such as wood, cotton, flax, hemp, jute, ramie, cereal straws, rice straws, and sugarcane bagasse and it is insoluble in water and most organic solvents, due to the extensive network via numerous intermolecular and intra-molecular hydrogen bonds (Ching and Ng, 2014). Chemically, cellulose is a linear, stereo-regular natural homo-polymer composed and the glucose unit is linked together by β -1, 4-glycosidic bonds. The β isomers are arranged in parallel row and the hydroxyl groups in adjacent chains are held together by forming the hydrogen bonds, to hydrolysis than starch (Nuruddin *et al.*, 2013) and it is confirmed by the presence of three hydroxyl groups with different reactivity, secondary OH at the C-2, secondary OH at the C-3, and primary OH at the C-6 position, and, accordingly, by the formation of strong various intermolecular and intra-molecular hydrogen bonds (Debiagi *et al.*, 2018). Many factors play important roles in the properties of cellulose. These factors are internal fiber structure, chemical composition, micro fibril angle, cell dimensions, and defects, which vary from plant to plant (Ching and Ng, 2014).

It is also composed of large polymer chains with variable molecular weight and empirical formula $(C_6H_{10}O_5)_n$, where 'n' is the number of repeating sugar units or the degree of polymerization (DP). The degree of polymerization (DP) and molecular weight of cellulose depends on the cellulosic source, the processes and further treatments used in obtaining this biopolymer. The DP of cellulose can vary between 1500 and 3500. Generally, the DP of cellulose profoundly influences the mechanical, biological and physiological properties of cellulose (Nasir *et al.*, 2017). The cellulose polymer is a linear homo-polysaccharide consisting of D-an hydroglucopyranose units (AGU) linked together by β -1, 4-glycosidic bonds (Salameh, 2009). Every other AGU is turned 180° with respect to its neighbor and two AGU next to each other form a cello-bios unit, the smallest repeating unit in the polymer. The degree of polymerization is defined as a measure of how many AGUs there is in the polymer and since no polymer is homogenous in length, the molecular weight distribution will have an important influence on the

properties of the fiber. After degradation reactions and purification processes, the DP is reduced to about 300–1000 in wood cellulose(Zhao *et al.*, 2017).

Table 2.1: Chemical properties of cellulose

Chemical formula	$(C_6H_{10}O_5)_n$
Density	1.5 g/cm ³
Molecular weight	162.14 g/mol
Melting point	260°C – 270 °C
Solubility	Not soluble in water
Appearance	White powder

Source: (Granström, 2009 ; Heinze, 2016)

2.4.2 Hemicellulose

Hemicellulose is the second important constituent of wood and made only from glucose. It consists of glucose and other water-soluble sugars produced during photosynthesis. In hemicelluloses the degree of polymerization is lower and they are composed of shorter molecules than cellulose. It covers between 20%–35% of the dry weight of wood. Generally, hemicelluloses are in a relatively greater proportion in hardwoods than in softwoods (Asif, 2009). Hemicelluloses are grouped into four classes according to the main types of sugar residues present: xyloglucans, xylans, mannans, and mixed-linkage β -glucans. Hemicelluloses are linked to cellulose and lignin via hydrogen and covalent bonding, respectively, and they are less crystalline than cellulose because of non-uniformity and the presence of side groups insoluble in water but can be extracted with aqueous alkali and hydrolyzed into component mono-saccharides with diluted sulfuric acid (H_2SO_4) (Debiagi *et al.*, 2018).

2.4.3 Lignin

Lignin is a complex constituent that cements the wood (cellulose and hemicelluloses) together. It delivers rigidity to the cells, crucial for the growth of the tree. Lignin is thermoplastic, which means it becomes flammable at high temperatures and hard again when it cools. It makes up 15–

35% of the dry weight of wood (Asif, 2009). Lignin is generally the most complex and smallest fraction of lignocellulosic biomass. Lignin is composed of three major phenolic components p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, and it is synthesized by polymerization of these components. This ratio varies between different plants, wood tissues and cell-wall layers (Ibrahim, 2010). Lignin is theoretically considered adhesive, holding cellulose and hemicelluloses together and it is linked to both hemicellulose and cellulose to form a physical seal that is an impenetrable barrier in the plant cell wall. Lignin is present in the cellular wall to provide structural support, impermeability, and resistance against microbial attack and oxidative stress (Debiagi *et al.*, 2018).

2.4.4 Extractives

Extractives are various organic and inorganic chemicals found in the cell walls and cell lumens that are not structural components of wood. These substances are called extractives because they can be removed from wood through extraction with various solvents. Extractives contribute to such properties of wood as color, odor, taste, decay resistance, density, hygroscopicity (ability to absorb water) and flammability. Usually, they make up around 1–10% of the wood's dry weight (Asif, 2009 ; Ching and Ng, 2014). Extractives are deposited in the cell Lumina and are not constituents of the wood structure. The elements vary from organic to non-organic materials. Because they are deposits in cell walls they can easily be extracted by hot water or organic solvents, such as benzene, acetone, ether or alcohols (Raatz, 2018).

2.5 Extraction of Cellulose from Ligno-cellulosic Materials

The first step in the extraction of cellulose is the removal of lignin and other extractives. Lignin is a component that provides rigidity to wood enables water conduction and reduces impregnation from outside elements. It is different from cellulose and hemicelluloses in that it is an aliphatic and aromatic hydrocarbon polymer consisting of phenyl propane units. They are generally not susceptible to acid hydrolysis, but it can be oxidized in hot alkali solutions (Raatz, 2018). The extraction of cellulose was done by different methods such as chemical treatment, mechanical treatment, cyrocrushing, high-pressure homogenization, steam-exploded, ultra sonication and etc. (Moon *et al.*, 2011; Mzimela *et al.*, 2018). The simple and effective method is chemical treatment. This can be done by using hot water treatment and the delignification step. In the delignification step different chemicals were used by different researchers. These

chemicals are acidified sodium chlorite, sodium hypochlorite, hydrogen peroxide, chlorine and etc (Mandal and Chakrabarty, 2011)

2.6 Factors Affect the Yield of Cellulose

The yield of cellulose can be affected by different alkaline hydrolysis conditions. These are reaction time, reaction temperature, concentration and fiber to solution ratio. As different works of literature show that the concentration of sodium hydroxide used is between (1 and 20)% w/v (Raatz 2018 ; Salameh 2009) the reaction time between (1 and 5) hour, the reaction temperature from room temperature to 100°C and the fiber to solution ratio between 1:20 and 1:50 and reported that the ratio and string speed has not to affect the yield of cellulose (Kumar et al. 2016 ; Chin et al. 2017). There are also reported literature that produces cellulose without stirring the solution (Sisak *et al.*, 2015). Different works on process conditions of cellulose done by different researchers were presented in Table 2.2.

Table 2.2: Different works on the extraction of cellulose

Raw material	Conditions	Yield (%)	Reference
OPEFB	10% NaOH and 10% H ₂ O ₂ at 60°C for 90 minutes	87	(Sisak <i>et al.</i> , 2015)
Rice straw	4% NaOH at 80°C for 2 hours	90	(Chin <i>et al.</i> , 2017)
SCB	17.5% NaOH at 80 °C for 5 hours	67	(Mandal and Chakrabarty, 2011)
SCB	17.5% NaOH at 45°C for 3 hours	73	(Wulandari <i>et al.</i> , 2016)
OPEFB	6% NaOH at room temperature for 24 hours and 80°C for 2 hrs	83.4	(Ching and Ng, 2014)
Tea leaf waste	4% NaOH At 80°C for 3 hours	70.9	(Hayati <i>et al.</i> , 2017)
IBG	5% NaOH at 70°C for 1 hour	83.4 %	(Kelly <i>et al.</i> , 2018)

2.7 Cellulose Nano-crystals

Cellulose Nano-crystals (CNC) or Nanocellulose (NC) are rod or whisker shaped particles seen in the crystalline regions of the cellulose fibrils produced by different methods from wood fibers, microcrystalline cellulose, and micro-fibrillated cellulose. CNCs are highly crystalline particles with high aspect ratios (Nasir *et al.*, 2017). Cellulose nano-crystals have been also called whiskers rod-like cellulose, micro-crystals and nano-wires. Materials reinforced with nanoparticles have better physical and mechanical properties than those filled with a micron-sized particle of the same filler (Alamri and Low, 2012). Moreover, some exclusive properties, which traditional micro-particles cannot attain, make nano-composites be prominent and draw attention. Greater stiffness and strength have resulted from the considerable surface area developed when nano-particles are randomly distributed in the matrix. Nanocellulose with small particle size and high crystallinity has better properties and usually used as a nanofiller for some polymer materials. It is used in various fields such as a barrier in the separation process of hazardous waste, food wrappers which replace the non-biodegradable plastics, and as nano-composite to improve properties such as mechanical, thermal, ionic conductivity properties of the polymer. An important characteristic of CNCs prepared using sulfuric acid (SA) is the negative particle charge due to the formation of sulfate ester groups, which enhances the phase stability of the nanocrystalline particles in an aqueous medium. It has been reported that nanocrystalline particles extracted from tunicates and bacterial cellulose (BC) are usually larger compared to CNCs obtained from wood or cotton. This is because tunicates and BC are highly crystalline and contain longer nano-crystallites. CNCs extracted from pure cellulose materials exhibit increased crystallinity (Moon *et al.*, 2011). The ribbon-shaped CNCs from tunicates have typical aspect ratios between 70 and 100, and crystallinity ranging from 85% to 100%.

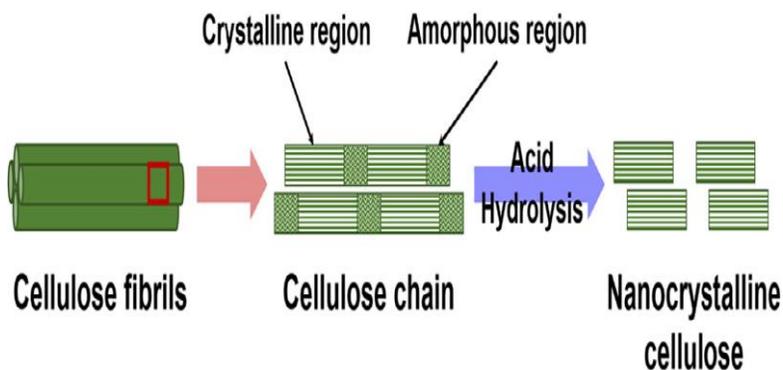


Figure 2.2: Schematic diagram of nanocrystalline cellulose

2.8 Extraction Methods of Nanocellulose

As different works of the literature show, that nanocellulose can be extracted by different methods. These methods include acid hydrolysis (Hubbe *et al.*, 2018 ; Habibi *et al.*, 2010), enzymatic hydrolysis (Hubbe *et al.*, 2018), a mechanical treatment (Hubbe *et al.*, 2018 ; Khawas, 2016).

2.8.1 Acid Hydrolysis

In this process, chemicals are used to isolate the cellulose nano-fillers and it consists of strong acids to promote hydrolysis of the amorphous regions of cellulose. The crystalline regions remain intact under acid attack while the amorphous regions are hydrolyzed. Due to the higher resistance of crystalline regions to acid attack than the amorphous region, the amorphous regions hydrolyzed first (Bondeson *et al.*, 2006). A material with a high degree of crystallinity produced as a result of the difference in kinetics between amorphous and crystalline regions. Acid hydrolysis of cellulose induces a rapid decrease in its degree of polymerization and consequently leads to the production of nano-sized particles through a reduction in the cellulose chain size which produces nano whiskers or cellulose nano-crystal particles (Bondeson *et al.*, 2006). Depending on the required degree of separation and the purpose for which they are intended the lignin and hemicelluloses are removed from the fiber by thermal, chemical, biological, physical and by combinations of any of these methods (Santos *et al.*, 2016). In the acid hydrolysis process first, the lignocellulosic material is treated with alkali and bleached with bleaching agents to remove impurities and lignin from it then, the lignin-free holo-cellulose undergoes acid hydrolysis under controlled conditions. To release CNCs, acid hydrolysis of purified cellulosic

material is conducted using strong mineral acids under controlled temperature, time, agitation, and acid/cellulose ratio conditions (Santos *et al.*, 2016). Different mineral acids can be used for this purpose, such as sulfuric, hydrochloric, phosphoric and hydro bromic, maleic, nitric, and formic acid (Habibi *et al.*, 2010). A mixture composed of hydrochloric and organic acids (acetic or butyric) has also been reported. Sulfuric acid is the most extensively used acid for CNC preparation. The CNC dispersion in a strong acid is diluted with water and washed using successive centrifugations. Neutralization or dialysis with distilled water is performed to remove free acid from the dispersion. Additional steps such as filtration, centrifugation, or ultracentrifugation, as well as mechanical or ultrasound disintegration, have also been reported. If CNCs are prepared using cellulose hydrolysis with hydrochloric acid, the uncharged nanocrystalline particles tend to flocculate in aqueous dispersions.

2.8.2 Enzymatic Hydrolysis

Enzymatic hydrolysis is the other method used to produce CNC. It is carried out by using cellulase (Hubbe *et al.*, 2018). Like the acid hydrolysis method, the treatment used to obtain the nanofiller is based on the enzymatic attack of amorphous regions of the cellulose substrate, while maintaining the crystalline regions (Fattahi and Dadashian 2014). Henriksson and coworkers employed an enzymatic treatment to isolate cellulose nanoparticles, where they treated the wood-bleached pulp with the endo-glucanase enzyme and reported that the treatment made it easier to separate the material into micro-fibrillated cellulose (MFC) under mechanical shearing when compared to the isolation of the nanofibers obtained by acid hydrolysis (Henriksson *et al.*, 2007).

2.8.3 Mechanical Treatment

This process includes the high-pressure homogenization, micro-fluidization, cyro-crushing, high-intensity ultra-sonication treatments that used to extract cellulose fibrils from microcrystalline cellulose, wood, tunicate, algae, and bacterial source materials (Chakraborty *et al.*, 2005). Generally, these processes produce high shear, which causes transverse cleavage along the longitudinal axis of the cellulose micro-fibrillar structure, resulting in the extraction of long cellulose fibrils, also called micro-fibrillated cellulose. Among these processes, those based on the use of high-pressure homogenizer and micro-fluidizer equipment is most used in extracting MFC from pulp fibers. The high-pressure homogenization process consists of passing cellulose slurry into a vessel through a very small nozzle at high-pressure. High velocity and pressure

produced in the process, as well as the impact of the shear forces on fluid, generate shear rates in the stream, therefore decreasing the size of fibers into the nano-scale. This process has been used by many researchers as a strategy to break up cellulosic fibers into nano-sized component structures, often in combination with other treatments.

High-pressure homogenization can be considered as an efficient method for refining cellulose fibers, because of its efficiency and lack of organic solvents. However, one of the most important aspects, which can be observed in this process, is that the small size of the orifice of the instrument can cause clogging. Thus, it is necessary to reduce the fiber size before passing samples through the system in order to overcome this limitation. Similar to the high-pressure homogenization process, micro-fluidization can also be used to produce micro- fibrillated cellulose. A micro-fluidizer includes an intensifier pump to increase the pressure, as well as an interaction chamber to defibrillate the fibers through shear and impact forces against the colliding streams and the channel walls. All of the mechanical methods listed involve a high consumption of energy, which can cause a dramatic decrease in both the yield and fibril length (Nakagaito and Yano, 2004). Thus, current research has focused on environmental conservative, high efficiency, and low-cost methods to isolate nanocellulose. The pretreatment of cellulose or a combination of two or more methods has produced positive results in this regard.

2.9 Factors Affect the Nano Cellulose Yield in Acid Hydrolysis Process

The yield of nano cellulose is affected by different parameters during the extraction process of acid hydrolysis. The main parameters are reaction time, reaction temperature, acid concentration, and acid to a straw ratio (Peng *et al.*, 2011). Reaction time is one factor that affects the nanocellulose characteristics such as yield, crystallinity, and size. Depending on reaction times used for hydrolysis, the hydrolysis could also occur on the crystalline regions as reaction times become long and some of the hydroxyl groups on the crystalline surface will convert into sulfate groups. Too long reaction time will hydrolyze cellulose crystals completely which reduces the yield. Too short reaction time will give a high degree of polymerization due to large undispersed fibers and also results in the production of nano-celluloses with larger diameters and amorphous regions. In some pieces of literature, reaction time vary from 30 minutes to 8 hours, depending on the temperature used in the reaction (Torres *et al.*, 2013). The sulfuric acid concentration has also played a significant role in the properties of nanocellulose. The Sulfuric acid concentration of 60 to 65 w/v% has been used in most studies for the isolation of cellulose whiskers(Santos *et al.*, 2016). The acid concentration has a significant effect on nanocellulose yield, crystallinity and size. Acidic hydrolysis using hydrochloric acid is less common compared to hydrolysis with sulfuric acid but has also been used in some studies(Yu *et al.*, 2013). A reaction temperature has a significant effect on the yield and other properties of the nanocellulose. At low temperatures, the reaction may take a long time to get the desired yield and at high temperatures, the reaction is hard to control. The temperature can range from room temperature to 70°C. The acid hydrolysis conditions used by different researchers and the particle size, yield and crystallinity index were summarized in Table 2.3.

Table 2.3: Different works on the extraction of nanocellulose

Raw material	Conditions	Particle size	Yield (%)	CI (%)	Ref
Sugarcane bagasse	Acid hydrolysis at 45°C for 30 min	L=255±55 nm D= 4±2 nm	65.97	-	(Mashego, 2016)
Commercial MCC	H ₂ SO ₄ , 2hr	L=200-400 nm D=10 nm	30	77	(Bondeson <i>et al.</i> , 2006)
SCB	H ₂ SO ₄ (64%)	L= 250-480 nm D= 20-60 nm	-	72.5	(Kumar <i>et al.</i> , 2014)
OPEFB	H ₂ SO ₄ (56%) at 45°C for 2 hours	D= 300 nm	34.9	75±1	(Burhani and Septevani, 2018)
Sisal	H ₂ SO ₄ 60% at 45°C for 30 min for 108 min	D = 30.9 nm	-	75 ±1	(Morán <i>et al.</i> , 2008)
MCC	H ₂ SO ₄ 33% at 43°C	L= 200 – 400 nm D = 20-30 nm	83.5%	-	(Ioelovich, 2012)

2.10 Polyvinyl Alcohol

PVA is a polymer that has been used during the first half of the 20th century worldwide. It has been applied in the industrial, commercial, medical, and food sectors and has been used to produce many end products, such as lacquers, resins, surgical threads, and food packaging materials that are often in contact with food. PVA is a widely used thermoplastic polymer that is benign to living tissues, harmless, and non-toxic (Lisboa, 2018). PVAs are very common polymers, widely used as surface materials, which should be retained on the water surface, in a huge range of fields as films and glues because of their exceptional chemical and physical properties, biocompatibility, and stability to temperature variation (Takasu *et al.*, 2004). PVA polymer is selected due to its amazing properties such as high optical transmission, water-solubility, and noncorrosive nature that make it a good matrix for optoelectronic and a variety of other applications. PVA is a creamy or whitish, tasteless, odorless, non-toxic, biocompatible, thermo stable, granular or powdered semi-crystalline or linear synthetic polymer. It possesses astonishing optical properties, large dielectric strength, and excellent charge storage ability (Hajeessa *et al.*, 2018). Its mechanical, optical and electrical attributes can readily be tailored by doping with nanofiller.

