UNIVERSITÉ DE SHERBROOKE
Faculté de génie
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EXTRACTION DE CELLULOSE NANOFIBRILLÉE À PARTIR DE BIOMASSE AGRICOLE ET ÉTUDE DES APPLICATIONS POTENTIELLES

Thèse de doctorat

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Sherbrooke (Québec) Canada January 2020

And once the storm is over, you don't remember how you made it through, how you managed to survive. You won't even be sure, whether the storm is really over. But one thing is certain. When you come out of the storm, you won't be the same person who walked in. That's what this storm's all about.

Haruki Murakami

DEDICATED TO

My parents and family, husband Dr. Nagalakshmaiah for believing in me even before I did. Your motivation and constant help made all this possible. Thanks for being there for me always.

RÉSUMÉ

La production de matériaux cellulosiques est en forte augmentation et doit évoluer vers des matières premières renouvelables, durables et respectueuses de l'environnement. La cellulose est souvent considérée comme l'une des ressources naturelles les plus importantes. Avec l'avènement de la nanotechnologie, les chercheurs et les industries se concentrent dans la production de nanocellulose en très grandes quantités. L‘intérêt des recherches sur la nanocellulose repose sur ses propriétés prometteuses telles que sa faible densité et sa grande résistance mécanique. Les nanofibrilles de cellulose (FNC), également connues sous le nom de cellulose nanofibrillée (NFC), de cellulose microfibrillée (MFC) ou nanofibres de cellulose et la cellulose nanocristalline (NCC) sont des matériaux aux propriétés barrières, mécaniques et colloïdales importantes. De telles propriétés rendent la nanocellulose prometteuse pour des applications telles que la fabrication du papier, les composites, les emballages, les revêtements et la biomédecine.

La cellulose se trouve dans différentes sources telles que le bois, les fibres naturelles (biomasse agricole), les animaux marins (tuniciers), les algues et les champignons. La composition de cette biomasse lignocellulosique est différente pour chaque source. Avec la demande croissante en ressources renouvelables, la récupération des déchets de récoltes est appropriée en permettant de protéger l'environnement et de bénéficier d’une matière à faible coût. La biomasse des déchets agricoles est une ressource importante car elle est respectueuse de l’environnement, ne coûte presque rien, est très résistante, facilement disponible et renouvelable. Ces déchets, de sources variables (ex. tiges de coton, feuilles d’ananas, paille de riz, de lin, de chanvre, d’asclépiade, de carottes, de soja, de balles de riz) contiennent une quantité abondante de fibres naturelles.

L'accent est actuellement mis sur le marché des NFC en raison de l'attention accrue portée par les gouvernements, les industries, les agences de financement et les universités. La bioéconomie croît rapidement, ce qui entraîne des investissements plus importants. Les industries qui produisent les NFC sont Paperlogic, l’Université du Maine, Borregaard Norvège, American Process, Nippon Paper Japon, Innventia Suède, CTP / FCBA France, Oji Paper, Japon.

Cette étude est dédiée à l'extraction de la nanocellulose à partir de fibres naturelles telles que celles de carotte, de lin, de chanvre et d'asclépiade. La biomasse a été purifiée à l'aide d'un procédé à

étape unique qui comprend par ailleurs divers traitements avec de nombreux produits chimiques, ce qui est discuté dans la revue bibliographique.
La toute première étape de l'extraction de la nanocellulose est la purification de la biomasse afin d'éliminer toute trace de contaminants comme la lignine et les cires. Dans une étude typique, cela inclurait de nombreuses étapes telles que les traitements à l'acide et aux alcalis et le blanchiment. Dans l'étude présentée, la biomasse (lin, chanvre et asclépiade) purifiée a été obtenue en une seule étape à l'aide du peroxyde d'hydrogène. La longueur des fibres est restée inchangée pendant le processus. Les résultats de DRX ont montré que la cristallinité des fibres n'était pas affectée lors de la purification.

Les NFC et les NCC ont été extraits des déchets de carottes par un broyage à billes suivi d'une hydrolyse acide. L'effet du temps de broyage à billes sur la fibrillation et la morphologie des NFC a été étudié. Les propriétés mécaniques des NFC issus de la carotte ont également été étudiées. Les films de nanocellulose (NF) ont également été préparés en coulant les suspensions extraites (NFC et NCC). Les propriétés mécaniques, fonctionnelles et thermiques, ainsi que la cristallinité des NFC et des NCC obtenus ont été caractérisées. Les résultats ont montré que la longueur et le diamètre des NCC préparés à partir de la carotte étaient compris entre 54 et 610 nm. Une amélioration significative de la cristallinité a été observée pour NFC (69 %) et NCC (78 %) par rapport à celle des fibres brutes (36 %). Par ailleurs, les propriétés optiques et la morphologie des films nanocellulosiques préparés en utilisant les NFC et les NCC ont été analysées. Les films ont montré une amélioration significative en termes de transparence et d'homogénéité avec une augmentation du temps de broyage.

En général, les films de nanocellulose ont une faible perméabilité à l'oxygène et une grande résistance à l'huile en raison de leur structure en toile dense ressemblant à un réseau. Cependant, ces films ne sont pas stables dans des milieux à humidité élevée. Afin d'améliorer leur caractère hydrophobe, les films ont été recouverts d'un revêtement TiO_2 par technique sol-gel avec et sans oxydation TEMPO. Les NCF purs et oxydés ont été revêtus de dioxyde de titane (TiO_2) via approche sol-gel par revêtement par immersion. Les NCF revêtus de TiO_2 ont été séchés à 65 °C pendant deux heures, puis traités à 95 °C pendant une heure pour former du TiO_2 à la surface des films. L'effet du revêtement de TiO_2 sur les NCF purs et oxydés a été caractérisé afin de comprendre les propriétés morphologiques, optiques, fonctionnelles et barrière. La mesure de

l'angle de contact a montré que la nature hydrophobe des films revêtus de TiO_2 non oxydé et ceux revêtus de TiO_2 oxydé augmente considérablement, avec un angle de contact passant de 89 ° à respectivement 41 ° et 29 °. En particulier, l'hydrophobicité et les propriétés optiques des films revêtus ont été considérablement améliorées par rapport à celles des films de NCF purs.

ABSTRACT

The production of cellulosic materials is increasing tremendously in need to change towards the renewable raw materials and eco-friendly sustainable material. Cellulose is often considered one of the most important natural resource. With the advent of nanotechnology, the researchers and industries focus in the production of nanocellulose in huge quantities. The trailing purpose behind the growth of research in nanocellulose lies in their promising properties such as low density and high mechanical strength. Cellulose nanofibrils (CNF), otherwise known as nanofibrillated cellulose (NFC), micro fibrillated cellulose (MFC) or cellulose nanofibers and Nanocrystalline cellulose (NCC) are the materials with significant barrier, mechanical and colloidal properties. The above properties make nanocellulose promising for applications in such fields as papermaking, composites, packaging, coatings and biomedicine.

Cellulose can be found in different sources like wood, natural fibers (agriculture biomass), marine animal (tunicate), algae and fungi. The composition of this lignocellulosic biomass is different for each source. With the ever-increasing demand in renewable resource, the crop waste is meant to be an appropriate material. The recovery of waste makes it possible to protect the environment and to benefit from low cost reinforcements. Agriculture waste biomass is significant resource for the reason it is environmentally friendly, cost next to nothing, high in strength, readily available and renewable. The crop waste constitutes abundant natural fiber. The agriculture waste can be obtained from cotton stalk, pineapple leaf, rice straw, flax, hemp, milkweed, carrot, soy pods, rice husk etc. These materials can be used in multitude applications like paper and textile industry, composites, building, furniture and medical fields.

The NFC market is currently emphasized because of the augmented focus of the governments, industries, funding agencies and Universities. The bio-based economy is rapidly increasing resulting in the higher investments. The industries producing NFC are Paperlogic, University of

Maine, Borregaard Norway, American Process, Nippon Paper Japan, Innventia Sweden, CTP/FCBA France, Oji Paper, Japan.

This study is dedicated to the extraction of nanocellulose from nat6ural fibers viz carrot, flax, hemp and milkweed. The biomass was purified using single step process which otherwise includes various treatments with many chemicals which is discussed under literature review. The very first step in the extraction of nanocellulose is the purification of biomass to remove any traces of lignin, waxes etc. In a usual study, this includes many stages like acid and alkali treatments, bleaching etc. In this research work, the purification of biomass (flax, hemp and milkweed) was achieved in single step using Hydrogen peroxide. The fiber length remained unaffected during the process. The XRD results showed that the crystallinity of the fibers was not affected when purified.

NFC and NCC was extracted from carrot waste by ball milling and acid hydrolysis respectively. The effect of ball grinding time on the fibrillation and morphology of the NFC was studied. The mechanical properties of carrot NFC was also studied. The nanocellulose films (NFs) were also prepared by casting the extracted NFC and NCC suspensions. The structural, functional, crystalline and thermal properties of resulted NFC and NCC was characterized. The results exhibited that length and the diameter of the NCC prepared from carrot was in the range of 54 - 610 nm. Significant improvement in crystallinity was observed for NFC (69 %) and NCC (78 %) compared to that of raw fibers (36 %). The nanocellulosic films prepared by using NFC and NCC, optical and morphological properties were analyzed. The films exhibited the significant improvement in the transparency and homogeneity with increase in the grinding time.

Generally, the nanocellulose films has low oxygen permeability and high oil resistant due to their dense web like network. However, these films are not stable at high moisture medium. In order to improve the hydrophobic nature of the films, coated with TiO2 sol-gel coating with and without oxidation of TEMPO. The neat and oxidized NCF were coated with Titanium dioxide sol-gel (TiO_2) by dip coating. The TiO_2 coated NCF was dried at 65 ºC for two hours and then treated at 95 ºC for one hour to form the TiO_2 on the surface of the films. The effect of TiO_2 coating on neat and oxidized NCF was characterized to understand the morphological, optical, functional, and barrier properties. The contact angle measurement showed that the hydrophobic nature of the non-oxidized TiO_2 coated and oxidized TiO_2 coated films were increased drastically from 89° to 41° and 29° respectively. Notably, the barrier and optical properties of the coated films were significantly improved compared to that of the neat NCF films. Importantly, the tensile strength and elasticity of the TiO_2 coated NCF films were improved considerably compared to neat NCF.