However, brittleness and other properties such as low thermal stability, high flammability, medium gas barrier properties and low solvent resistance of the pure PVA are often insufficient for its applications. PVA is available on the market in different grades on the basis of viscosity and the degree of hydrolysis (Aslam *et al.*, 2018). Nano-fillers (<5 wt%) are most widely used to enhance the properties of polymers including toughness, strength, modulus, heat and scratch resistance, dimensional stability, thermal, and electrical conductivity due to their high aspect ratio. Nanofillers have the advantage of possessing a large surface area for interaction with a surrounding matrix that is the key concept for the enhancement of the properties of polymeric nanomaterial (Kord *et al.* 2016) (Lisboa, 2018). In addition, nanofillers possess a quantum confinement effect which makes nanofiller–polymer interaction of great importance. Over the last many years, PVA has been a candidate material for diverse applications. PVA nanocomposites may include nanofillers made from metals, nonmetals, metal oxides, metal sulfides, inorganic, or combinations of these materials. Inorganic nanofillers may include carbon nanofibers, carbon nanotubes, clays, silicates, and others. PVA is used as an embedding mat and

matrix for metal/inorganic nanofillers for sensing, designing of optoelectronic devices and many other applications (Aslam *et al.*, 2018).

Table 2.4: Chemical properties of Polyvinyl Alcohol

Chemical properties of Polyvinyl alcohol	
Chemical formula	$(\text{CH}_2\text{CHOH})_n$
Density	1.19-1.31 g/cm ³
Melting point	200°C
Flashpoint	79.44°C
Solubility	Soluble in water
Appearance	White powder

Source: (Lisboa, 2018)(Takasu *et al.*, 2002)

2.11 Preparation of Nanocellulose/PVA Composite

2.11.1 Fabrication of Nano-Cellulose Composites Using Solvent Casting

This is a good method when the solvent used is less toxic (chloroform, acetone, alcohol or water). In this method, different quantities of nanoparticles can be dispersed due to the good interaction with the solvent and polymer. This is the easiest method to obtain good nanocomposites (Lani *et al.*, 2014). Some care must be taken in the manipulation of the solvent since it must be completely eliminated afterward. The necessary apparatus is very simple (Inês *et al.*, 2017). The main advantage is that the dispersion state of the micro or nanoparticles is kept when using an aqueous medium for the processing. After the dissolution of the hydro-soluble or hydro-dispersible polymer, the aqueous solution can be mixed with the aqueous suspension of cellulosic micro or nanoparticles. The resulting mixture is generally cast and evaporated to obtain a solid micro or nanoparticle film. It can also be freeze-dried and hot-pressed. Hot distilled water is used as standard solvent and cellulose is first dispersed in this standard casting solution of hot water and ultra-sonication takes place. Glycerol is used to avoid sticking of the composite on the petri dish or the material used to cast the films. The polymer solution is prepared by dissolving it in hot water which is finally to be mixed with cellulose suspension for cellulose suspension reinforcement of the polymer. After manually mixing (stirring) for a required period at constant speed the solution will be poured/cast onto a glass petri dish and

freeze-dried or dried at reduced pressure inside a vacuum oven or air-dried to remove the solvent (Kord *et al.*, 2016 ; Khalili *et al.*, 2019). But if at large scale it can be extruded and injection molded. This method is selected for this research because of simplicity and manually done at a laboratory scale without searching for automated machines.

2.11.2 Fabrication of Nano-Cellulose Composites Using Melt Extrusion

This method has a major advantage in relation to the others since no solvent is necessary. However, the quantity of nanoparticles to be dispersed is very important. This method requires close monitoring of the nanoparticles' dispersion because of these agglomerate easier than in other methods (Islam *et al.*, 2014). The apparatus is the same used for polymer processing without nanoparticles. Therefore, the researcher needs to pay attention to the temperatures used so as not to degrade the polymer during extrusion and also must pay attention to the time necessary for the nanoparticles to disperse properly. For natural polymers and few biopolymers, the degradation and melting temperatures are very close (Inês *et al.*, 2017).

2.11.3 Fabrication of Nano-Cellulose Composites Using *In situ* Polymerization

This method normally is suitable for polymers that cannot be produced economically or safely by solution methods because the solvents used to dissolve them are highly toxic. This method promotes good dispersion and distribution of the nanoparticles in the polymer matrix. Some important aspects of this method should be pointed out (Islam *et al.*, 2014). The first is related to the cost of the process, which can require some changes compared to the normal polymer synthesis. Care is also necessary to choose the most appropriate catalyst. The apparatus used can be the same for polymerization without nanoparticles (Inês *et al.*, 2017).

2.12 Production of Teff and its Straw in Ethiopia

Ethiopia has abundant availability of natural fibers such as Sugarcane, cotton, pineapple, bamboo, banana, wheat straw, barley husk, and teff straw (Bultosa, 2016). Their use can provide value-added novel applications of natural fibers based composites and in the end, it gives social benefits and major income for communities who cultivate them. Among various agricultural crops, teff is famous for its production volumes and large amounts of residues. Teff is a warm-season annual cereal and the only cultivated species in the genus *Eragrostis*. Ethiopia considered the center of origin of teff (Abeje et al., 2019). In Ethiopia, teff is a major staple. It is the most important crop in terms of cultivation area and production value (Minten B, 2016). In 2017, teff accounted for about 24% of the nationwide grain-cultivated area followed by maize 17% and sorghum 15%. Amhara and Oromia are the two major regions, and collectively, the two regions account for 85.5% of the teff area and 87.8% of the teff production respectively.



Source: (Chufu *et al.*, 2015)

Figure 2.3: Teff straw

The most common utilization of teff in Ethiopia is the fermented flatbread called Injera. The most preferred form of the Injera is one made from pure teff flour. Other utilizations of teff include local alcoholic beverages called *tela* and *katikala*, and porridge. Additionally, teff plant residues could be used as fodder for livestock, and often incorporated as construction materials, for bedding and mushroom compost. The majority of the teff straw is used for mulching (59%) and animal feed (28.1%). Others are used as firewood and leftover the root (10.1%) (Tesfaye A, 2006), which has been primarily disposed of through burning in the field. This treatment method, in fact, could cause environmental pollution specifically air pollution. Different uses of different types of residues of agricultural products are presented in Table 2.5.

Table 2.5: Different uses of some agricultural residues

Residue type	Percentage score for uses				
	Firewood	Animal feed	Mulching	Construction	Not used
Wheat straw	9.5	16.6	62.6	1.4	8.1
Barley straw	8.13	19.3	62	-	8.6
Maize stover	59.8	9.5	26.1	-	4.6
Teff straw	2.4	18.1	59.2	2.5	10.1
Sorghum stover	54	5.2	26.6	-	14.1
Harricot bean haulms	10.4	12.5	65	-	12.2

Source: (Bart *et al.*, 2016 ; Abeje *et al.*, 2019)

2.13 Chemical Composition of Teff straw

Like different lignocellulosic materials, teff straw also has its own composition like lignin, cellulose, hemicellulose, and extractives. According to different works of literature, hardwoods have a higher content of cellulose from (95-60) % and known as primary sources of cellulose. Softwoods have moderate content of cellulose which ranges from (25 – 50) % and known as a

secondary source of celluloses. Teff straw has (35-39) % cellulose content as described by (Chufu *et al.*, 2015). The cellulose and other component composition of different lignocellulosic materials are described in Table 2.6.

Table 2.6: Chemical composition of lignocellulosic materials

Source	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractives (%)
Wheat straw	30	50	15	5
Sisal	50-74	10-14	8-11	3
OPEFB	40-50	20-30	15-20	-
SCB	43.6	33.5	18.1	3.1
Cornstalk	35	25	35	5
Cotton	95	2	1	0.4
Flax	71	21	2	6
Hemp	70	22	6	2
Jute	71	14	13	2
Bamboo	55	30	10	5
Pineapple	30	35	24	9
Teff straw	38	27	18	10

Source: (Chung and Washburn, 2016; Morán *et al.*, 2008; Sisak *et al.*, 2015; Chufu *et al.*, 2015)

3 Methodology

3.1 Chemicals and Equipment Used

Materials and Methods

Raw materials: the raw material, teff straw, was collected from the agricultural field near Jimma Agaro town.



Figure 3.1: Collected and grinded Teff straw

Chemicals: Sodium hydroxide (97%), sulfuric acid (98%), sodium chlorite (80%), glycerol were purchased from Ranchem industry and trading plc, Addis Abeba. PVA powder (95%), acetic acid glacial (96%), filter paper (90mm) in diameter were purchased from Alkane Plc, Addis Abeba. All chemicals are analytical grade and used as received. Different solutions were prepared according to the required concentrations in a laboratory and the experimental works for production were conducted at Addis Abeba Institute of Technology, School of Chemical and Bio-engineering laboratory.

- ❖ Sodium hydroxide was used for the removal of hemicellulose and the preparation of cellulose.
- ❖ Sodium chlorite was used to remove lignin and bleach the raw material.
- ❖ Acetic acid was used to acidify the sodium chlorite solution.
- ❖ Sulfuric acid was used to prepare nanocellulose suspension.
- ❖ Glycerol was used to avoid the sticking of films on Petri dishes.
- ❖ Polyvinyl alcohol was used to prepare composite films.

Equipment used

Table 3.1: List and description of equipment used for laboratory work

Equipment	Use
Grinder	to grind raw material
Oven	to dry samples and determine moisture content
Furnace	to determine ash content and volatile matter content
Water bath	to produce products by controlling temperature
Ultrasonicator	to produce homogenous solution
pH meter	to determine and adjust the pH of the solution
Centrifuge	to centrifuge and collect the nanocellulose suspensions
Mechanical stirrer	to stir and prepare solutions
Vacuum filter	to filter the product from the solution
Filter paper	used as filter media with vacuum filter
Plastic bags	to hold raw materials and dry products
Fourier transform infrared spectroscopy	for functional group analysis
Freeze dryer	to dry nanocellulose suspensions
X-ray diffractometer	to determine the crystallinity index
Dynamic light scattering	to determine the average particle size
Thermogravimetry analysis	to determine the thermal stability

3.2 Proximate Analysis of Teff Straw

3.2.1 Determination of Moisture Content

The moisture content of the teff straw was determined by the oven drying method. This was carried out at a temperature of 103 ± 2 °C for 2 hours in accordance with the ASTM D 1037 (1991). Then it was calculated by the equation,

$$\text{Moisture content} = \frac{W_i - W_f}{W_i} \times 100\% \quad (3.1)$$

Where, W_i is initial mass before drying and W_f is the final mass after drying

3.2.2 Determination of Ash Content

Ash content was determined using ASTM D 2017 (1998). 3g of straw placed in a pre-weighed crucible was incinerated in a muffle furnace at 600°C until complete ash was achieved (2 hours). The crucible was then transferred into desiccators for cooling and calculated by;

$$\text{Ash Content} = \frac{W_a - W_c}{W_b - W_c} \times 100\% \quad (3.2)$$

where, W_a , is the weight after complete ashing + crucible

W_b is the weight before ashing + crucible

W_c is the weight of the empty crucible

3.2.3 Determination of Volatile Matter Content

The volatile matter was determined according to ASTM, E-872. 2g of the samples of the straw was incinerated in a crucible at a temperature of 650 °C for 6 minutes and allowed to cool down in desiccator. Based on a dry basis the volatile matter content was calculated by using equation;

$$\text{Volatile content} = \frac{W_i - W_f}{W_i} \times 100 \quad (3.3)$$

Where W_i is the initial weight of the sample and W_f is the final weight of the sample

3.2.4 Determination of Fixed Carbon Content

The fixed carbon of the straw was calculated according to standard (ASTM D3172 – 13) by subtracting the sum of ash content (%) and volatile matter (%) from 100. The fixed carbon is defined as the residue left after removing the volatile matter and the ash from the substance.

$$\text{Fixed Carbon} = 100 - (\text{Ash content} + \text{Volatile matter}) \times 100\% \quad (3.4)$$

3.3 Component Characterization of Teff straw

3.3.1 Determination of Extractive Content of the Straw

The water and ethanol extractives were determined according to the method used by (Vijayanand *et al.*, 2016). 10 g of sample was taken and mixed in 200 ml of distilled water. Then, the solution was kept in a boiling water bath at 80°C for a period of 3 hours then cooled and vacuum filtered. After that, it was dried at 105°C in the oven until a constant weight was obtained. To determine the ethanol extractives, 5% ethanol was prepared and the water extractive free sample (5g) was added and mixed. Then, the solution was kept in a water bath of 80°C for 3 hours. Then, cooled and filtered. After that, it was dried at 105°C until constant weight obtained. The amount of total extractives was calculated as,

$$\text{Extractives}(\%) = \frac{\text{Initial mass} - \text{Mass after water and ethanol extraction}}{\text{Initial mass}} \times 100 \quad (3.5)$$

3.3.2 Determination of Hemicellulose Content

The hemicellulose content was determined according to the method ASTM D5896-96 (2012). 1g of the sample from the dried extractive free sample was taken and 10 ml of 0.5 mol of NaOH solution was added to it. Then the solution was kept in a boiling water bath for 3 hours at 80°C. After that, the residue was washed with distilled water and filtered until neutral pH was achieved. Then, the sample was dried at 105°C and the amount was calculated by the equation;

$$\text{Hemicellulose content} = \text{Initial weight} - \text{Final weight} \quad (3.6)$$

3.3.3 Determination of Lignin

Lignin content was estimated according to the method of the institute of paper chemistry, Appleton, Wisconsin as described on (Halim, 2014). About 2 g of extractive sample was treated with 20 ml 72% sulfuric acid and the acid was added to the sample drop-wise with constant stirring. After that, the sample was allowed to stand and left overnight at room temperature. The sample was then transferred to a round flask, diluted to 3% sulfuric acid and boiled for 4 h. The lignin was filtered on a pre-weighed filter paper and washed with hot distilled water until neutrality. The lignin was then dried at 105°C for 6 h and estimated according to the following equation.

$$\text{Lignin content (\%)} = \frac{\text{weight of dried sample}}{\text{initial weight of sample}} \times 100 \quad (3.7)$$

3.3.4 Determination of Cellulose Content

The cellulose content was determined by considering the other constituents of lignocellulose and by subtracting the sum of extractives, hemicellulose, and lignin from a hundred.

$$\text{Cellulose \%} = 100 - (\text{hemicellulose} + \text{lignin} + \text{extractives}) \quad (3.8)$$

3.4 Extraction of Nanocellulose from Teff Straw

3.4.1 Delignification Process

Delignification is the process in which lignin, pectin, and other extractives were removed and this process was conducted according to the procedure described by (Mandal and Chakrabarty 2011) and (Lani *et al.*, 2014). The fiber was treated with hot distilled water prior to the delignification process to remove water extractive materials. The fiber was treated at 75 °C when a ratio of fiber to water is 1:20 g/ml for an hour. Then the fiber was treated with acidified sodium chlorite solution (0.7%) w/v at 75°C in a water bath for 2 hours under continuous mechanical stirring (400 rpm). The pH of sodium chlorite was adjusted to 4 by glacial acetic acid (5% v/v). The ratio of fiber to acidified sodium chlorite solution was 1:25 g/ml. This process was repeated four times until the color of the fiber was turned to white. The residue was vacuum filtered and washed with distilled water and this process was repeated until the pH of the filtrate becomes neutral. Then the residue was oven-dried overnight at 50°C and kept for further process.

3.4.2 Isolation of Cellulose

The cellulose was extracted from holo-cellulose by an alkaline hydrolysis process using sodium hydroxide solution. The optimum conditions of process parameters on this process were studied to observe the optimum points by using the Design-Expert software (11.0) version. The studied parameters were temperature, time and sodium hydroxide concentration under constant string speed (400 rpm) and straw to NaOH solution ratio of 1:20 g/ml. The design was done by surface response methodology (central composite design) with five levels.

Table 3.2: Levels of three independent variables studied.

Variables	Factor coding	Unit	(-1) low level	(+1) high level	- α	+ α
Temperature	A	°C	40	70	29.7	80.3
Time	B	Hour	1	3	0.318	3.681
NaOH concentration	C	(w/v) %	4	10	1.95	12.04

The studied levels were between 40°C and 70°C for temperature, 1 hour and 3 hours for time and 4 (w/v) % and 10 (w/v) % for sodium hydroxide. In this research, design variables were selected based on previous work (Li et al. 2018) and (Yong et al. 2019). The twenty (20) experiments were conducted and cellulose yield was calculated by dividing the cellulose powder obtained after drying the residues in an oven at 50°C for 24 hours to the initial mass of delignified straw. The design parameters were screened by the software and all experiments were conducted according to run order to minimize the effect of unexpected variability in the observed response due to extraneous factors.

A polynomial regression method was used to fit the experimental data by a quadratic equation and the second-order polynomial equation can be expressed as (Li et al. 2018) and given as,

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC \quad (3.9)$$

where Y is the response (yield) A, B and C is temperature, time and sodium hydroxide concentration

β_0 is intercept coefficient, β_1 β_2 and β_3 are linear coefficients, $\beta_{11}\beta_{22}\beta_{33}$ are squared coefficients and $\beta_{12}\beta_{13}\beta_{23}$ are interaction coefficients.

Table 3.3: Selected and screened design parameters for the alkaline process by CCD.

Std.	Run	Temperature (°C)	Time (hour)	NaOH concentration%(w/v)	Yield (%)
9	1	29.77	2.00	7.00	
17	2	55.00	2.00	7.00	
14	3	55.00	2.00	12.05	
1	4	40.00	1.00	4.00	
16	5	55.00	2.00	7.00	
8	6	70.00	3.00	10.00	
3	7	40.00	3.00	4.00	
4	8	70.00	3.00	4.00	
6	9	70.00	1.00	10.00	
20	10	55.00	2.00	7.00	
12	11	55.00	3.68	7.00	
11	12	55.00	0.32	7.00	
19	13	55.00	2.00	7.00	
2	14	70.00	1.00	4.00	
10	15	80.23	2.00	7.00	
15	16	55.00	2.00	7.00	
13	17	55.00	2.00	1.95	
5	18	40.00	1.00	10.00	
18	19	55.00	2.00	7.00	
70	20	40.00	3.00	10.00	

3.4.3 Preparation of Nanocellulose

The nanocellulose extraction was conducted under a modified procedure adopted by (Wulandari *et al.*, 2016) and (Mandal and Chakrabarty, 2011). The 10 grams of cellulose was hydrolyzed with a sulfuric acid solution (48% v/v) under continuous mechanical stirring (500 rpm) at 35 °C in a water bath for 30 minutes. The ratio of cellulose to a sulfuric acid solution was kept 1:25 g/ml. To stop the hydrolysis process 10-fold of distilled water (2500 ml) was added to the reaction mixture.