ACKNOWLEDGMENTS

I would like to express my sincere gratitude to my supervisors Professor Mathieu Robert and Professor Saïd Elkoun for accepting me for this PhD position. I appreciate their guidance, supervision and persistent support throughout my PhD. I also extend my thanks to Pr. Saïd Elkoun for his constant care and help.

I would like to thank the Jury members for their valuable time in evaluating my thesis and for their suggestions.

My sincere thanks to the technical staffs at Center for characterization of Materials (CCM) of the Université de Sherbrooke, Mme. Sonia Blais, M. Charles Bertrand, M. Carl St. Louis, and M. Stephane Gutierrez for helping me in the characterizations. Also, I would like to appreciate all of my colleagues in Carrefour of Innovative Technologies and Eco-design (CITÉ) for helping in settling down both at home and lab.

Finally, yet ultimately, my gratitude to my parents Mr. Chakravarthy and Mrs. Vasantha Chakravarthy who always wants to see me in the happy place. I can never thank enough my darling son Ram Suhaas who understands and stands by me forever and my little angel daughter Amrutha who kept quiet and let me sit and write this thesis. I also thank my entire family for their support. I am forever grateful for the almighty for showering me with the blessings.

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ABBREVIATIONS

AFM	Atomic Force Microscopy
BC	Bacterial cellulose
CNC	Cellulose nanocrystals
CNF	Cellulose nanofibres
FE-SEM	Field Emission Gun Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
TGA	Thermogravimetric analysis
X-RD	X-ray diffraction
LCA	Life Cycle Assessment
MFC	Microfibrillated cellulose
NCC	Nanocrystals of Cellulose
NFC	Nanofibrillated cellulose
OTR	Oxygen Transmission Rate
PE	PolyEthylene
SEM	Scanning Electron Microscopy
TEM	Transmission electron microscopy
UV	Ultra-Violet
WVTR	Water Vapor Transmission Rate
WVP	Water Vapor Permeability
OP	Oxygen permeability

OTR	Oxygen transmission rate

CHAPTER 1

GENERAL INTRODUCTION

1.1 INTRODUCTION

The materials with dimensions (either the length or width or the diameter) in the 1-1000 nanometer (nm) scale (10^{-9}meter) are called as nanomaterials. From last two decades nanomaterials emerged as highly attractive research areas due to their remarkable physical and mechanical properties. The nanomaterials can be extracted from both organic (natural) and inorganic materials. Chitin, protein, starch and cellulosic derivatives are derived from natural materials (in nanometric scale) often also called as biomaterials. Whereas nanoclays, carbon nanotubes, nanographene, hydroxyapatite and graphene oxide are derived from inorganic materials. However, nanomaterials derived from the inorganic materials are not biodegradable.

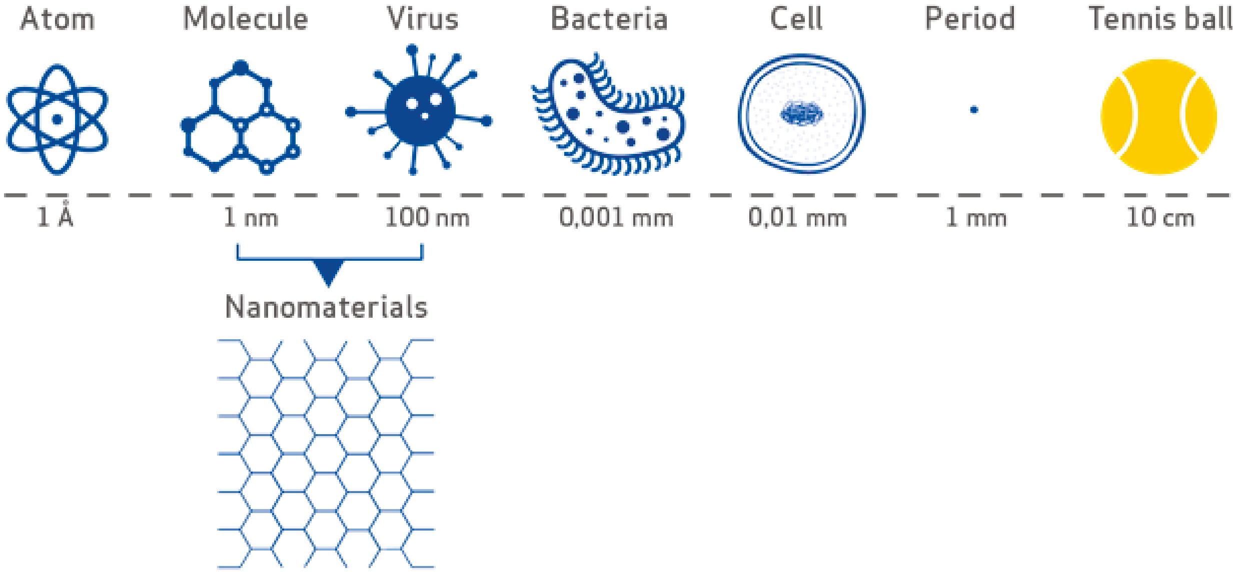

Figure 1. 1 Hierarchical structure of materials from macro to atomic scale (courtesy of European chemical agency)