Then the suspensions were centrifuged at 3000 rpm for 5 minutes to remove the acids. Then, the suspensions collected from the centrifugation process undergo the dialysis process to remove the remaining acids and the dialysis process was done with a dialysis tube with a specification of 12-14 kDa MWCO. The suspensions were kept under dialysis in distilled water for 10 days by changing the water daily and collected after the pH of the product near to neutral. After that, it was sonicated using probe ultrasonicator at 25 kHz for 5 minutes at (LIDI, Ethiopia) to obtain uniformly dispersed nanocellulose suspension to avoid agglomeration of the nano cellulose particles. Finally, the yield of nanocellulose was calculated by dividing the final weight of nanocellulose after freeze drying for the initial weight of the cellulose submitted to hydrolysis.

$$Yield = \frac{\text{Final weight of Nanocellulose after hydrolysis}}{\text{Initial weight of Cellulose before hydrolysis}} \times 100\% \quad (3.10)$$

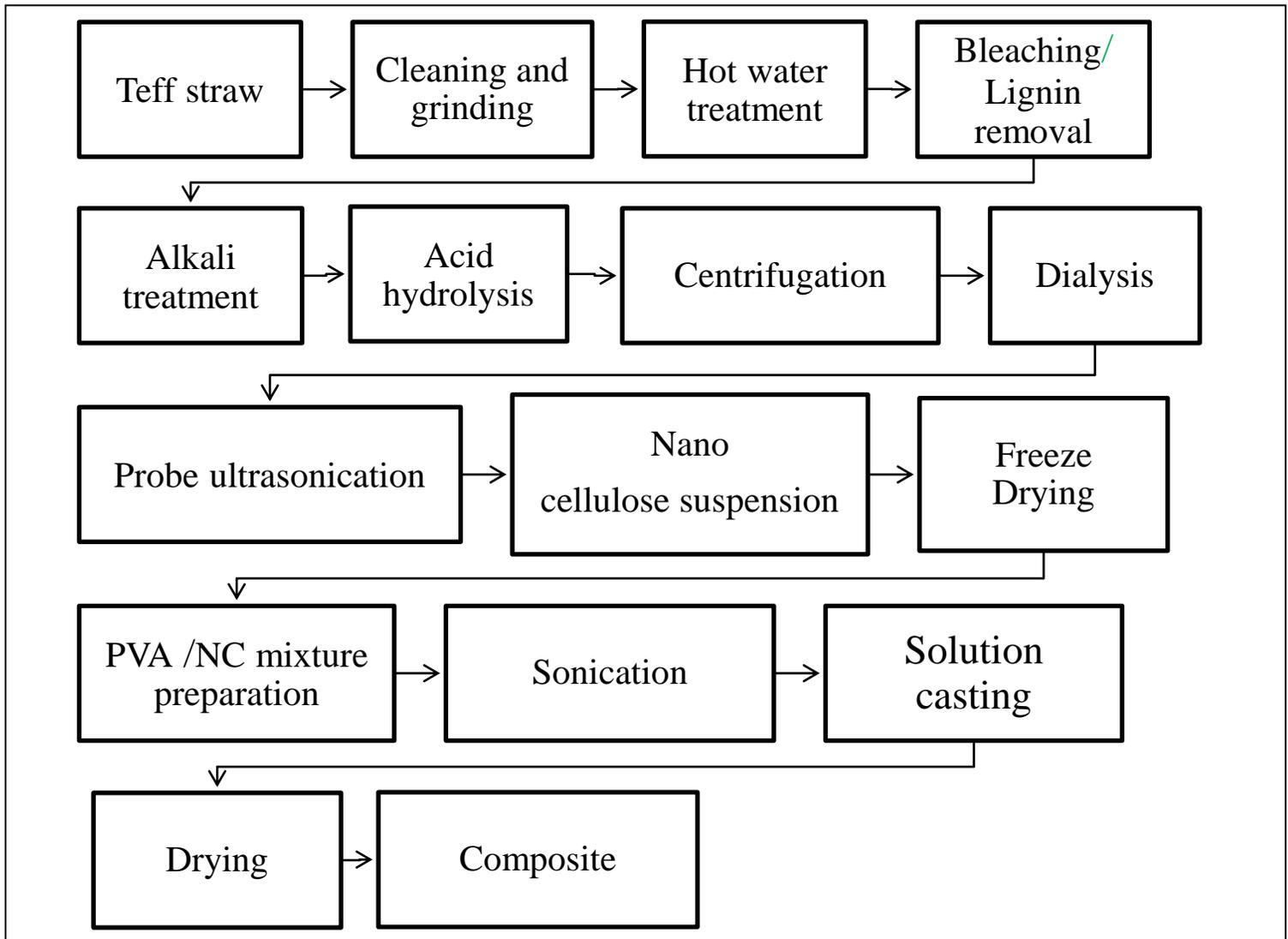


Figure 3.2: Overall flow diagram of the production process of composite from Teff straw.

3.5 Characterization of Nanocellulose

The characterization of nanocellulose obtained from experimental works was determined by using different methods such as Fourier Transform Infrared Spectroscopy (functional group analysis), Dynamic Light Scattering (particle size distribution and average particle size) analysis and X-ray diffractometer (Crystallinity) analysis.

3.5.1 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Fourier transform infrared spectroscopy (FTIR) analysis is commonly used to study a functional group of lignocellulosic biomass and the changes caused due to different treatments. The spectra offer the qualitative and semi-quantitative information suggesting the absence and presence of lignocellulosic compounds and whether the intensity of the absorption band has changed.

The chemical composition assessment of teff straw, cellulose, and the nanocellulose suspensions were conducted using Fourier transform infrared spectroscopy (FTIR). FTIR spectra were obtained using the Perkin Elmer FTIR spectrometer (Perkin Elmer, 65, USA) at Addis Ababa University, Department of Chemistry (Addis Ababa, Ethiopia). This analysis was done for the three materials to see the changes happened to the functional group of the straw after different steps of pretreatments. The analysis was done with the range of $4000 - 400 \text{ cm}^{-1}$ and KBr is used for solid samples (teff straw and cellulose) and the NaCl window was used for nanocellulose suspension.

3.5.2 Particle Size Distribution

Dynamic Light Scattering Analysis is one of the well-known methods to determine the particle size distribution and average particle size of the nanoparticle. Due to the different treatments on the teff straw, there is a change in dimensions since the fiber chains breakdowns into smaller particles. The determination of particle size distribution and average particle size of nanocellulose was done at Addis Ababa Science and Technology University (Addis Ababa) by using the Zetasizer Nano instrument (ZE3600).

It can measure particle size when it is in solution by using the Brownian motion of the particles. Particles suspended in liquid experience random Brownian motion and light that is passed through the suspension is scattered off the particles. The refractive indices are continually

changing due to this motion, which is detected by a sensor, which uses the Stokes-Einstein equation to determine the size distribution of the suspension.

3.5.3 Crystallinity Analysis

The X-ray Diffractometer instrument was used to see the changes in the crystallinity of the teff straw, cellulose and nanocellulose. It is the most common method to determine the crystallinity of materials. The XRD analysis was done at Jimma Institute of Technology, School of Materials Science and Engineering, Jimma. DW-XRD-Y7000 instrument was used with Cu K α radiation. The scanning range was $2\theta = 10$ to 70 degrees at a scanning speed of $0.03^\circ/\text{s}$.

To conduct the XRD analysis the samples need to be dried in advance, which will affect the results as the structure changes upon drying. The nanocellulose suspension used for XRD analysis was freeze-dried at (-30°C) at Addis Ababa Science and Technology University (Addis Ababa, Ethiopia) to obtain dry powder nanocellulose particles. The crystallinity of teff straw and cellulose also determined to see the difference between the crystallinity of these materials. The crystallinity of each sample was determined based on the observed peak and the degree of crystallinity was taken as the ratio of the sum of areas under the crystalline diffraction peaks to the total area under the curve between $2\theta = 10$ to 70 degrees. The crystallite sizes of the lattice planes were estimated by using the well-known Scherrer equation.

The following equations were used to calculate the crystallinity and crystallite size from the different peaks obtained. The Origin Pro (8.5) a version was used to analyze and fit the peak observed.

$$\text{Crystallinity} = \frac{\text{Area of crystalline peaks}}{\text{Total area of all peaks}} \times 100\% \quad (3.11)$$

$$D = \frac{\kappa\lambda}{\beta \cos \theta} \quad (3.12)$$

Where D is crystallite size k is Sherrer constant = 0.9 λ is wavelength = 0.154 nm

β = Full width at half maximum (FWHM) in radians

3.6 Production of Nanocellulose/PVA Composite

Composite materials are one of the application areas of nanocellulose and cover the great percent of total nanocellulose production. To see the effectiveness of reinforcing nanocellulose in their different applications different composites films were prepared with different loading of nanocellulose according to procedures described by (Lani *et al.*, 2014) and (Silvério *et al.*, 2013). These composites were prepared by differing the loading ratio of nanocellulose and reinforcing with polyvinyl alcohol and the change in the properties of PVA after reinforcing with nanocellulose was observed.

Polyvinyl alcohol (PVA) with a degree of hydrolysis of 90 % and a molecular weight of 88 kg/mol with 96.7 % purity was purchased from Alkane Plc. (Addis Ababa, Ethiopia) and used as a matrix for the preparation of the composite. For avoiding sticking of the film to the Petri dish during drying, glycerol was used on the surface of the Petri dish. Three different composites were prepared by using the nanocellulose suspension (2%, 5%, and 7%) prepared with different ratios. Then, to compare their properties three other composites were prepared by using neat PVA, PVA reinforced with cellulose and PVA reinforced with Teff straw.

The nanocellulose–PVA composite films were prepared by the solvent casting method. The aqueous solution 5% w/v of PVA was prepared by dissolving 5g of PVA powder in distilled water at 80°C kept in a water bath for 2 hours under mechanical stirring (400 rpm) until the PVA was fully dissolved and the clear jelly-like solution was formed. The solution was cooled to room temperature while stirring and different amounts of nanocellulose suspensions (2%, 5%, and 7%) were added to PVA solution under continuous manual stirring until the solution became viscous. Then, the ultra-sonication process was taken place by using sonicator in water for 15 min to obtain a homogenous solution and to avoid agglomeration of nanocellulose in the PVA matrix at Addis Ababa Institute of Technology, Department of Chemical and Bioengineering. Then, the solutions were kept for 24 hours to obtain bubble-free solutions before casting on the Petri dish. Then, different films were cast on the petri dish according to their perspective ratio and left for 7 days to obtain dry films. Then, the films were kept in plastic bags for further characterization and comparison. The different ratios used for film preparation were described in table 3.4.

Table 3.4: Formulation ratio for the preparation of composite films

Ratios	Amount of PVA used (%)	Amount of reinforcement used (%)	Amount of glycerol used (ml)
PVA/0%NC	100	0	2
PVA/2% NC	98	2	2
PVA/5% NC	95	5	2
PVA/7% NC	93	7	2
PVA/5% C	95	5	2
PVA/5% TeS	95	5	2

To evaluate the effectiveness of nanocellulose other composites were also prepared from an equal amount of teff straw and cellulose by following the same procedure followed for PVA/NC based composite preparation. The ratio of these materials was given in table 3.4.

3.7 Characterization of Nanocellulose/PVA Composite

The characterization of composite films was done by performing mechanical tests, thermal stability, and water absorption tests.

3.7.1 Water Absorption Capacity

This test was done to determine the water intake capacity of the films after the addition of nanocellulose. It was done at Jimma Institute of Technology, School of Chemical engineering laboratory, Jimma, Ethiopia.

The water absorption tests were done by the Water Immersion method and carried out by following the procedures described by (Lani et al. 2014) with slight modifications. For this test oven, scissors, beaker, distilled water, and balance were used. Each composite sample was dried in an oven for 24 hours at 50°C to remove surface moisture on the samples before weighing. The weight of the oven-dried samples was taken as the initial weight of the composites. The samples were then placed in distilled water maintained at room temperature (25°C) and at time intervals of 24 hours, the composite samples were removed from the water, cleaned using a dry cloth and weighed. The weight measurements were taken periodically at time intervals of 24 hours for up to 168 hours (7 days).

$$\text{Water Absorption Capacity} = \frac{W_t - W_o}{W_o} \times 100\% \quad (3.13)$$

Where W_t is the weight of the film after immersed in water and W_o is the weight of the film before immersed in water.

3.7.2 Mechanical Properties

The mechanical properties of composite films were performed to see the improvement in the properties of PVA after reinforcing the nanocellulose particles. This was done at Leather Industry Development Institute (LIDI), Addis Ababa, Ethiopia. The tests were conducted as per standard methods ASTM D 882-92 (ASTM 2012). The tensile strength and elongation at a break of the composite films were measured on a tensile testing machine. Samples with rectangular shapes were cut into 20mm× 13mm from the films. The test was carried out at room temperature until the film was broken by an applied force. As the film breaks, the distance between the two

grips was measured and the maximum forces were taken. The following equations were used to calculate tensile strength and elongation at break of the films respectively.

$$\text{Tensile strength} = \frac{\text{Maximum breaking load applied}}{\text{Cross sectional area of the film}} \quad (3.14)$$

$$\text{Elongation at break} = \frac{\text{Final length at break} - \text{Initial length}}{\text{Initial length}} \quad (3.15)$$

3.7.3 Thermal Stability

The thermal stability of neat PVA and PVA reinforced with 5% nanocellulose was determined by using a Thermogravimetry analysis instrument. Thermal degradation is a molecular deterioration as a result of overheating. The ability to resist degradation is called stability. So, in this work, the TGA analysis was done to see the effects of reinforcing the nanocellulose particles on the thermal stability of polyvinyl alcohol.

Thermal degradation was obtained by instrument TGA- 4000 Perkin Elmer at Jimma Institute of Technology, School of Material science and Engineering. The PVA and composite samples were heated from 25°C to 500°C under a flow of nitrogen gas. The flow rate of nitrogen gas was 20 ml/min with a heating rate of 10°C/min. The Derivative Thermogravimetry data also recorded. Then, the data obtained were analyzed with the help of the Origin Pro 8.5 version.

4 Result and Discussion

4.1 Proximate Analysis of Raw Material (Teff straw)

4.1.1 Moisture Content

To determine the moisture content of the teff straw three samples were used and three different data were recorded. Then, the moisture content for the sample was calculated according to the equation (3.1) and the mean value was found to be 8.46. Different authors were reported that the moisture content of other straw on a dry basis ranged from (5-16) % (Sisak *et al.*, 2015)

4.1.2 Ash Content

The ash content determined according to the standard method described in section (3.2) and the values of the three samples were recorded. As different literature show the ash content of teff straw ranges between 3% and 7%. The mean value of ash content obtained from this experiment was 5.11% which is in the normal range with literature (Chufo *et al.*, 2015). The high ash content may lead to reduced cellulose yield.

4.1.3 Volatile Matter

The volatile matter determined and the mean value obtained was 74.2%. The values reported for a volatile matter of different straws range from 61% to 92% by different authors. (Chufo *et al.*, 2015) reported that the volatile matter of teff straw as 84.3%

4.1.4 Fixed Carbon

The fixed carbon content was determined according to equation (3.4) and the mean value of three samples was 15.6 %. The results were presented in table 4.1 and the result was in agreement with the literature (Chufo *et al.*, 2015)

Table 4.1: Results of proximate analysis for Teff straw with literature values

Analysis type	Obtained average value (%)	Literature value (%)	Source
Moisture content	8.46	5-16	(Chufo <i>et al.</i> , 2015)
Ash content	5.11	3-14	(Kalderis and Diamadopoulou, 2008)
Volatile matter content	74.2	61-78	(Chufo <i>et al.</i> , 2015)
Fixed carbon content	15.6	13-23	(Chufo <i>et al.</i> , 2015)

4.2 Component Characterization of Teff Straw

4.2.1 Extractives

Extractives are a part of the plant and lignocellulosic materials that contain pectins, phenols, waxes, and other minor organic compounds. They are also responsible for the color and smell of a material. It may cover up to 15% of the whole plant part based on the origin and type of the plant. The extractive amount of teff straw calculated was 8.5% based on a dry basis. The extractive content of sugarcane bagasse was reported as (3.1-4.5)%. The high amount of extractives produces a high amount of colors and it needs a repetitive treatment process to remove these extractives from raw material and to obtain a product with good purity.

4.2.2 Hemicellulose

Hemicellulose is the second part of plants that contains several types of sugar units such as galactose, mannose, and glucose. It covers (24-32)% of a total plant component. The hemicellulose content of teff straw was found to be 29.5%. The high amount of hemicellulose may affect the crystallinity of the samples and require repetitive treatment process and consume more chemicals than that of raw materials with lower hemicellulose content.

4.2.3 Lignin

Lignin is a rigid and stiffer part of the plant component and it has an ability to protect the cellulose and hemicellulose. The lignin obtained was 17.5% and when compared to other raw materials teff straw had a good amount of lignin. If a high amount of lignin found in raw material, it makes them rigid that difficult in the decomposition of plants to obtain cellulose products. The processes of extraction of cellulose from plants that have a high amount of lignin requires long treatments and consume more time and chemicals to remove the lignin.

4.2.4 Cellulose

It is the main component in plants. It is advised to have raw material with a good amount of cellulose for nanocellulose production. The cellulose content of cellulose calculated and found to be 36.57. The high amount of cellulose content results in the best yield of cellulose products extracted from lignocellulosic materials.

Table 4.2: Value of component analysis with literature values

Sample analysis	Obtained result (%)	Value of literature (%)	Source
Extractives	8.50	<10	(Silvy et al. 2018)
Lignin	17.50	6.05-27.60	(Mohanty <i>et al.</i> , 2000)
Hemicellulose	29.50	10.80-40.60	(Mohanty <i>et al.</i> , 2000)
Cellulose	36.57	29.19-67.60	(Chufu et al. 2015)

4.3 Extraction of Nanocellulose from Teff Straw

White cellulose powder was obtained after hot water treatment, alkali treatment, and delignification steps. At the end of the above three stages, the product obtained was white. There were color changes at each step of the process. At the first stage of the process or hot water treatment, the residues filtered was dark black and after the delignification process, it was

changed to dark yellow color. After the repeated process of bleaching step, the product was changed to white and residues water turned to light yellow color. The black color from the first step was due to the presence of the different components of the fiber such as pectin and xylan. Those are almost removed at the first step. The yellow color was due to the presence of lignin and hemicellulose presented in the fiber. The color disappearance of those color implies the effectiveness of the series treatment steps. The yield of cellulose was calculated after drying the product and dividing the final mass of the cellulose to the initial mass of straw subjected to the treatment steps multiplied by 100.