Due to the vast attention towards sustainability and green materials, research institutes and private organisations are focussing on biomaterials. In this context plant-based materials especially cellulose, Lignin and starch playing vital role to replace non-degradable materials in the market. Nevertheless, in the present thesis work we focussed mainly on cellulose and its advanced derivatives such as nanofibrillated and nanocrystalline cellulose. It is well known the most copious material on the earth is cellulose. Nanocellulose is the advanced derivative of cellulose and it is widely produced in large scale by industries through mechanical, enzymatic and chemical process. However, industries are using only wood fibers and leaving the rest such as agricultural biomass and industrial waste. Largely agricultural biomass is simply burned in the field due to insufficient novel products. In this framework nanocellulose was produced from agricultural biomass such as flax, hemp, milkweed and carrot waste as primary source material.

1.2 PROBLEMATIC AND PROJECT PLAN

Agriculture biomass is rich in lignocellulosic materials. Though, industries are not interested to use them in applications such as paper, packaging, composites due to their multiple purification steps. The main constraints to purify the agricultural biomass is their diversity in the composition of the plant constituents such as cellulose, pectin, hemicellulose (HC) and lignin. Importantly the minerals such as silica, potassium, calcium and magnesium present in the biomass is a huge barrier to separate the fibers (1).

Generally, the wood-based fibers are purified by alkali treatment to remove pectin and HC followed by two stage bleaching process to eliminate lignin (2). Whereas in the case of the agriculture biomass it is completely different due to unlike composition. Previously, reported that different biomass such as flax, hemp and milkweed fibers are purified in multiple steps (3–5).

1. Fibers refining (separating the fibers from the peat)
2. Acid treatment (Such as hydrochloric acid, sulfuric acid, nitric acid and chromic acid)
3. Soxhlet extraction with different combinations of solvents
4. Alkali treatment (Sodium hydroxide often called as soda cooking) to remove the HC and pectin
5. Bleaching treatment to obtain the purified cellulose fibers by eliminating the lignin

Essentially bleaching treatment can be done by using sodium hypochlorite, hydrogen peroxide, oxygen and ozone process. However, to purify the biomass by using the aforementioned methods is very challenging for industries as these processes are very expensive and not feasible with industries to produce at bulk scale production. In this context, we proposed single step purification to obtain the pure fibers in this thesis work. By purifying the biomass in single step, it will give great opportunity for industries to focus and use the agricultural biomass in different applications such as insulation, packaging, composites etc.

Importantly this will be single gate way for the production of advanced cellulose materials such as NFC and NCC by mechanical and acid hydrolysis process. The NFC and NCC were characterized to understand the physical, thermal and morphological properties by mean of different techniques.

In order to understand the scope of potential applications the extracted nanocellulose was used to prepare the films for packaging with high oxygen barrier properties. The detailed description of each chapter is detailed in the project outline and objectives section.

1.3 PROJECT MOTIVATION AND OBJECTIVES

Every year merely in Canada farmers are harvesting 11million metric tons of agriculture biomass (6). Predominantly, this lignocellulosic biomass is mostly from diverse crops such as wheat, flax, hemp, corn, durum, oats, barley, rye, canola, soybeans and rice. However, after harvesting the food grains the leftover of all these crops remained a huge problem for the farmers before moving to next cultivation. In developing countries this biomass is simply burnt in the fields. Which caused lots of colloidal dust pollution along with carbon dioxide and carbon monoxide. Some of these harvested stems less than 40% is used in various low value applications like fabrics, ropes and twines. By valorizing high value-added products from this biomass will be great advantage for the farmers, manufacturers and entrepreneurs as it will be open the gates for new applications. Moreover, this biomass can replace the traditional sources as wood, cotton and recycled fibers.

In this perspective different agricultural (flax, hemp and milkweed) and vegetable (carrot) biomass was selected as potential source. Initially biomass was refined and purified in order to make the process easy and fibers were disintegrated by industrial mechanical process. The disintegration of the fibers will facilitate to penetrate the chemicals into the fiber network and help to reduce the cost and time. Further the purified fibers were used to prepare the nanocellulose by mechanical and chemical process. The prepared nanocellulose was dedicated to use in different applications.