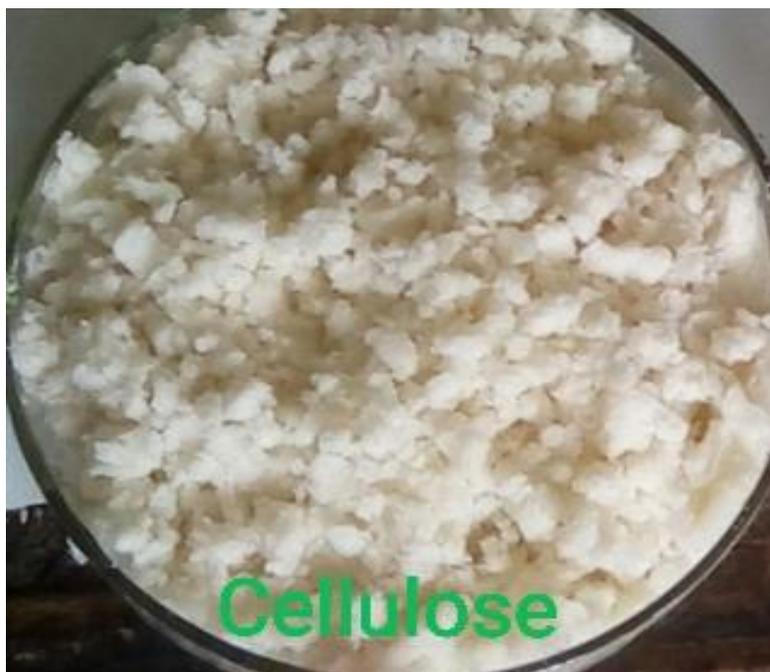


Figure 4.1: Produced cellulose after delignification and alkali treatment.

The nanocellulose suspension was produced from the obtained cellulose by acid hydrolysis was given in Figure 4.2. The product was in suspension form and light white than cellulose. A strong acid has the ability to dissolve the amorphous parts of fiber cellulose. There are some parameters that affect the yield, crystallinity, size, and color of the nanocellulose. These parameters are time, acid concentration and temperature. In this study, different experiments were conducted to get a better point of these parameters to obtain a better product. Acid has the ability to disperse in the fibers and dissolve the amorphous part quickly than the crystalline part. When the acid concentration was low the suspensions were left with the amorphous parts because of the low

ability of dilute acids to dissolve the amorphous. Too long reaction times have resulted in the lower yield of nanocellulose suspensions because as the acid diffuses through the fibers it also dissolves the crystalline region of the cellulose. Too short reaction times resulted in the production of nano cellulose with larger diameters and amorphous parts. Reaction temperature also has a significant effect on nanocellulose yield. Higher temperatures were lead to uncontrollable and hard reactions and the color of suspension was turned to black just after a few minutes. At lower temperatures, it took too long reaction times to produce the nanocellulose suspensions. Finally, the yield of nanocellulose was calculated after drying the suspension in the freeze dryer was 42.87%.



Figure 4.2: Produced nanocellulose suspension

4.4 Statistical Analysis of the Experimental Results

4.4.1 Experimental Data

After the experimental work, the yield of cellulose was calculated and analyzed with the software. The results from design expert 11 were discussed in the following section.

Table 4.3: The value of experimental data and predicted data at selected parameter values.

Std.	Run	Temperature (°C)	Time (hour)	NaOH concentration (w/v)%	Actual Yield (%)	Predicted Yield (%)
9	1	29.77	2.00	7.00	76.05	75.72
17	2	55.00	2.00	7.00	76.58	77.47
14	3	55.00	2.00	12.05	71.45	71.60
1	4	40.00	1.00	4.00	76.77	76.97
16	5	55.00	2.00	7.00	72.26	73.00
8	6	70.00	3.00	10.00	75.56	76.33
3	7	40.00	3.00	4.00	76.86	77.47
4	8	70.00	3.00	4.00	78.85	78.17
6	9	70.00	1.00	10.00	73.01	73.59
20	10	55.00	2.00	7.00	78.57	77.47
12	11	55.00	3.68	7.00	72.05	72.21
11	12	55.00	0.32	7.00	77.45	77.44
19	13	55.00	2.00	7.00	74.58	74.25
2	14	70.00	1.00	4.00	75.88	76.23
10	15	80.23	2.00	7.00	74.07	73.26
15	16	55.00	2.00	7.00	74.91	74.93
13	17	55.00	2.00	1.95	77.86	77.47
5	18	40.00	1.00	10.00	77.15	77.47
18	19	55.00	2.00	7.00	77.98	77.47
7	20	40.00	3.00	10.00	71.72	71.07

4.4.2 Model Summary Statistics

The model suggested by software for this work was the Quadratic model. The application of RSM gives an empirical relationship between the response function and the independent variables.

Table 4.4: Suggested model for the design.

Source	Std. Dev.	R ²	Adjusted R ²	Predicted R ²	PRESS	
Linear	1.91	0.4494	0.3462	0.1707	88.32	
2FI	1.78	0.6142	0.4361	0.2664	78.12	
Quadratic	0.7964	0.9404	0.8868	0.7055	31.36	Suggested
Cubic	0.9190	0.9524	0.8493	-3.5585	485.46	Aliased

4.4.3 Analysis of Variance

The Model F-value of 17.54 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case, A, B, C, AB, BC, A², B², C² are significant model terms while AC is insignificant to the response. Values greater than 0.1000 indicate the model terms are not significant. The Lack of Fit F-value of 1.20 implies the Lack of Fit is not significant relative to the pure error. There is a 42.32% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good. The reaction time has the highest effect than other parameters. There is also an interaction effect between time and temperature as well as between time and NaOH concentration. The ANOVA values from the software were given in Table 4.5.

Table 4.5: Analysis of variance (ANOVA) for Response Surface Quadratic Model

Source	Sum of squares	Df	Mean square	F-value	P-value	
Model	100.15	9	11.13	17.54	< 0.0001	Significant
A-Temperature	8.39	1	8.39	13.23	0.0046	
B-Time	20.48	1	20.48	32.28	0.0002	
C-NaOH Concentration	19.88	1	18.99	29.94	0.0003	
AB	11.6	1	11.76	18.54	0.0015	
AC	0.0338	1	0.0338	0.0533	0.8221	
BC	5.75	1	5.75	9.06	0.0131	
A ²	11.82	1	11.82	18.63	0.0015	
B ²	18.46	1	18.46	29.11	0.0003	
C ²	11.8	1	11.18	17.63	0.0018	
Residual	6.34	10	0.6343			
Lack of Fit	3.46	5	0.6919	1.20	0.4232	Not significant
Pure Error	2.88		0.5767	17.54		

4.4.4 Model Adequacy

The regression coefficient (R^2) quantitatively evaluates the correlation between the experimental data and the predicted responses. Results of $(R^2) = 0.9404$ and $Adj-(R^2) = 0.8868$ obtained implies that the predicted values were found to be in good agreement with experimental values. The values of (R^2) should be between 1 and 0. Since the (R^2) value is closer to 1.0 it indicates that the regression line perfectly fits the data. Similar to that in this investigation, (R^2) obtained was 0.9404, which was close to 1. The values of (R^2) almost equal to 1.0 were indicated that a high correlation between the experimental and predicted data (Li et al. 2018). The Predicted R^2 of 0.7055 is in reasonable agreement with the Adjusted R^2 of 0.8868 that means the difference is less than 0.2. Adeq precision measures the signal to noise ratio and a ratio greater than 4 is desirable. The ratio of 12.612 indicates an adequate signal. This model can be used to navigate the design space. Low values of coefficient of variation demonstrate reliability and good precision of the experiments since it is the error expressed as a percentage of the mean. In this case, the value of C.V was 1.06%.

Table 4.6: Model statics of the design

Std. Dev.	0.7964	R^2	0.9404
Mean	75.48	Adjusted R^2	0.8868
C.V.%	1.06	Predicted R^2	0.7055
		Adeq Precision	12.6120

Diagnostic Plot

From the normal probability plot as shown below, the normal probability plot indicates that the residuals following by the normal % probability distribution. Residual is the difference between the value of actual results from experiments and the value of predicted results from the software. In the case of this experimental data the points in the plots show fitted to the straight line in the figure, this shows that the quadratic polynomial model satisfies the analysis of the assumptions of variance.

Design-Expert® Software

Yield

Color points by value of Yield:

71.45  78.85

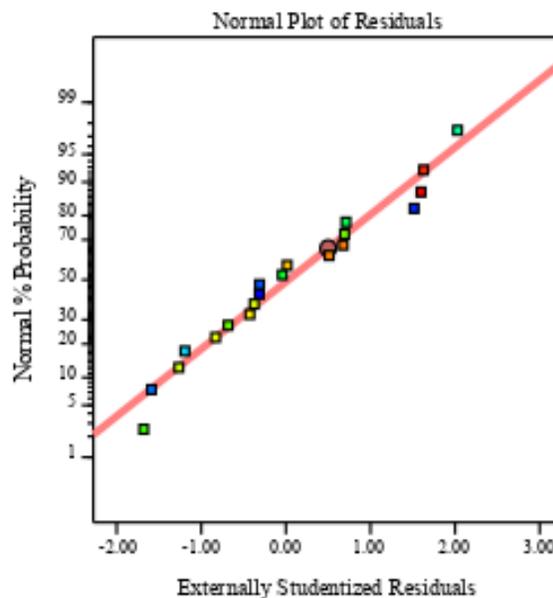


Figure 4.3: Normal plots of residuals for cellulose yield

If the model is correct and the assumptions are satisfied, the residuals should be structure less in particular, they should be unrelated to any other variable including the predicted response. A simple check is to plot the residuals versus the fitted (predicted) values. A plot of the residuals versus the rising predicted response values tests the assumption of constant variance. The plot shows random scatter which justifying no need for any alteration to minimize personal error.

Design-Expert® Software

Yield

Color points by value of Yield:

71.45  78.85

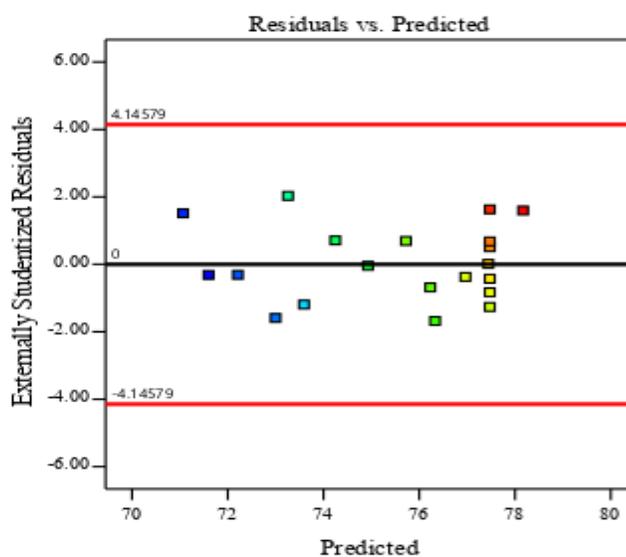


Figure 4.4: Plot of predicted versus residuals for the yield.

Design-Expert® Software

Yield

Color points by value of Yield:

71.45  78.85

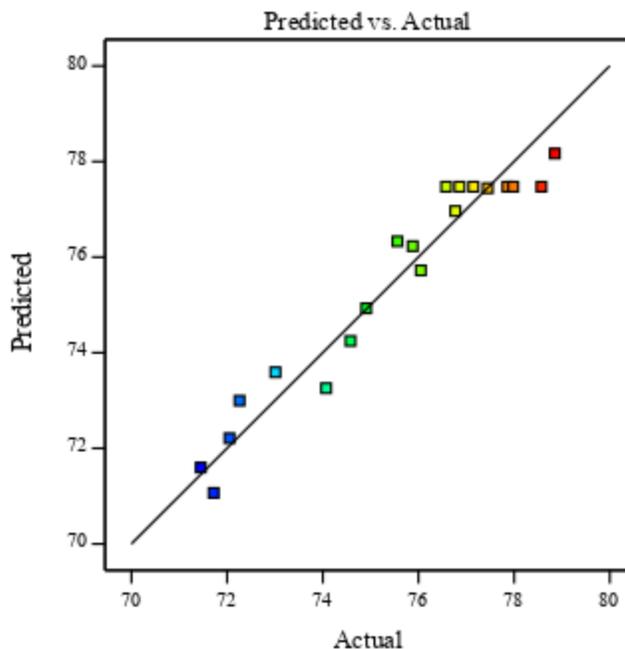


Figure 4.5: Plot of actual yield versus the predicted yield of cellulose

4.4.5 Development of Model Equation

The model equation that correlates the response to the alkaline hydrolysis process variables in terms of independent variables was obtained. From the model summary statistic section, a quadratic model is selected from other models because it has a high accuracy of fitting the data. Therefore, the second-order polynomial model was used to express yield as a function of independent variables given in equation (4.1).

$$Y = +77.47 - 0.784 * A - 1.22 * B - 1.18 * C - 1.21 * AB + 0.8475 BC + 0.065 AC - 0.9056 A^2 - 1.13 B^2 - 0.8809 C^2 \quad (4.1)$$

Where Y is yield, A is temperature, B is time and C is alkali concentration.

4.4.6 Effects of Significant Individual Factors

Effect of Temperature

There are three significant individual effects on the cellulose yield. The effects of temperature from ANOVA show the p-value with 0.0046 which is less than 0.05 and significant. Heat is required to speed up the reaction between holo-cellulose and sodium hydroxide solution. But, it requires controlled conditions to obtain the desired result. As the temperature increases from

40°C to 58.364°C, the yield was increased to around 77.5% and when the temperature becomes beyond 58.364°C the yield was decreased to around 75%. This implies the over-degradation of cellulose at high temperatures.

(a)

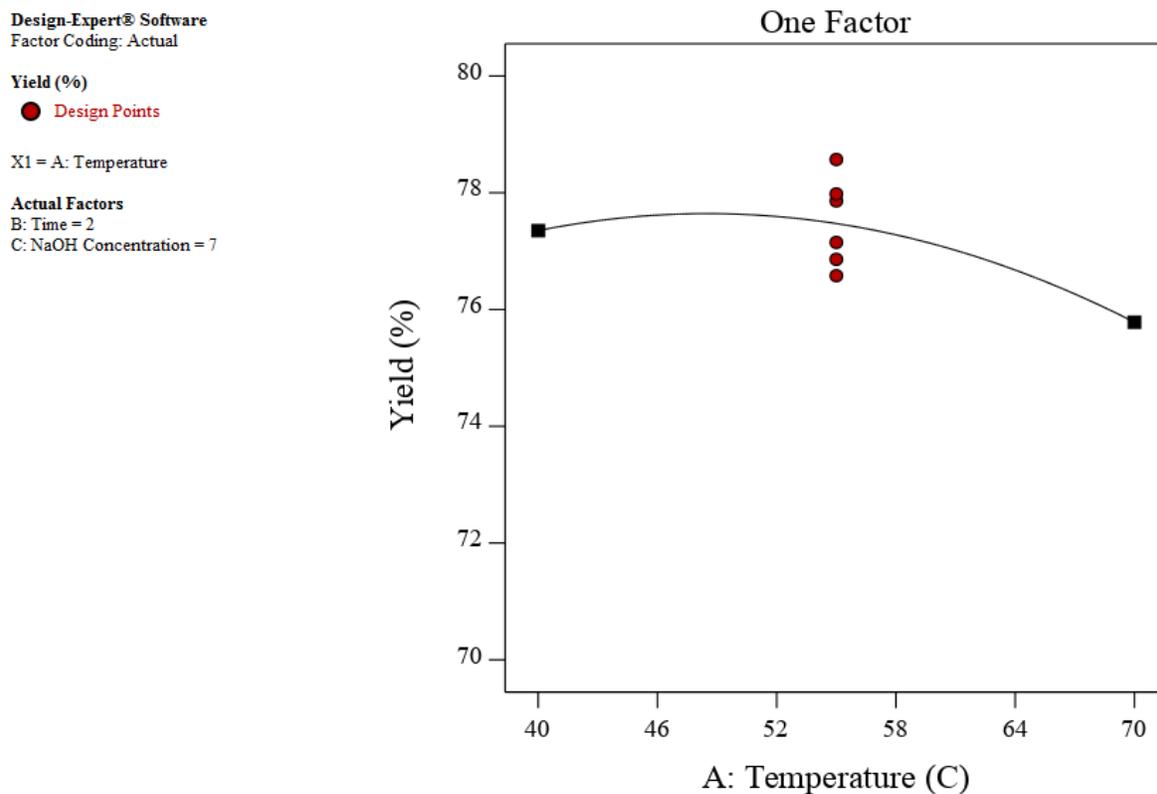


Figure 4.6: Plot of the effect of temperature (a) and time (b) on a yield of cellulose

Effect of Time

Figure 4.6b shows the one-factor effect of time on the yield of cellulose. At constant temperature and concentration, the yield was increasing for the first two hours. After the time reached 2 hours the yield starts slightly decreased from 77.8% to 75.2% with increasing time. This occurs due to the longer contact time between holocellulose and sodium hydroxide concentration the solution diffuses into the cellulose component and dissolves the required product which results in the decrement of the yield.