1.3.1 Single stage purification of flax, hemp, and milkweed stem and their physical and morphological properties

Initially the delignification agents were screened, and hydrogen peroxide was selected. Firstly, the disintegrated fibers were cooked with hydrogen peroxide at 7.5% in water. Thanks to disintegration step which helps hydrogen peroxide to penetrate into the inner cell wall to react directly with lignin. Basically, hydrogen peroxide oxidizes the lignin and then dissolve in the water (7). The visual appearance of flax, hemp and milkweed fibers before hydrogen peroxide was rough due to the presence of lignin, wax and constituents (8). However, after treatment the fibers were clean and white. The results were ensued through the morphological observation by SEM. In order to understand the thermal, chemical, crystalline and morphological properties the fibers were characterized before and after treatment by means of TGA, FT-IR, X-RD and SEM.

1.3.2 Homogenous and transparent nanocellulosic films from carrot

Firstly, the carrot fibers were separated by removal of juice from the carrots and further dried and treated with previously developed hydrogen peroxide single step purification. The successively extracted cellulose fibers was used to prepare the Nano fibrillated cellulose (NFC) and nanocrystalline cellulose (NCC) by using non-conventional ball milling and acid hydrolysis process respectively. Initially, hot water washed carrot raw fibers treated with hydrogen peroxide, yielded the cellulose rich fibers in the absence of β-carotene and lignin. The scanning electron microscopy (SEM) of raw and bleached fibers showed that carrot consisting of both classical and unusual spring shaped fibers (9).

The purified cellulose pulp was fibrillated by ball milling process at three different grinding time to obtain NFC. The consequence of grinding time on fibrillation and morphology of the resulted NFC was investigated by SEM. In parallel, alkali treated pure carrot fibers were used to extract the NCC by acid hydrolysis process. The structural, functional, crystalline and thermal properties of resulted NFC and NCC was characterized by means of transmission electron microscopy (TEM), atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and thermogravimetric analysis (TGA).

In the final step the NFC and NCC suspensions were separately cast into nanocellulosic films (NCF). The final optical and morphological properties of the resulted films were analyzed systematically by ultraviolet-visible spectrophotometry (UV-vis) and SEM respectively.

1.3.3 Enhancement of surface properties of the nanocellulosic films by Tio_2 sol-gel coating

The main aim of this work is to dedicate the nanofibrillated cellulose films for the packaging applications. The global research interest towards NFC is growing due to their mechanical, physical, barrier and biodegradable properties. In this context, highly percolated nanocellulose films (NCF) were prepared by filtration and hot-pressing process. Further, the prepared neat NCF surface were oxidized using 2, 2, 6, 6-tetramethylpiperidine-N-oxyl (TEMPO).

The neat and oxidized NCF were coated with Titanium dioxide sol-gel (TiO_2) by dip coating. The TiO_2 coated NCF was dried at 65ºC for two hours and then treated at 95ºC for one hour to form the TiO_2 on the surface of the films. The effect of TiO_2 coating on neat and oxidized NCF was characterized by means of scanning electron microscopy (SEM), ultra violet (UV), Fourier transform infra-red spectroscopy (FT-IR), Oxygen transmission rate (OTR) to understand the morphological, optical, functional, and barrier properties.

1.4 THE LAYOUT OF DISSERTATION:

This dissertation is based on articles (published/submitted) which is consists of five chapters as shown in the figure 1.2. Chapter 1 is a brief introduction to the project describing the framework, motivation and objectives.

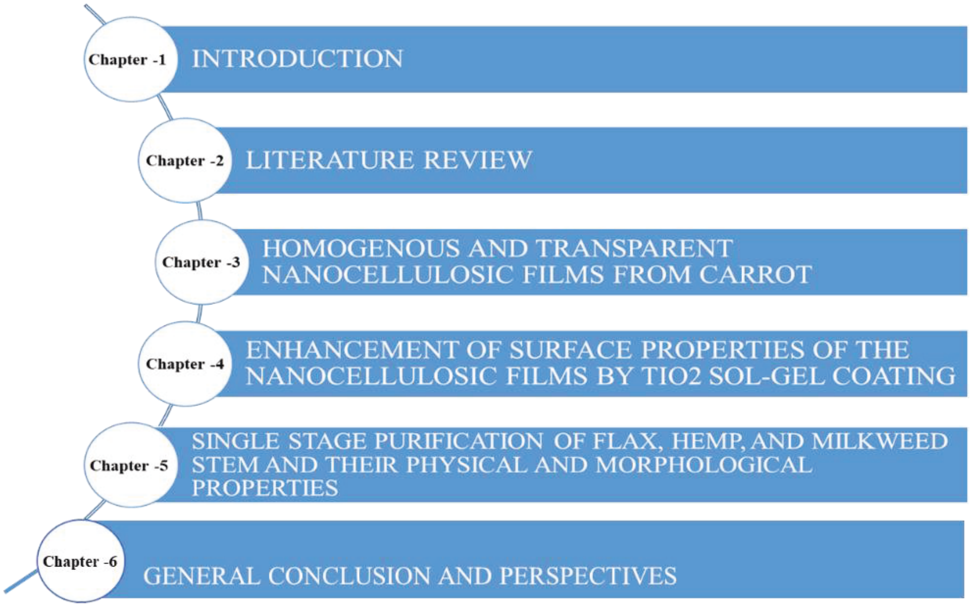

Figure 1. 2 Structural organization of the reported thesis work

Chapter 2 is completely dedicated to the extensive literature review of different agricultural and vegetal biomass composition, purification techniques reported in the literature was reported along with the nanocellulose production methods and their final properties based on the process was detailed. Finally, the production cites present in the world also listed to understand the importance of nanocellulose in the high value-added applications in the modern world (10).

Chapter 3 is devoted for the extraction of cellulose and nanocellulose from carrot waste. Additional to this the ensued nanocellulose was used to prepare the films to compare the mechanical properties with wood based nanocellulose films. Chapter 4 was detailed the impact of TiO_2 sol-gel coating on nanocellulose films for packaging applications were reported. In this chapter the influence of TiO_2 coating on surface properties of the hydrophilic nanocellulose films were characterized. In order to understand the mechanical and barrier properties of the coated films were analysed by tensile test and oxygen transmission rate tester. Chapter 5 the single stage purification of different agricultural biomass (flax, hemp and milkweed) procured from Canada was reported. Finally, the thesis work was concluded with future perspectives.

CHAPTER 2
LITERATURE REVIEW

Importance of Agricultural and Industrial Waste in the Field of Nanocellulose and Recent Industrial Developments of Wood Based Nanocellulose: A Review

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Published date: February 3, 2018
Current status: Published
Journal: ACS sustainable chemistry and engineering
Citation: (10)

DOI : https://doi.org/10.1021/acssuschemeng.7b03437

2.1 RÉSUMÉ

Les nanomatériaux de cellulose sont récemment devenus d'actualité dans le domaine des matériaux durables. Les deux principaux groupes de nanocelluloses (NCs) sont les (1) nanofibres fibrillées (NFC) et la (2) cellulose nanocristalline (CNC). Ces groupes sont souvent considérés comme des ressources renouvelables de deuxième génération, qui servent aussi d'alternatives aux produits à base de pétrole. Une grande attention a été accordée à ces matériaux en raison de leur faible densité, de leurs propriétés mécaniques élevées et de leur caractère renouvelable et biodégradable. Il existe beaucoup de travaux dans la littérature portant sur l'extraction des NFC et CNC à partir de différentes sources comme le bois dur/mou et la biomasse agricole. Parallèlement, le travail actuel représente uen revue bibiliographique consacrée aux propriétés des NFC et CNC extraites uniquement de l'agriculture et des déchets industriels en utilisant des méthodes mécaniques, chimiques et enzymatiques. Cet article explore en détail l'importance des déchets de l'agriculture et des prétraitements et méthodes utilisées dans production de NC, ainsi que les propriétés de la NC préparée à partir de déchets de récolte et industriels. Les applications potentielles de la NC provenant des différentes sources sont discutées. Les plus importantes initiatives industrielles actuelles dans la production de NC sont aussi présentées. Cette revue de littérature attirera probablement l'attention des chercheurs vers des cultures et des déchets industriels jusqu'alors considérés dans valeur comme de nouvelles sources dans le domaine de la NC.

2.2 ABSTRACT

Nano-sized cellulose materials have recently become topical in the sphere of sustainable materials. The two key groups of nanocelluloses (NCs) are (1) nanofibrillated cellulose (NFC) and (2) cellulose nanocrystals (CNC). They are often considered as second-generation renewable resources, which also serve as better replacements for petroleum-based products. More attention has been given to these materials because of their low density and high mechanical, renewable, and biodegradable properties. There are many works in the literature on the isolation of NFC and CNC from different sources like hard/soft wood and agriculture biomass. However, this is a comprehensive literature review dedicated to the properties of NFC and CNC extracted only from agriculture and industrial waste using mechanical, chemical, and enzymatic methods. This article explores in detail the importance of agriculture waste and pretreatments, methods involved in the

production of nanocellulose, and the properties of NC prepared from crop and industrial wastes. The potential applications of nanocellulose from different sources are discussed. The current extensive industrial activities in the production of nanocellulose are presented. This review will likely draw the attention of researchers toward crop and industrial wastes as a new source in the realm of nanocellulose.

2.3 INTRODUCTION

The production of cellulosic material increases tremendously to fulfil the need for renewable and eco-friendly sustainable materials.(11) Cellulose is often considered as one of the most important natural resource. With the advent of nanoscience, the researchers and industries focus in the production of NC in huge quantities. The trailing purpose behind the growth of research in NC lies in their promising properties such as low density and high mechanical strength.(12) Cellulose can be found in different sources like wood, natural fibers (agriculture biomass), marine animal (tunicate), algae and fungi.(13) The composition of this lignocellulosic biomass is highly dependant on the source.(14) This review deals with the crop waste as a core source for the extraction of NC.

With the ever-increasing demand for renewable resource, the crop waste is meant to be an appropriate material. The recovery of waste makes it possible to protect the environment and to benefit from low cost reinforcements. Agriculture waste biomass is significant resource for the reason it is environmental friendly, low cost, readily available, renewable and exhibit somehow acceptable mechanical properties.(15) The crop waste constitutes abundant natural fibers.(16) The agriculture waste fibers can be obtained from cotton stalk, pineapple leaf, rice straw, flax, hemp, soy pods, rice husk, garlic straw, potato peel, grape skin etc. Agri biomass can be used in multitude applications like paper, textile industry, composites, building, furniture and medical fields.