(b)

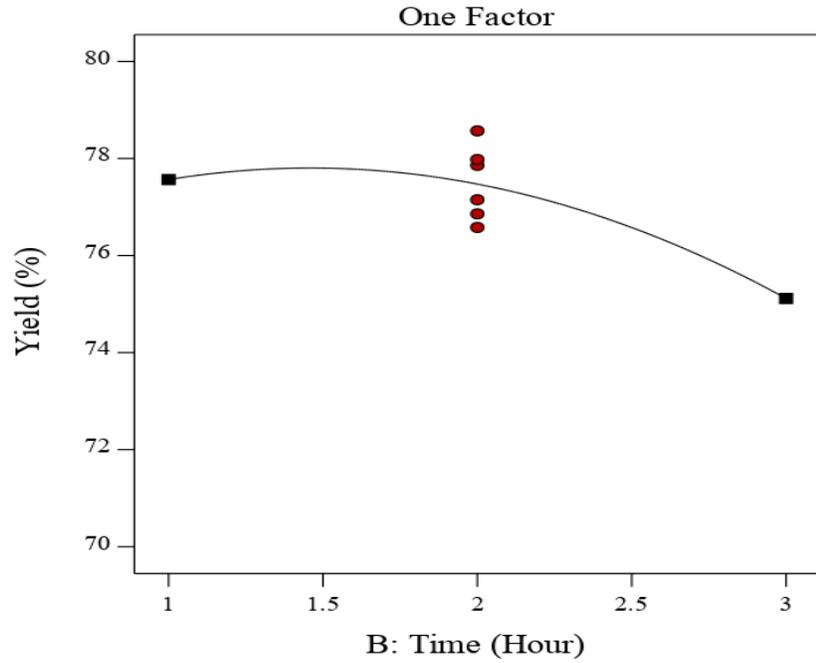
Design-Expert® Software
Factor Coding: Actual

Yield (%)

● Design Points

X1 = B: Time

Actual Factors
A: Temperature = 55
C: NaOH Concentration = 7



Design-Expert® Software
Factor Coding: Actual

Yield (%)

● Design Points

X1 = C: NaOH Concentration

Actual Factors
A: Temperature = 55
B: Time = 2

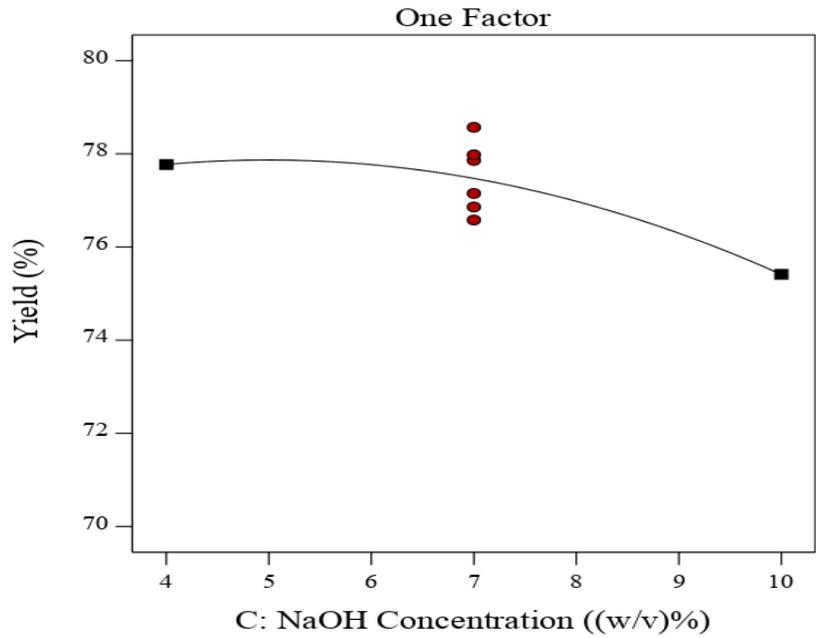


Figure 4.7: Effect of NaOH concentration on the yield of Cellulose

Effect of NaOH Concentration

The cellulose yield was very sensible to the alkali concentration. Figure 4.7 shows the effect of alkaline concentration at constant time and temperature. At a constant time and temperature, the yield was increasing for alkali concentration up to 7 w/v%. Then, it was slightly decreased. This was due to the ability of NaOH diffusion through the holocellulose, at high concentration, the solution diffuses faster and degrades the cellulose as well.

4.4.7 The Interaction Effects of Factors

The interaction effects between time and temperature have a significant effect on cellulose yield. Figure 4.8 shows the response surface of a three-D graph comprising the effect of time and temperature at fixed alkali concentration. The interaction effect occurs when the effect of one variable depends on the value of another variable.

Temperature is used to speed up the degradation of hemicellulose and other amorphous parts in the holo-cellulose. At normal and lower temperatures the degradation process was slower and take long reaction times. An increasing temperature, decrease the time used for the production process. But using the high temperature and long reaction times, in this case, beyond around 55°C and 1 hour respectively resulted in the decrement of yield. This occurs because of the ability of NaOH to degrade the cellulose parts. As the contact time between holo-cellulose and NaOH became longer it diffuses in the cellulose and degrades it, which results in the decrement of cellulose yield.

The other interaction effect was BC (time and NaOH) interactions. Sodium hydroxide has the ability to dissolve the holo-cellulose components. At constant temperature, the yield was observed with the interaction between time and NaOH concentration. The yield was increased at lower concentrations and short reaction times. When reaction time increases to 3 hours and alkali concentration increases about greater than 7% w/v the yield was decreased. This may arise from the high concentration that had an ability to degrade the cellulose as the contact time between holocellulose and alkali increases the rate of degradation increases which results in a decrement of yield.

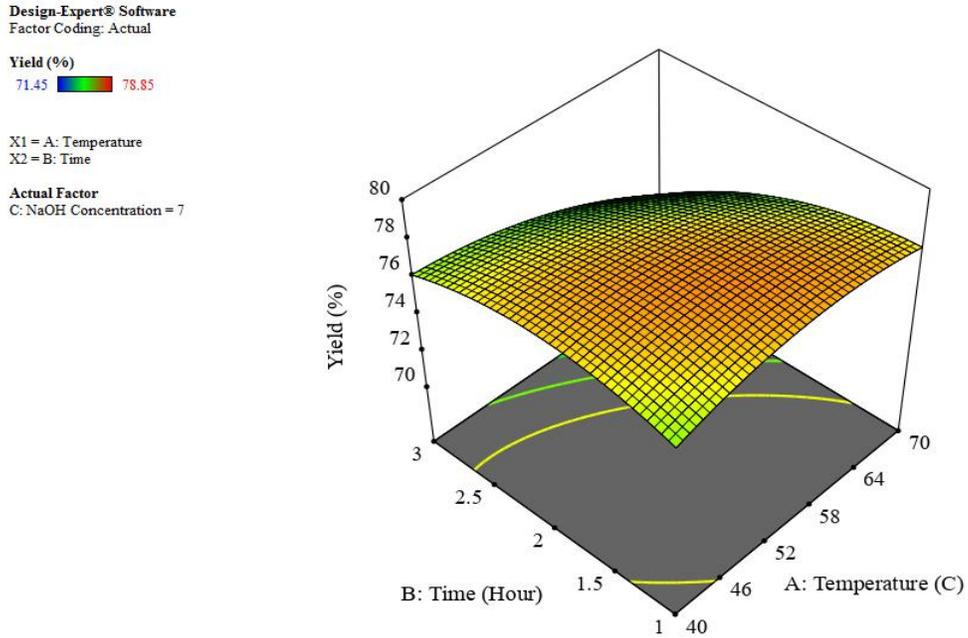


Figure 4.8: The 3D graph of time and temperature interaction effects on yield.

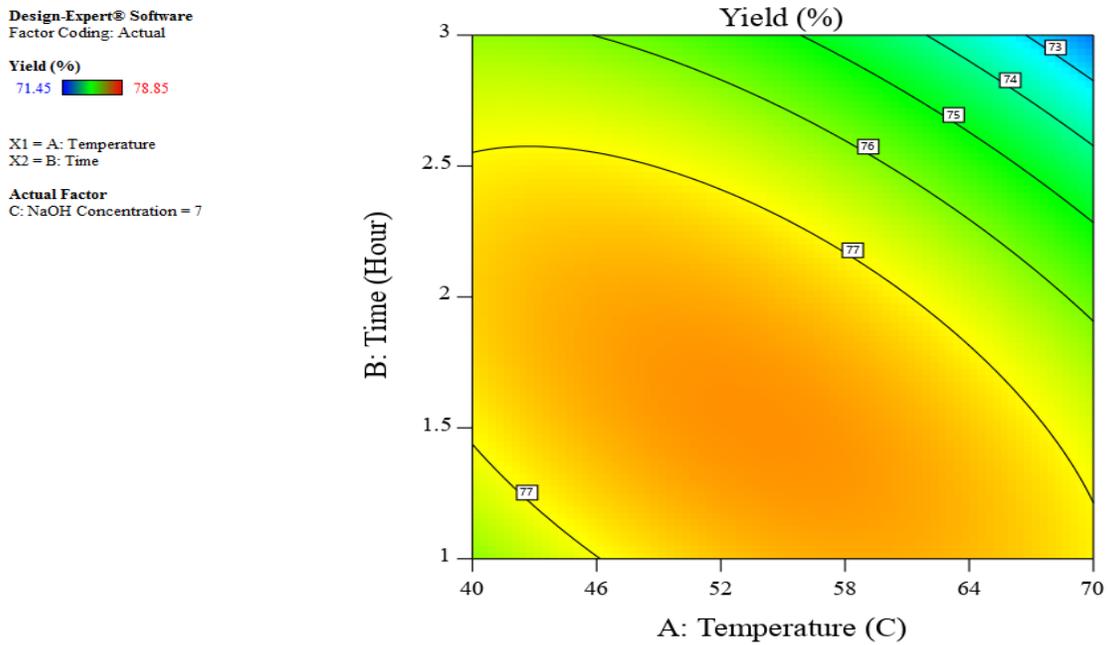


Figure 4.9: The contour plot of time and temperature interaction effects on yield.

Design-Expert® Software
 Factor Coding: Actual
 Yield (%)
 ● Design Points
 71.45 78.85
 X1 = B: Time
 X2 = C: NaOH Concentration
 Actual Factor
 A: Temperature = 55

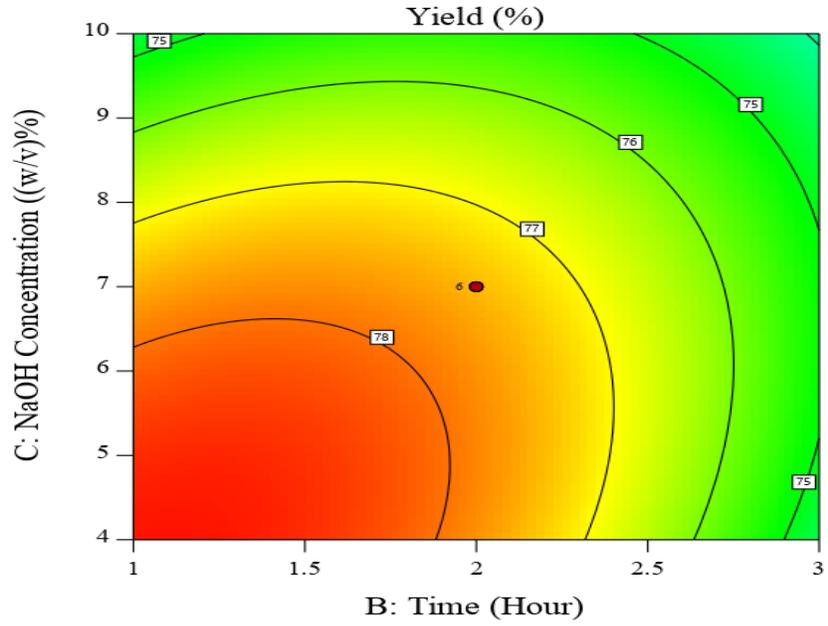


Figure 4.10: The contour plot of time and NaOH concentration effects on yield.

Design-Expert® Software
 Factor Coding: Actual
 Yield (%)
 71.45 78.85
 X1 = B: Time
 X2 = C: NaOH Concentration
 Actual Factor
 A: Temperature = 55

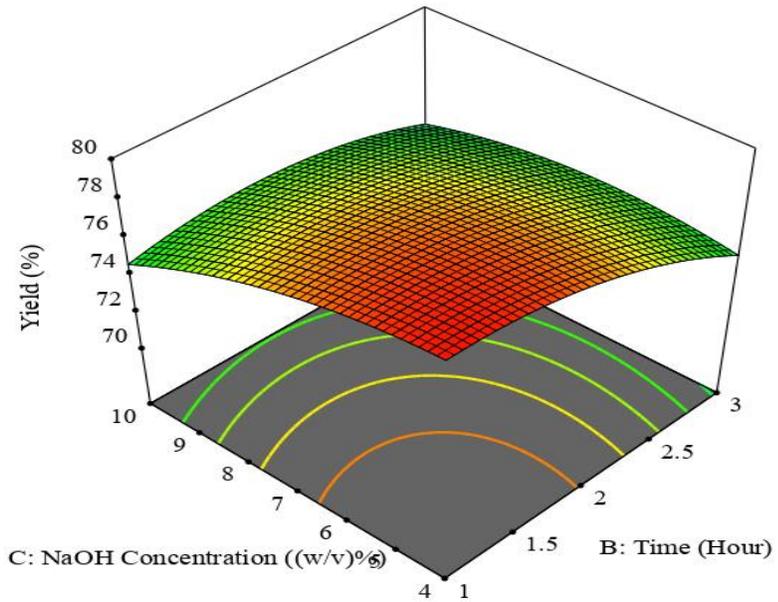


Figure 4.11: The 3D graph of interaction effects of time and NaOH concentration on yield.

4.4.8 Optimization of Process Parameters for Alkaline Hydrolysis.

The optimum process parameters for temperature, time and NaOH concentration were obtained by CCD. To perform the analysis the parameters were kept in range while the yield was kept at a maximum. Table 4.7 exhibits the desired combinations of process parameters that would provide the highest response by using numerical optimization. Numerical optimization was used to optimize any combination of one or more goals. The model capable of predicting the maximum cellulose yield showed that the optimum values of the process variables were the operating process variables are putting on the range.

Table 4.7: Adjusted process parameters in range to maximize the yield.

Name	Goal	Lower limit	Upper limit	Importance
Temperature	in range	40	70	3
Time	in range	1	3	3
NaOH concentration	in range	4	10	3
Yield	Maximize	71.45	78.85	3

The numerical analysis from CCD gives thirteen (13) possible solutions with the desirability of 98.6%. All possible solutions were given in table 4.8. The maximum yield was 78.748% which was obtained at a temperature of 57.676°C, time of 1 hour and NaOH concentration of 4 w/v% and the desirability was 98.6%.

(Ching and Ng, 2014) used 6% sodium hydroxide concentration for 2 hours reaction time duration at 80°C to extract cellulose from OPEFB. The obtained cellulose yield was 81.5%. (Chin *et al.*, 2017) reported the extraction of cellulose from rice straw with 90% yield by using 4% NaOH at 80°C for 2 hours. (Wulandari *et al.*, 2016) reported that the use of 17.5% NaOH at 45°C for 3 hours for extraction of cellulose from sugarcane bagasse gives the yield up to 73%.

Compared to the data from the literature, the optimum value of the cellulose yield obtained in this work lies in acceptable limits with the values extracted from different raw materials as suggested by (Wulandari *et al.*, 2016 and Ching and Ng, 2014). Therefore, this work shows that teff straw waste is a potential source for the extraction of cellulose and the optimum alkaline parameters and yield were in acceptable range with literature.

Table 4.8: Optimal possible solutions

Number	Temperature	Time	Concentration	Yield	Desirability	
1	58.003	1.000	4.000	78.748	0.986	
2	58.119	1.000	4.000	78.748	0.986	
3	57.896	1.000	4.000	78.748	0.986	
4	57.675	1.000	4.000	78.748	0.986	Selected
5	57.902	1.009	4.000	78.748	0.986	
6	58.061	1.010	4.000	78.748	0.986	
7	58.201	1.011	4.000	78.747	0.986	
8	57.955	1.016	4.000	78.747	0.986	
9	57.696	1.022	4.000	78.747	0.986	
10	58.439	1.000	4.010	78.747	0.986	
11	57.320	1.021	4.000	78.746	0.986	
12	57.806	1.034	4.000	78.746	0.986	
13	57.392	1.034	4.000	78.745	0.986	

4.4.9 Model Validation

Based on the results of RSM the optimum process conditions in the alkaline hydrolysis were 57.6°C, 1 hour and 4w/v%. In order to confirm the validity of the RSM model results, a confirmation experiment with the triplicate set was conducted at the specified optimum process conditions predicted by the model and the average yield was taken. The obtained average yield was found to be 78.453%. This show the experimental values were found to be close to the predicted values and hence the model was validated. Thus the model was useful to predict the yield of cellulose and also to obtain optimum process parameters for the alkaline process.

4.5 Characterization of Nanocellulose suspension

4.5.1 Functional group Analysis

The study of the functional group of the raw materials, cellulose, and nanocellulose was done by FTIR and the results were interpreted based on the peak observed at each functional group.

As the spectra observed from the result shows there are different spectral bands. FTIR spectra of nanocellulose having sharp bands but almost similar to that observed in cellulose. A similar result was reported by (Kumar *et al.*, 2014). The peak at 3344-3490 cm^{-1} shows that the stretching of intramolecular hydrogen bonds of O-H groups of cellulose which became narrower after the different treatments due to the removal of part of the amorphous components which is in agreement with (Ahmed, 2017; Hayati *et al.*, 2017). The peak around 2852 cm^{-1} – 2942 cm^{-1} corresponds to the C-H stretching of methyl and methylene groups in cellulose which decreased after alkaline and bleaching treatments (Sofla *et al.*, 2016). The other peak located at 1730 cm^{-1} shows the presence of acetyl and uronic ester groups of the hemicellulose or the ester linkage of the carboxylic group of ferulic and p-coumaric acids of lignin and hemicelluloses (Garcia, 2006). This was reduced and practically disappeared after the treatment process. The peak at 1632 cm^{-1} is due to the water absorbed to the teff straw (Liu *et al.*, 2006). The other located at 1512 cm^{-1} in the teff straw sample is due to the C-H deformation of methyl, methoxyl groups of lignin and aromatic C=C ring stretching. This peak was disappeared in cellulose and nanocellulose which shows the absence or reduction of lignin and hemicelluloses after bleaching and alkali treatment. The spectral bands at 1427 cm^{-1} and 1384 cm^{-1} are due to CH₂ scissoring and C-H bending in cellulose respectively (Kumar *et al.*, 2014). The peaks observed at 1253 cm^{-1} and 1045 cm^{-1} in teff straw and disappeared in cellulose and NC were due to the C-O out of plane stretching due to the aryl group of lignin and C-O-C pyranose ring stretching respectively (Kallel *et al.*, 2016). This shows the effectiveness of the chemical treatments to remove lignin and hemicellulose. The spectral bands at 1155 cm^{-1} and 1118 cm^{-1} are due to the C-C stretching in cellulose and C-OH skeletal vibration in lignin respectively (Kallel *et al.*, 2016).

Table 4.9: FTIR characteristic peaks of Teff straw, cellulose, and nanocellulose

Wavenumber (cm ⁻¹)	FTIR spectra of the samples			Assignment of the peaks
	Teff straw	Cellulose	Nanocellulose	
3300	3300	3300	-	O-H stretching of intramolecular hydrogen bonds of hydroxyl groups
2942-2852	2942-2852	-	-	C-H stretching of methyl and methylene groups in cellulose and hemicellulose
1730	1730	-	-	C-H stretching vibration for acetyl and uronic ester group from pectin, hemicellulose, etc.
1632	1632	-	-	Water absorbed to straw and cellulose
1512	1512	1512	-	C-H deformation of methyl, methoxyl groups of lignin and aromatic C=C ring stretching
1427	1427	1427	-	CH ₂ scissoring motion in cellulose
1384	1384	1384	1384	C-H bending
1253	1253	-	-	C-O out of plane stretching due to aryl group of lignin
1155	1155	1155	-	C-C stretching in cellulose
1118	1118	-	-	C-OH skeletal vibration
1045	1045	-	-	C-O-C pyranose ring stretching
896	896	896	896	β -glycosidic linkages

The peak observed at 892 cm^{-1} shows the presence of β -glycosidic linkages in cellulose (Mzimela *et al.*, 2018). The appearance of the new small spectral band at 1205 cm^{-1} in nanocellulose is due to the presence of S=O vibration after the acid hydrolysis process (Duygu 2018). The spectral bands at 1427 cm^{-1} and 895 cm^{-1} represent Cellulose I content. The peaks at 1322 cm^{-1} , 1431 cm^{-1} , and 1372 cm^{-1} are typical of pure cellulose (Ahmed, 2017). Figure 4.12 shows the spectral bands at each functional group. Generally, the same results were reported by (Kargarzadeh *et al.*, 2012 ; Kallel *et al.*, 2016) and (Liu *et al.*, 2006)

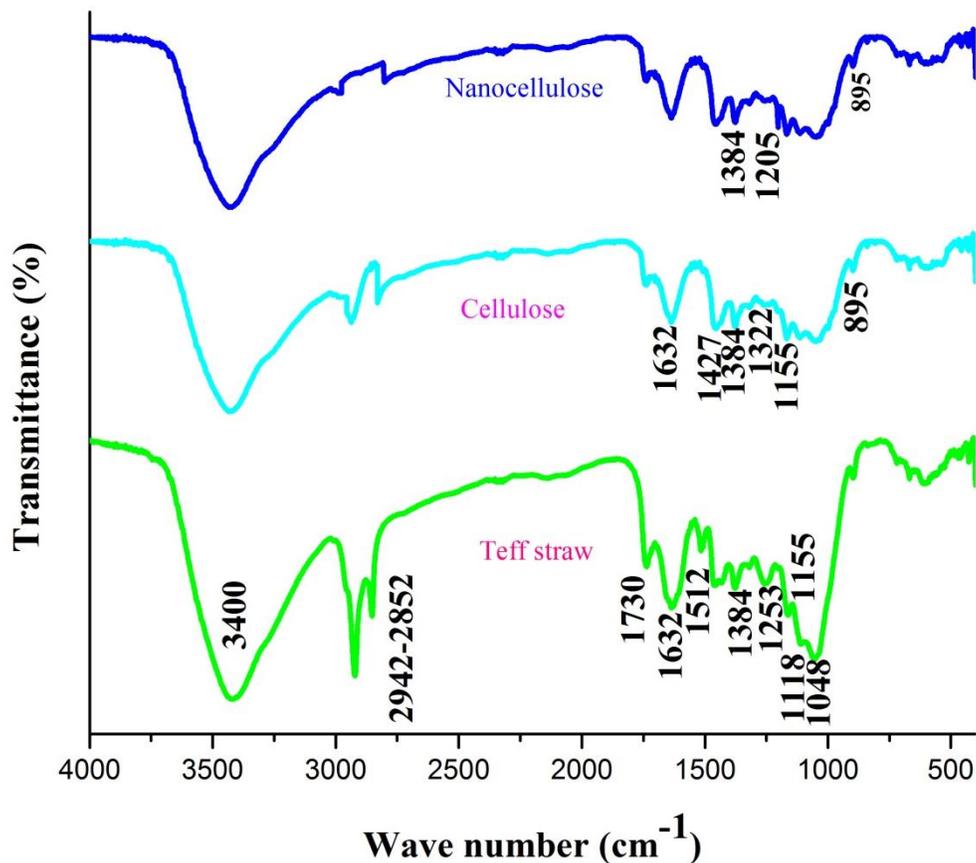


Figure 4.12: FTIR spectra for Teff straw, Cellulose and Nanocellulose suspension

4.5.2 Particle Size

Dynamic Light Scattering was the method used in this work to determine particle size distribution and average particle size. This instrument gives particle size distribution, the average particle size of nanocellulose suspension and Polydispersity index of the sample. The results derived by DLS were given in Figure (4.13) and Table (4.10). As the below figure shows the peak obtained was Uni-modal and the particle size distribution was in a range of 50 nm to 200 nm. The Z-average particle size given by the instrument was 102.6 nm and this shows that the obtained nanocellulose suspension from experimental work by acid hydrolysis of cellulose is in the nanometer scale. Z-average is the mean particle size as weighted by intensity. The polydispersity index (PDI) describes the uniformity of the sample in suspension. The higher the PDI, the less the uniform the sample is. In general, samples with PDI less than 0.1 (<0.1) corresponds to mono disperse and gives the Unimodal peak. Samples with PDI greater than 0.1 (>0.1) are poly disperse and can give the bimodal or tri-modal peaks. The PDI for this product was 0.047 which is less than 0.1 and confirms that the nanocellulose suspension had good uniformity.

Table 4.10: Z-Average particle size from DLS instrument

		Size (d.nm)	% Intensity
Z- average (d.nm) : 102.6	Peak 1:	91.99	100.0
PDI : 0.047	Peak 2:	0.000	0.0
Result quality : Good	Peak 3:	0.000	0.0

Different authors reported the particle sizes between 3 nm to 600nm ranges. (Zhou *et al.*, 2012) and (Fattahi and Dadashian 2014) reported the nanocellulose size of 115 nm and 70 nm respectively with bimodal peak. (Sofla *et al.*, 2016) and (Chattopadhyay D 2016) reported the nanocellulose size of approximately 100 nm and 348 nm respectively with unimodal peak. (Heriberto *et al.*, 2015) extracted nanocellulose from discarded cotton fibers with an average particle size of 235 nm with a unimodal peak by using a dynamic light scattering instrument.

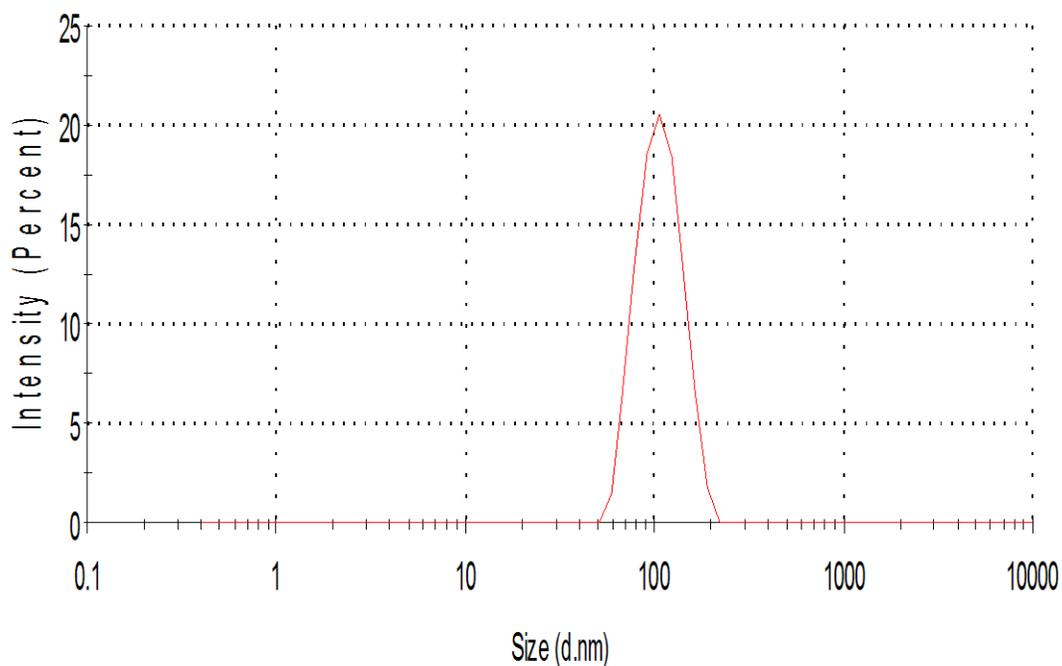


Figure 4.13: Particle size distribution obtained by Dynamic Light Scattering

The particle size distribution, Z-average particle size and Poly Dispersity index (PDI) of nanocellulose obtained in this work show that the product obtained was in the nanometer range and also in an acceptable range with the nanocellulose obtained by other researchers. The comparison of particle size with different works of literature was given in table 4.11.

Table 4.11: Comparison of average particle size with literature

Raw material	Average particle size (nm)	Source
Discarded cotton fiber	235	(Heriberto <i>et al.</i> , 2015)
Commercial MCC	115	(Zhou <i>et al.</i> , 2012)
Cotton fiber	70	(Sofla <i>et al.</i> , 2016)
Pineapple Peel	657.8	(Fattahi and Dadashian, 2014)
Teff straw	102.6	This work

4.5.3 Crystallinity Index

The diffractometer peaks obtained from XRD analysis scanned over 10 to 70 degrees with a step increment of $0.03s^{-1}$ were given in Figure 4.14. It was done for three samples, teff straw, cellulose, and nanocellulose to see the difference in their crystallinity after chemical treatments. The high-intensity peak located at 22.79° for nanocellulose describes the crystalline nature of the material and the intensity value shows the amount of crystalline structure. There are two major peaks for all samples around 2θ of 15 degrees and 22 degrees.

The crystallinity index was calculated by equation 3.11 and for nanocellulose sample crystallite size also calculated by equation 3.12. First, the crystallinity and crystallite size of nanocellulose was calculated and the crystalline peak area and total area for all samples were calculated. The crystallinity index was found to be 77.185% and the crystallite size at two peaks was found to be 39.106 nm for the first peak and 51.913 nm for the second. The crystallinity index of cellulose and teff straw was also calculated in the same way as calculated for nanocellulose and found to be 60.802% and 47.736% respectively.

The crystallinity indexes of three materials were given in Table 4.12. The CI of teff straw was 47.736% without any chemical treatment and it had the lowest CI compared to the chemical treated samples. The CI of cellulose was 60.802% which increased by 13.066% after alkali treatment and bleaching of teff straw which confirms the removal of amorphous regions of lignin and hemicellulose in straw results in the reduction of amorphous parts in the straw. After acid hydrolysis of cellulose, the crystallinity index was 77.185 % which increased by 16.38%. This means the acid hydrolysis process had played an important role in the degradation of the remained amorphous parts.

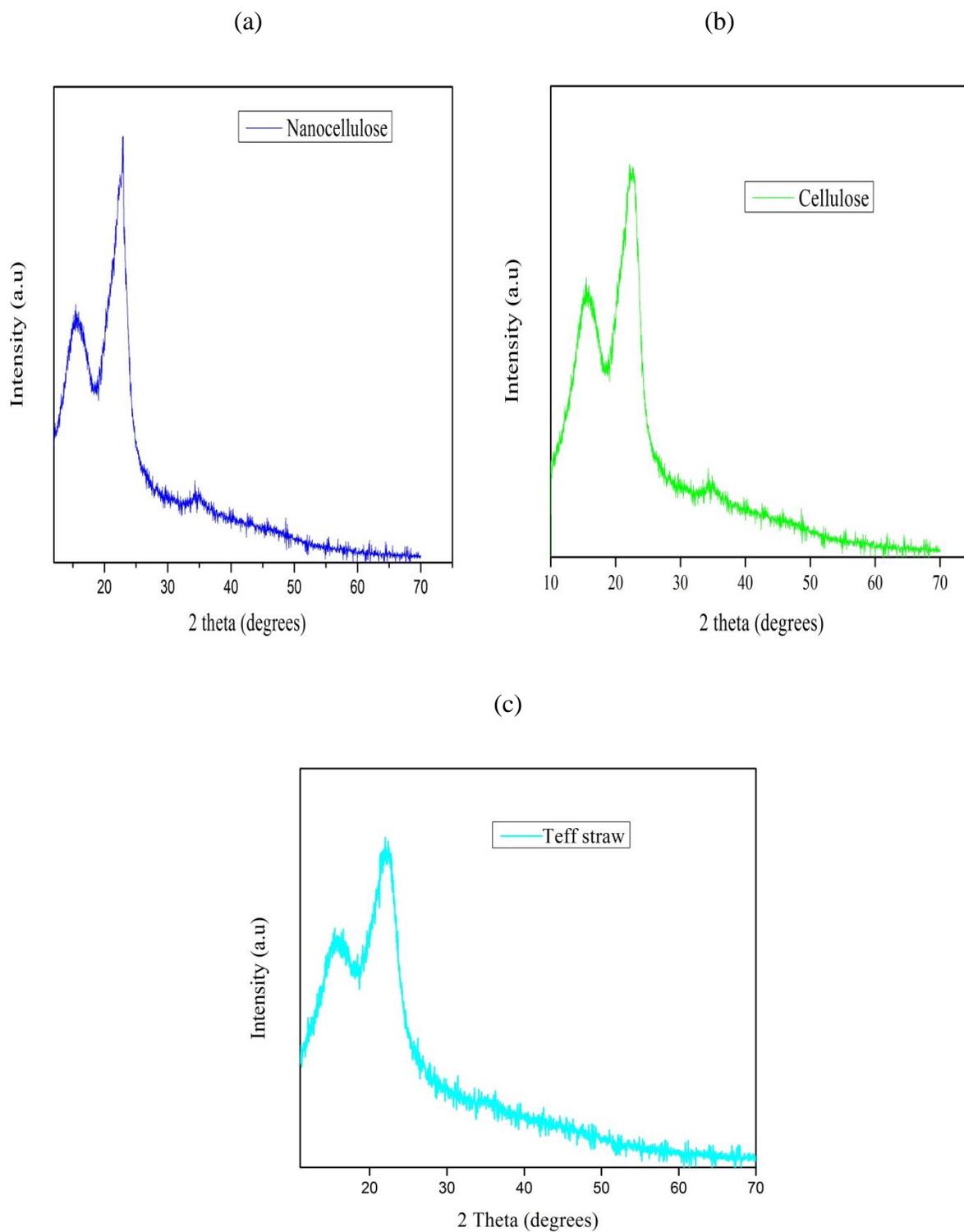


Figure 4.14: X-ray Diffraction patterns for nanocellulose (a), cellulose (b) and teff straw (c).

Table 4.12: Crystallinity index values for Teff straw, cellulose, and nanocellulose

Samples	Crystallinity Index (%)
Teff straw	47.73
Cellulose	60.80
Nanocellulose	77.18

(Kumar *et al.*, 2014) reported that the nanocellulose extracted from sugarcane bagasse with a crystallinity index of 72.5% that characterized by XRD. (Ioelovich, 2012) also extracted nanocellulose with a 76% crystallinity index from commercial MCC. (Burhani and Septevani, 2018) and (Sofla *et al.*, 2016) obtained the crystallinity index of 96% and 73% from OPEFB and SCB respectively. As different authors reported the nanocellulose obtained in this work had a good crystallinity index and in acceptable range with literature.

Table 4.13: Comparison of Crystallinity Index obtained in this work with previous works

Raw material	Crystallinity Index of Nanocellulose (%)	Source
Sugarcane bagasse	72.5	(Kumar <i>et al.</i> , 2014)
Commercial MCC	76	(Ioelovich, 2012)
OPEFB	96	(Burhani and Septevani, 2018)
Sugarcane bagasse	73	(Sofla <i>et al.</i> , 2016)
Teff straw	77.81	This work

4.6 PVA-Nanocellulose Composite Films

The composite films of PVA reinforced with nanocellulose of different ratios, neat PVA and reinforced with teff straw were presented in Figure 4.15. The films obtained were flexible and transparent.

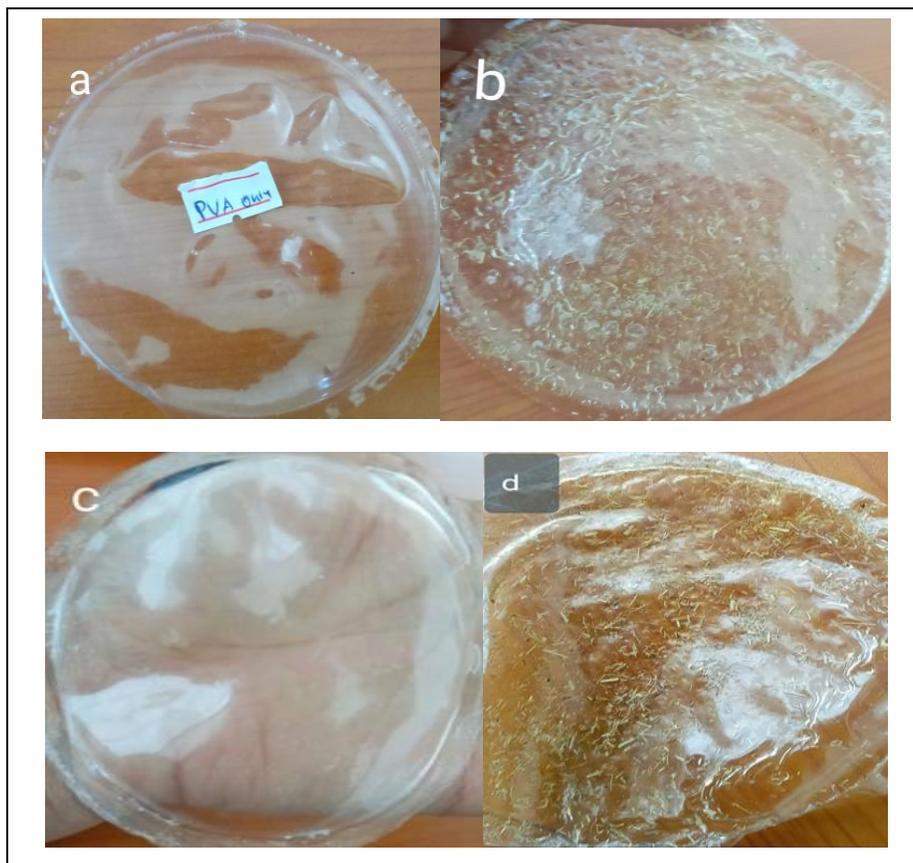


Figure 4.15: Prepared composite films.

a) Neat PVA, b) PVA/5% Cellulose c) PVA/5% NC d) PVA/5% Teff straw.

4.7 Characterization of PVA-Nanocellulose Composite Films

4.7.1 Water Absorption Test

The water absorption capacity of all samples was done and presented in the below section. As a result, obtained from the experiment shows the water absorption capacity of the composites decreases linearly with increasing the amount of nanocellulose loading. For neat PVA the highest amount of water absorption was obtained which was 84% and reduced to 73% by the addition of 2% NC. By increasing the nanocellulose loading to 7% the water absorption capacity was reduced to 61%.

Table 4.14: Water absorption capacity as a function of nanocellulose loading

Nanocellulose loading	Water absorption capacity (%)
PVA/0%NC	84
PVA/2%NC	73
PVA/5%NC	66
PVA/7%NC	61
PVA/5%C	76
PVA/5%TES	80

Figure (4.16) presents the relationship between the nano-cellulose loading rate and water absorption capacity. The reduction of water absorption capacity observed for all samples. This result shows the nano-cellulose reinforced films have lower water absorption which means they have good water preventive ability against water. The improvement of the properties of the films due to the presence of NC observed was related to several reasons. The first is, it shows and related to the formation of network structure between NC and PVA components which prevented the water molecules from dissolving the films and improved the water resistance. The other is the presence of NC means the pathway for water molecules to diffuse into the composites is altered from the direct diffusion into the polymer matrix, which leads to the improvement in water

absorption properties. The extensive hydrogen bonding between the polymer matrix and NC may prevent the hydrogen bonding sites for water molecules. The high aspect ratio of nanocellulose also has its own contribution to the improvement of the properties. The high aspect ratio of nanocellulose reduces the void spaces generated which can absorb the water molecules.