The NC market is currently emphasized because of the augmented focus of the governments, industries, funding agencies and Universities. The bio-based economy is rapidly increasing resulting in the higher investments. The NC production includes high value added applications like composites, paper industry, packaging, paints, oil &gas, personal care, medical care etc.(17) The NC is first commercialised by celluforce Inc. in Quebec; a joint-venture between FP innovations and Domtar.(18) The NC industries are prominent in the areas of Asia Pacific, North America, Europe, Latin America and Middle East and Africa including leading names like Paperlogic, University of Maine, Borregaard Norway, American Process, Nippon Paper Japan, Innventia Sweden, CTP/FCBA France, Oji Paper, Japan.

This literature review aims to deliver the consolidate details on structure and multiple sources of cellulose, NC, their extraction from agri-based sources and the current industrial developments on NC production and applications. There are numerous literature which deal with various aspects of NC like source, production of nanofibrillated cellulose,(19,20) production of nanocrystals,(21–23) extraction methods,(20) pre-treatments,(24) and applications.(25) However, there is only limited review on the agriculture biomass for the extraction of NC.(15,26) Since the urge of converting agriculture waste into wealth is increasing for the reasons of waste management, improve ecofriendly resource and creating new source of economy, it is necessary to concentrate on the inside story of the agriculture biomass, extraction of NC from crop waste, different treatments, pre-treatments involved. It also deals with the properties and multiple applications of isolated NC. To conclude, the industrial evolution in the production of NC is also addressed.

2.4 SOURCE OF CELLULOSE

Cellulose is the amplest resource of natural fibers. Annually, the extraction of cellulose is assessed to be over 7.5 x 10^{10} tons.(21) Cellulose is extracted from various sources including wood (Hard or soft wood), seed (cotton), bast (Flax, hemp), cane (bamboo, bagasse), leaf (Sisal), straw (rice, wheat), fruit (Coir), tunicate, algae, fungi, bacteria and minerals.(27) Figure 2.1 shows the hierarchical representation of the chief sources from which cellulose can be extracted.

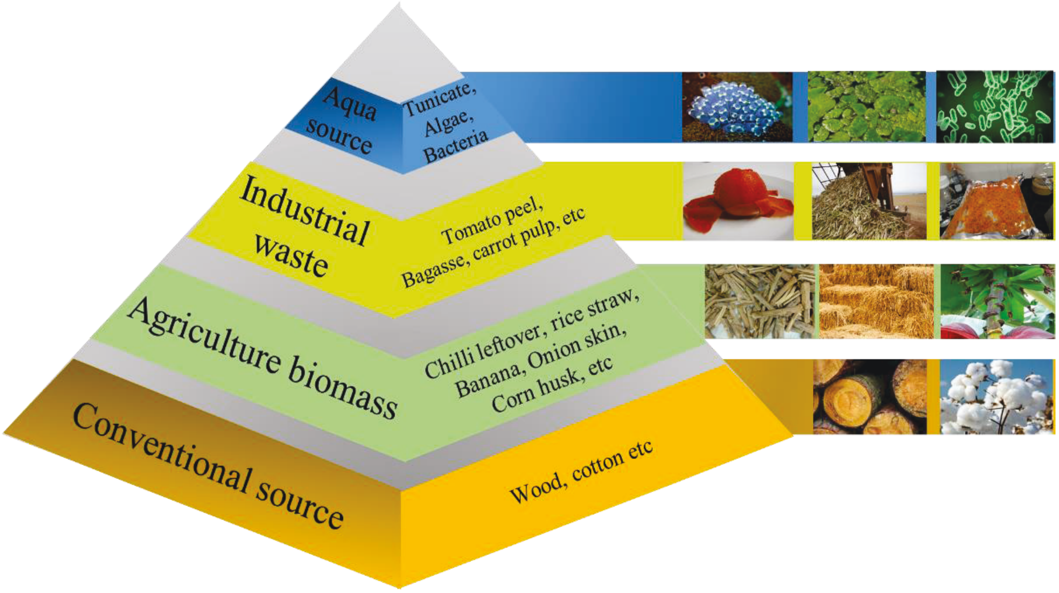

Figure 2. 1 Hierarchical representation various sources of cellulose.

The source is placed in the order of conventional source like wood and cotton, which is considered as the primary origin. Wood can be classified as soft/hard wood based on their structural aspect.(28) Then comes the agriculture waste like rice straw, banana rachis, corncob, onion skin etc. The crop waste is becoming the second highest source of cellulose. Also, the industrial wastes like sugarcane bagasse, tomato and garlic peels etc. is another source emerging lately. Cellulose can be obtained from some other small class of sources like marine animal (tunicate), algae, fungi and bacteria. The interest of this review lies on the second and third grid of the pyramid representation i.e. Crop and industrial waste for the fact that this source needs to be explored more. The basic constitution of the foretold fibers is cellulose, lignin and hemicelluloses. However, the chemical composition differs for each some of which are tabulated in table 2.1 on dry basis. Besides cellulose lignin and hemicelluloses, some sources contain pectin, waxes and other water soluble components.