The water absorption test is the most important character in the evaluation of composite effectiveness. Mechanical properties and moisture absorption behavior are related to each other. Films that absorb less water will show better mechanical properties. The other thing is the application of polyvinyl alcohol in food packaging applications were limited due to its properties to absorb water. The packaging materials that absorb water are suitable for the production of bacteria and micro-organisms. These properties affect and lead to the deterioration of food under storage. So, the incorporation of nanocellulose shows better improvement in the water preventability of the PVA matrix.

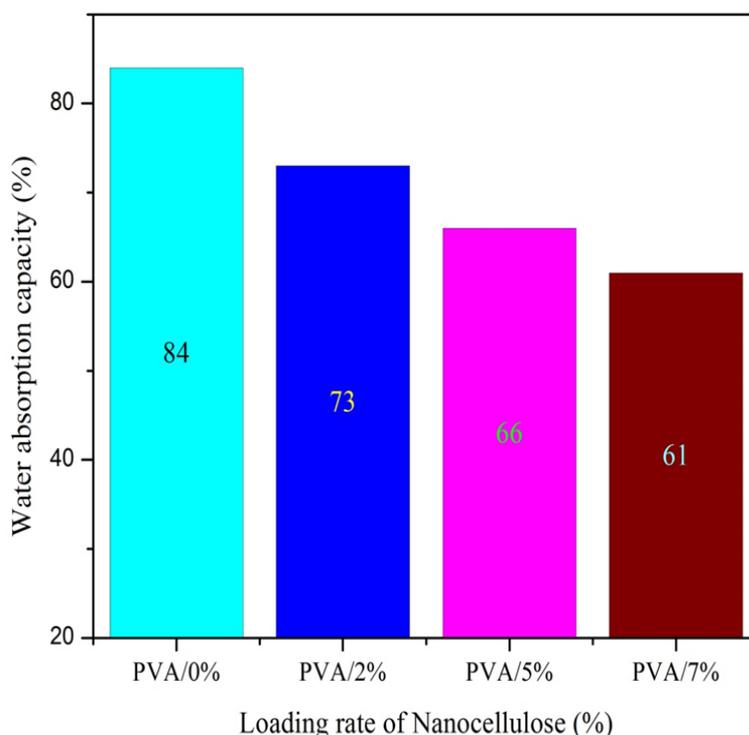


Figure 4.16: The plot of Nanocellulose loading versus Water Absorption capacity

The same results were reported by different authors. (Alhuthali, and Dong, 2012), produced Vinyl-ester eco nanocomposite by reinforcing with nano clay and reported that the addition of 5% nanocellulose reduces the water absorption capacity by 7.5%. (Lani et al, 2014) reported that increasing the nanocellulose content up to 10% reduces the water absorption capacity of PVA by 20%. The water absorption capacity results in this work were in agreement with different works of literature that described for other raw materials. (Alhuthali et al., 2012; Lani et al., 2014 ; Zanela et al. 2018)

Table 4.15: Comparison of a result of the water absorption capacity of composite materials with literatures

Nanocellulose loading	Water absorption capacity	Source
0% NC	50	
5% NC	17	
10% NC	23	(Lani <i>et al.</i> , 2014)
20% NC	35	
0%NC	12.81	
1%NC	11.13	(Alhuthali <i>et al.</i> , 2012)
3%NC	8.78	
5%NC	5.57	

4.7.2 Thermogravimetry Analysis

The TGA and DTGA curves obtained were given in Figure 4.17. TGA curves of both the films reveal three regions of mass loss. As observed from DTG curves, the first degradation occurs between the region of 30°C - 180°C which is due to the evaporation of absorbed water and accounts 10.86% for neat PVA and 7.4% for PVA composite. The second region was from 200°C-370°C due to the degradation of PVA intermolecular hydrogen bonding decomposition of PVA by a dehydration reaction on the polymer chain and by the degradation of the main backbones. The third region is above 400 °C which responsible for the carbonization of organic materials. As observed from the DTG curves the neat PVA film reached it is a maximum peak at a temperature of 286°C and the nanocellulose reinforced PVA film reached its maximum peak at 275°C. The thermal degradation temperature of the PVA film shifted to lower temperatures by 11 °C after reinforcement. The char residue is high for PVA composite film than that of neat PVA. This shows the reduction in thermal stability of polyvinyl alcohol after incorporating nanocellulose particles which results in low thermal stability of the composites. This may arise from the lower thermal stability of nanocellulose than PVA polymer. The nanocellulose extracted by sulfuric acid shows lower thermal stability than that of extracted by other methods. This may be from the presence of sulfate groups produced in nanocellulose during the acid hydrolysis process and the thermal degradation of sulfate groups starts at lower temperatures. There are different ideas related to the thermal stability of nanocomposites after reinforcing the nanocellulose extracted by sulfuric acid.

(Silvério *et al.*, 2013) reported that the addition of 9% nanocellulose to PVA did not improve the thermal stability of the nanocomposite material and discussed that the reduction of thermal stability in polyvinyl alcohol composites due to the presence of nanocellulose may arise from the sulfate groups in the nanocellulose.

(Kelly *et al.*, 2018) extracted nanocellulose and characterize the thermal stability of the nanocellulose. The nanocellulose extracted by sulfuric acid shows lower thermal stability than the cellulose and raw materials and they conclude that the presence of sulfate groups in the nanocellulose resulted in their low thermal stability.

(Wang *et al.*, 2007) reported the same argument and the neutralization of nanocellulose suspension by alkaline solution improves the thermal stability but the suspensions inclined to aggregate due to lacking electrostatic repulsion force between crystal particles.

So, the reduction in thermal stability of composite material observed in this work is in the agreement with that of previous works and that it is possible to say incorporation of nanocellulose to PVA polymer does not improve its thermal properties.

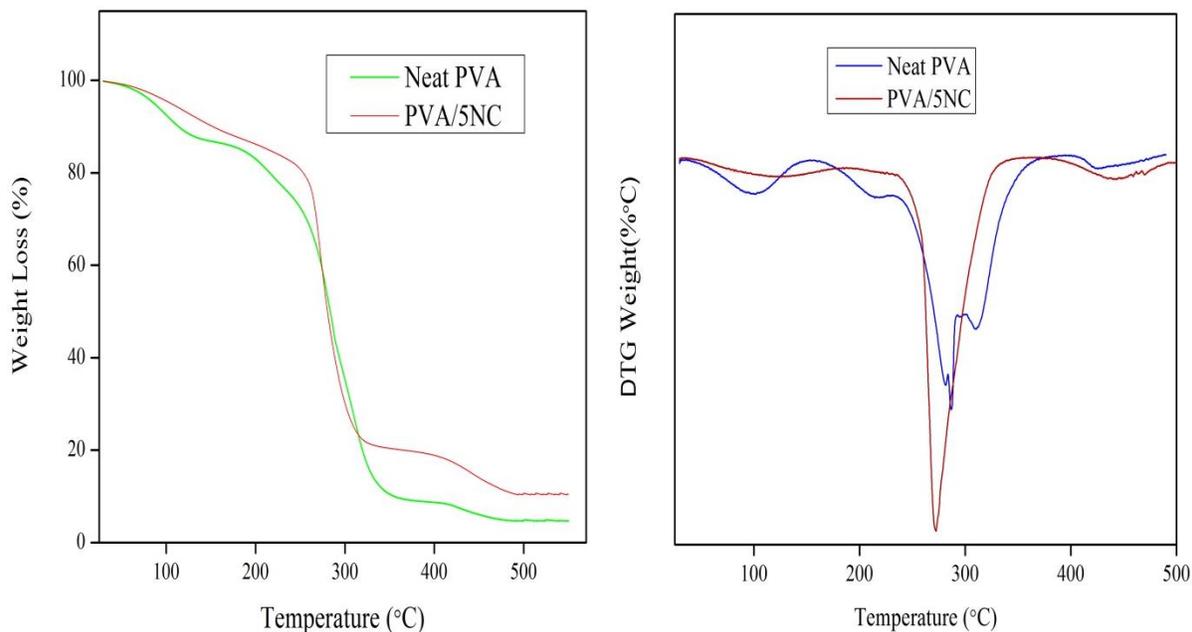


Figure 4.17: TGA and DTG curves of neat PVA and NC/PVA films

4.7.3 Mechanical Tests

Mechanical tests were done to see the improvement in the tensile strength and elongation at break of the composite films and compared with neat PVA. The results obtained were presented in table 4.16. The result illustrates that the addition of NC to PVA increases the tensile strength up to addition 5% NC and increases elongation at break at 2%NC loading rate. The addition of 2%NC, 5%NC increases the tensile strength from 24.5 MPa to 37.5MPa and 40.6 MPa respectively and then decreased to 38.5 MPa with the addition of 7% NC. The elongation at break was increased from 40% to 45.7% with the addition of 2% NC and reduced to 39.55% with the addition of 5% NC. After the addition of 7% NC, the elongation at break was decreased to 36.2%.

Table 4.16: Tensile strength and elongation at break of different composites

Composite samples	Tensile strength (MPa)	Elongation at break (%)
PVA only	24.5	40
PVA/2%NC	37.5	45.7
PVA/5%NC	40.6	39.55
PVA/7%NC	38.5	36.20
PVA/5%C	32	25.57
PVA/TES	29.5	22.67

According to Figure 4.18, there was an increase in the tensile strength of composite films. There is an increase in tensile strength up to nanocellulose loading of 5%. This is due to the presence of fine particles with high aspect ratio and dispersion of nanocellulose in the PVA matrix. It also indicates the presence of intermolecular interactions between nanocellulose and PVA. When nanocellulose contents are low the NC particles were surrounded thoroughly by PVA chains. So, the tensile strength of composites increased. The mutual affinity of the PVA matrix and NC with hydroxyl rich surface also leads to the strong interactions between them. The strong bonding between the hydroxyl groups of NC and matrix could explain the improved mechanical properties of composites. The decrement of tensile strength also observed after the addition of 7% nanocellulose to the PVA solution. The reason for this decrement is, due to the excess amount of nanocellulose leads to an increase in intermolecular interactions that might compete between the interactions of polyvinyl alcohol and nanocellulose. Therefore, compatibility between PVA and nanocellulose decreased, which results in the decrement of tensile strength at a higher loading amount of nanocellulose. The other reasons might be the number of flaws existing in nanocomposites including the weak boundaries between particles and bubbles trapped during sample preparation may increase with an increasing amount of reinforcement which causes the decrement in tensile strength of composites. Inhomogeneous dispersion also increases with increasing nanocellulose amount.

The increment in elongation at a break of composites at the nanocellulose loading reaches 2%. This was observed due to the presence of nanocellulose. However, after the addition of 5%NC, the decrement observed. This may arise from the stiffness of fibers. Strong interactions between nanocellulose and PVA chains could also restrict chain movement and consequently blocks its ability to flow and reduce ductility.

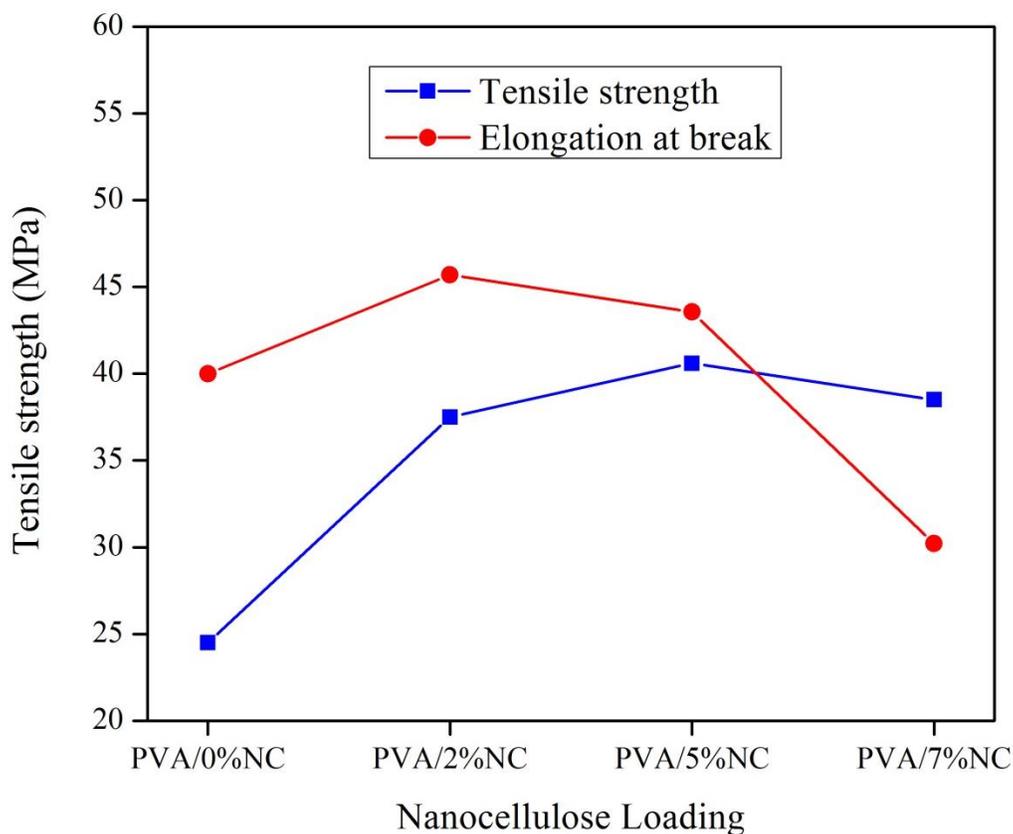


Figure 4.18: Tensile strength and elongation at break of composite versus nanocellulose

(Zhou *et al.*, 2012) reported that the tensile strength of nanocellulose reinforced PVA composite films increased up to the addition of 6% nanocellulose and decrement was observed after nanocellulose loading reaches 6%. The elongation at break was increased linearly with increasing the amount of nanocellulose added to the PVA matrix and decrement observed at the addition of 10% nanocellulose.

Table 4.17: Comparison of mechanical properties of PVA composite films with literature

Nanocellulose loading	Tensile strength (MPa)	Elongation at break (%)	Source
0%NC	100	25	
2%NC	108	40	
6%NC	104	50	(Zhou <i>et al.</i> , 2012)
10%	102	45	
0%NC	27	48	
1%NC	27.5	60	
2%NC	32	29	(Frone <i>et al.</i> , 2011)
3%NC	34	25	
4%NC	26	22	
5%NC	24	20	

4.8 Evaluation of Effectiveness of Reinforcing Nanocellulose

The evaluation of the effectiveness of the reinforcement was done to see the difference in properties of PVA composites by comparing them with the properties of neat PVA and PVA reinforced with other materials (cellulose and straw). The changes in tensile strength, elongation at break and water absorption capacity of composites based on reinforcement type were evaluated.

4.8.1 Improvement in Water Absorption Capacity

The water absorption capacity of neat PVA and reinforced PVA samples were presented in Figure 4.19. As the result shows that there is a difference in the water holding capacity of the samples. The reinforced samples have lower water absorption capacity than neat PVA which means they have a good prevent ability against water or moisture. The PVA reinforced with NC shows a good result than that of reinforced with cellulose and teff straw. The improvement in the properties of the films due to the presence of NC observed was related to particle size, high aspect ratio and the absence or reduction of amorphous regions in NC. The formation of network structure between NC and PVA components also prevented the water molecules from dissolving the films and improved the water resistance. The type of reinforcement and the amount of nanocellulose added to the PVA improves the water absorption properties and had their own effects.

As a result in Table 4.14 shows the water absorption capacity of the composites also decreased based on the different types of reinforcement of an equal amount. The addition of 5% untreated teff straw to neat PVA reduces the water absorption capacity by 4% and the addition of an equal amount of cellulose reduces by 8% and the addition of 5% NC to neat PVA reduces by 14%. This means the reinforcing type had also its own effect on the water absorption of the films. The untreated teff straw only reduces the water resistance by 4% that may be due to the presence of amorphous hemicellulose which has the property of absorbing water molecules. The addition of cellulose also reduces the WAC but not as much as nanocellulose. This may arise from the presence of amorphous parts or due to the semi-crystallinity of the cellulose molecules. The other thing is particle size and volume of the teff straw and cellulose. They have a lower aspect ratio than NC. This may lead to the formation of agglomeration and create high void spaces at the interfaces which help the water molecules to diffuse in the composite films made from

cellulose and teff straw than made from nanocellulose. As this result shows the reinforcing of 5% nanocellulose to neat PVA shows a good improvement in water absorption capacity in PVA than that reinforced with other ratios of NC and other reinforcement types (cellulose and teff straw).

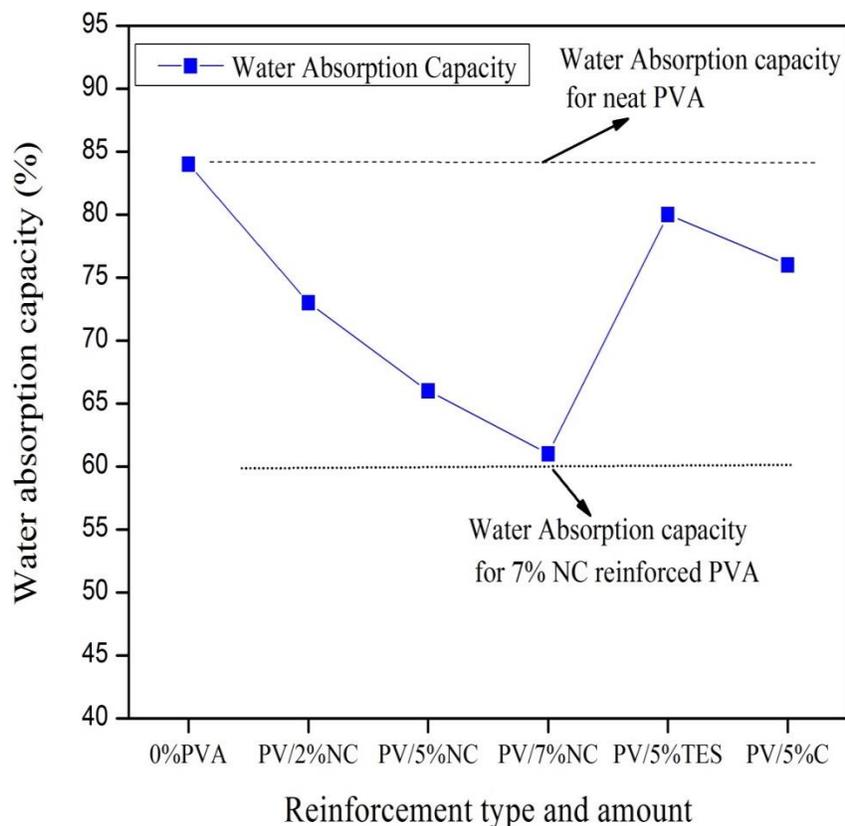


Figure 4.19: Plot of Water absorption capacity for Neat PVA and Reinforced PVA composite films

4.8.2 Improvement in Tensile Strength

The measured Tensile strength of neat PVA and reinforced PVA films were given in Figure 4.20. The result shows the improvement in tensile strength. This clearly indicates the variation induced on films by the incorporation of nanocellulose in PVA polymer, which resulted in higher tensile strength compared to neat PVA film as well as teff straw and cellulose reinforced PVA composite films. These results exhibit that the positive effect brought by incorporating nanocellulose in a polymer matrix to increase the tensile strength of the PVA matrix at lower nanocellulose loadings.

Figure 4.20 presents the changes in tensile strength based on the reinforcement type. The addition of 5% cellulose increases the tensile strength to 32 MPa and the addition of 5% untreated teff straw to 29.5MPa. But the addition of 5% NC increases to 40.6 MPa. There is a great difference with an equal amount of different reinforcement types. The good improvement observed with the addition of 5% NC was due to the small particle size of the nanocellulose, the intramolecular interaction between the components of composites and others. The stiffness and lower aspect ratio of teff straw and cellulose were responsible for the reduction in tensile strength of cellulose and teff straw reinforced composites.

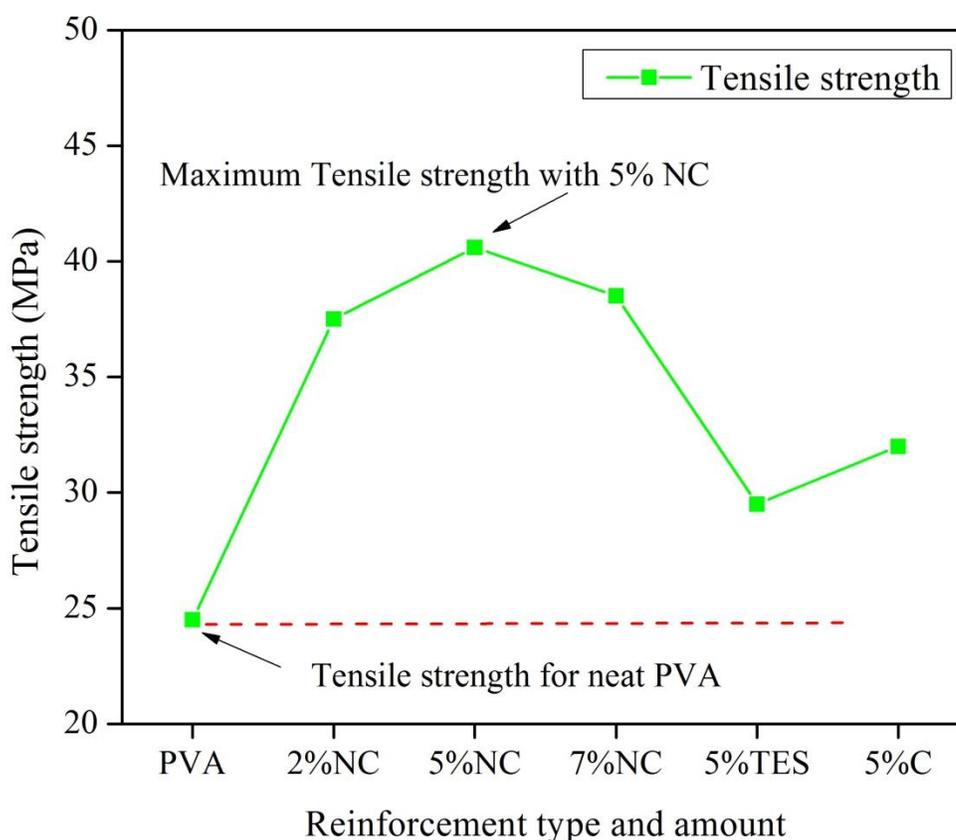


Figure 4.20: Plot of the tensile strength of neat PVA and reinforced PVA composite films.

The reason cellulose has good mechanical properties have from the removal of lignin, hemicellulose and other components in teff straw which causes the decrement in properties of teff straw reinforced PVA samples.

4.8.3 Improvements in Elongation at Break

The improvement in elongation at the break of PVA composite films observed only with the addition of 2% nanocellulose. At a higher concentration of nanocellulose, the elongation at break decreased.

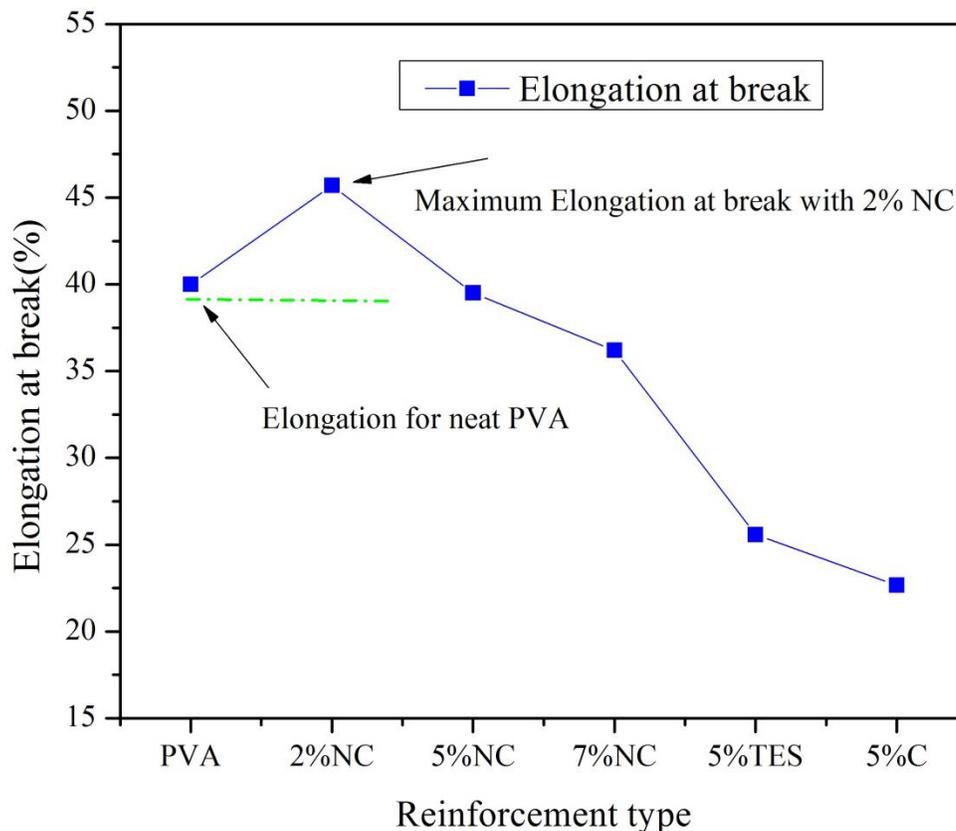


Figure 4.21: Plot of elongation at the break of neat PVA and reinforced PVA composites.

The mechanical properties of composites obtained in this work are in agreement with the literature (Ismail and Zaaba, 2011; Lani *et al.*, 2014) and (Zanela *et al.*, 2018). Therefore, the nanocellulose extracted from teff straw has an ability to reinforce and improve the mechanical properties (tensile strength and elongation at break) and water absorption capacity of polyvinyl alcohol.

5 Conclusion and Recommendation

5.1 Conclusion

In general, in this thesis the extraction and characterization of nanocellulose and reinforcing it with polyvinyl alcohol it leads to draw the following conclusions. The proximate analysis and chemical composition analysis of teff straw show a good amount of cellulose and show the ability to use as cellulose source. According to RSM analysis, time, temperature and alkali concentration affects the yield of cellulose and the optimum process condition for alkaline hydrolysis temperature, time and alkali concentration are 57.67°C, 1 hour and 4 (w/v) % respectively with cellulose yield of 78.74% and the extracted nanocellulose yield was 42.87%. The Fourier transform infrared spectroscopy result shows that the removal and reduction of lignin, hemicellulose and other unnecessary components. The average particle size from dynamic light scattering is 102.6 nm with a polydispersity index of 0.047. The crystallinity index of raw material, cellulose and nanocellulose was 47.73%, 60.80%, and 77.18% respectively. The composite films prepared by the solvent casting method were transparent and flexible. The water absorption capacity of the samples decreases linearly with increasing the addition of nanocellulose. The maximum tensile strength was observed with the addition of 5%NC which is 40.6 MPa and the minimum was 24.5 MPa without the addition of reinforcement. The elongation at break shows improvement only with the addition of 2% nanocellulose. Thermogravimetry analysis shows the lower thermal stability of the PVA composites than that of pure PVA. Generally, the composite material produced from polyvinyl alcohol and nanocellulose extracted from teff straw shows improved properties. The study has demonstrated that teff straw can serve as the best lignocellulosic feedstock for producing nanocellulose and reinforcing nanocellulose with polyvinyl alcohol with a lower ratio of nanocellulose improves the water absorption and mechanical properties of the composite materials and polymer films.

5.2 Recommendation

Further investigations are suggested on the processing of nanocellulose from teff straw. The process optimization on the extraction of nanocellulose needs further studies. For nanocellulose production pretreatments are most important and recommended to obtain purified cellulose but, during extraction and pretreatment steps extractive components, lignin and hemicellulose were removed and washed out but it is better to recover and change it into valuable materials. There is the generation of acid water that removed during the acid hydrolysis process which may cause an environmental effect. So, the way of neutralizing and recovering this acid wastewater needs another investigation. The further characterization of nanocellulose and composites by other characterization methods, that were not used in this work due to the shortage of time and unavailability, such as Scanning Electron Microscopy, Transmission Electron Microscopy and others also important. The government, researchers and universities should give attention to this area since it is a new and developing area in our country.

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Appendix

Appendix A: Results from Design Expert

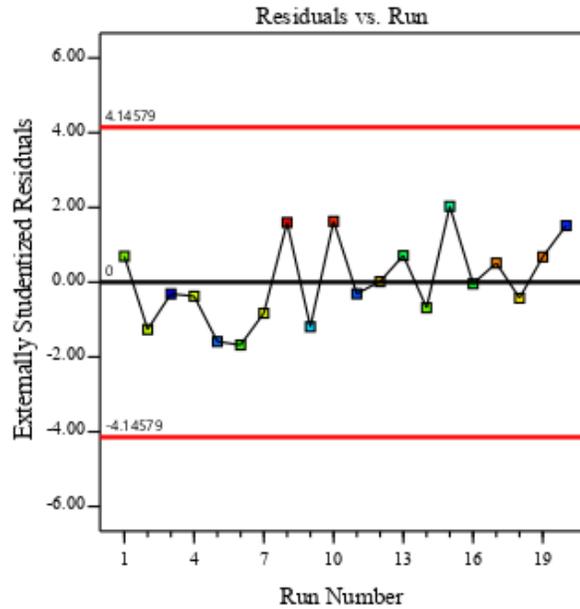


Figure A.1: Plot of residual versus run

Lack of Fit Tests

Table A.1: Lack of fit test from ANOVA

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Linear	55.75	11	5.07	8.79	0.0132	
2FI	38.21	8	4.78	8.28	0.0162	
<u>Quadratic</u>	<u>3.46</u>	<u>5</u>	<u>0.6919</u>	<u>1.20</u>	<u>0.4232</u>	
Cubic	2.18	1	2.18	3.79	0.1093	Aliased
Pure Error	2.88	5	0.5767	F-value	p-value	

Table A.2: Peak analysis from Origin Pro 8.5.

Samples	Peak Position	Integrated area	FWHM	Crystallite size (D) nm
Nanocellulose	15.49	6025.00	0.205	39.1098
	22.57	13,872.58	0.156	51.9136
	Area of crystalline	19,897.87	-	-
	Total area	25,779.23	-	-
Cellulose	15.475	5,954.08	-	-
	22.27	9,538.32	0.105	80.98
	Area of crystalline	15,492.4	-	-
	Total area	25,673.67	-	-
Teff straw	15.41	4,646.83	-	-
	22.15	7,608.87	0.098	82.63
	Area of crystalline	12,255.71	-	-
	Total area	25,673.67	-	-

Appendix B: Some pictures from laboratory work.

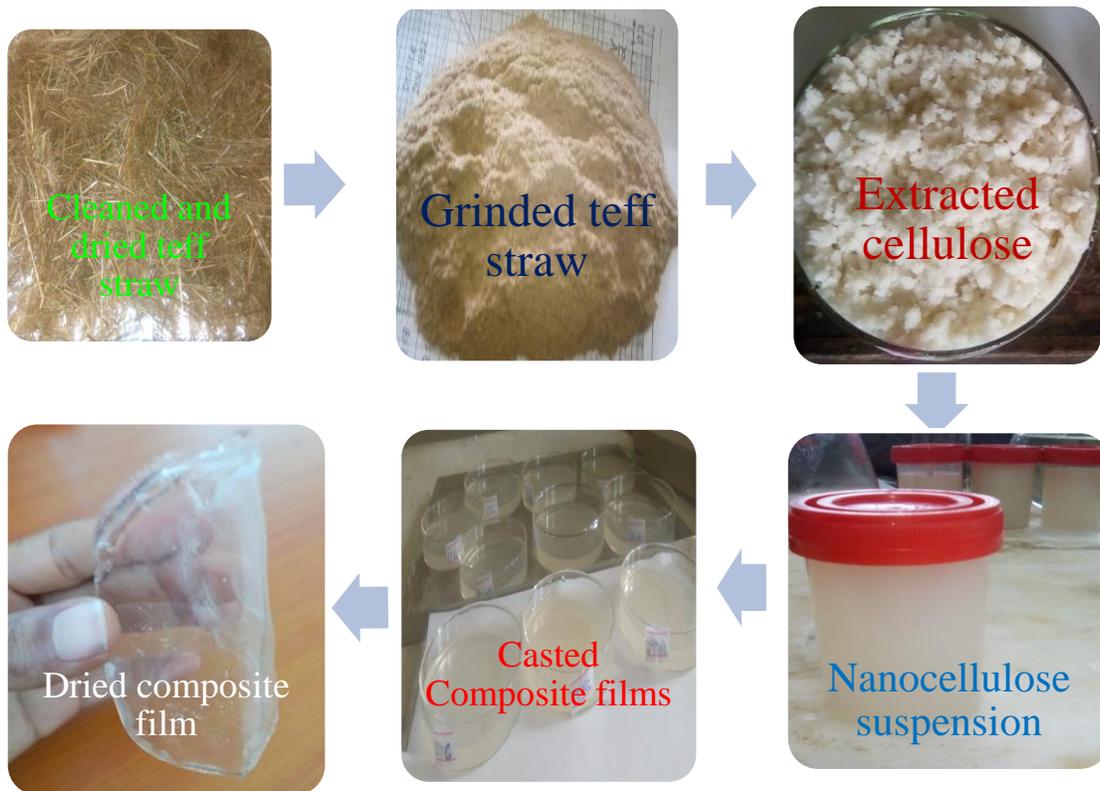


Figure B.1: Raw material and major products after each procedure

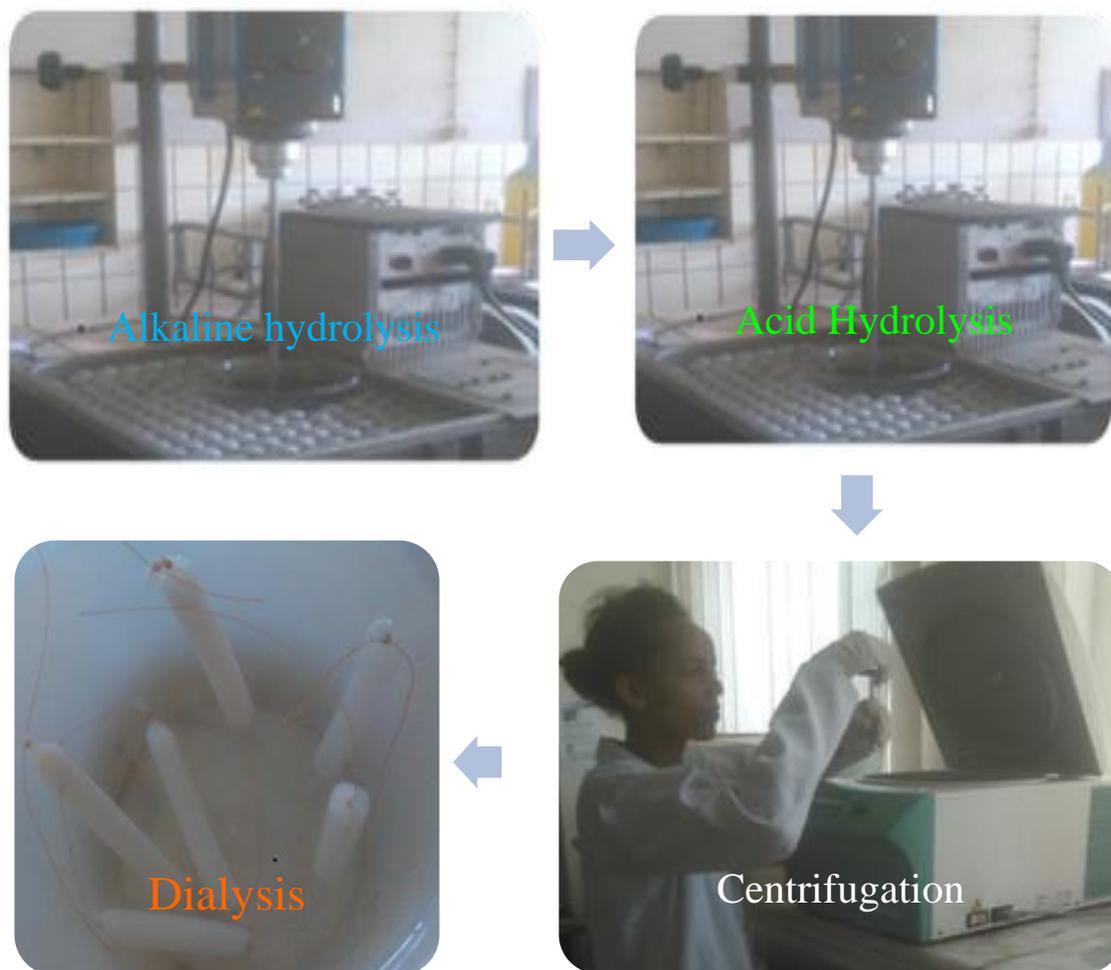


Figure B-2: Main Processes in nanocellulose production



Figure B-3: Production process of PVA composite