Table 2. 1 Chemical composition of different sources on dry basis.

Source	**Cellulose (wt.%)**	**Hemicellulose (wt.%)**	**Lignin (wt.%)**	***Reference***
Pine (softwood)	44.0	27.0	28.0	(29)
Yellow birch (hardwood)	47.0	31.0	21.0	
Jute	73.2	13.6	13.4	
Wheat straw	48.8	35.4	17.1	
Rice husk	45.0	19.0	19.5	
Bagasse	55.2	16.8	25.3	(30)

Banana	63–64	10	5	(31)
Flax	71	18.6-20.6	2.2	
Hemp	70-74	17.9-22.4	3.7-5.7	
Mulberry barks	37.38 ± 2.31	25.32 ± 2.45	9.99 ± 0.82	(32)
Garlic straw	41	18	6.3	(33)
Carrot residue	81	9	2.5	(34)
Ground nut shells	38.31	27.62	21.10	(35)
Onion skin	41.1 ± 1.1	16.2 ± 0.6	38.9 ± 1.3	(36)

2.5 CELLULOSE

Cellulose is the natural polysaccharide first isolated by Anselme Payen in 1838 from wood when treated with nitric acid.(21) They exist as microfibrils in the plant cell wall of multiple sources. The diameter of the fibrils varies from 3-35 nm depending on the source.(37) Cellulose contains linear polymer chain comprised of glucose monomer named β-1,4-linked anhydro-D-glucose units as shown in figure 2.2. The degree of polymerization of cellulose is up to 20000 units. For wood and cotton it is approximately 10000 and 15000 glucose units respectively.(38)

Anhydroglucose is the monomer and cellobiase is the dimer of cellulose. Each glucopyranose unit contains 3 highly reactive hydroxyl groups which are responsible for the hydrophilicity, chirality, biodegradability etc. of cellulose. The individual cellulose chain contains reducing end because of the hemiacetal unit with both aliphatic and carbonyl group and the non-reducing end with closed end group.(39) The higher mechanical properties of each microfibrils result from the strong hydrogen bonds.

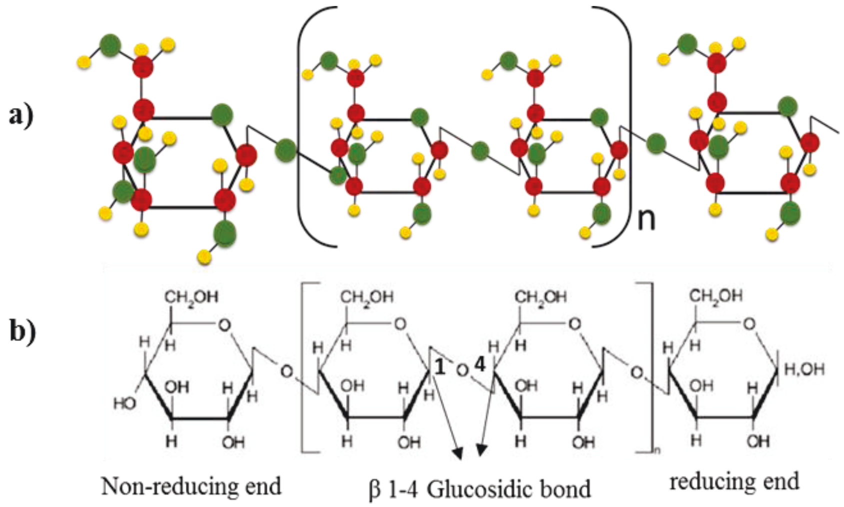

Figure 2. 2 a) **3D structure of cellulose.**b) **structure formula of cellulose. Adopted from Cave and Walker (1994).(39)**

The β-1,4-glycosidic bonds builds an ordered crystalline structure by Vander Waals forces and inter & intra molecular hydrogen bonding.(40) In these regions, the cellulose chains are strongly arranged into crystallites. The hydrogen bond existing between cellulose chains make it highly stable but poorly soluble in water and other solvents. These hydrogen bonding network and the molecular arrangement results in polymorphs or allomorphs of cellulose. There are six interconvertible polymorphs of cellulose had been identified id Est cellulose I, II,III_{I},III_{II},IV_{I} and IV $_{\text{II}}$.(41) In 1984 Atalla and Vander Hart proved that the native cellulose I can be subdivided into Iα and Iβ.(42) Cellulose II can be obtained from the chemical regeneration(43) or by mercerization.(44) Cellulose III is formed when cellulose I or II is treated with ammonia or various amines(45) and the polymorphs IV_{I} and IV_{II} are produced by heating cellulose III_{I} or III_{II} respectively at 260ºC in glycerol.(46)

The amorphous region results from the breakage and disordered hydrogen bonds.(47) Figure 2.3 shows the crystalline and amorphous regions of cellulose. The hydrogen bonding and orientation of cellulose differs extensively for the different source.

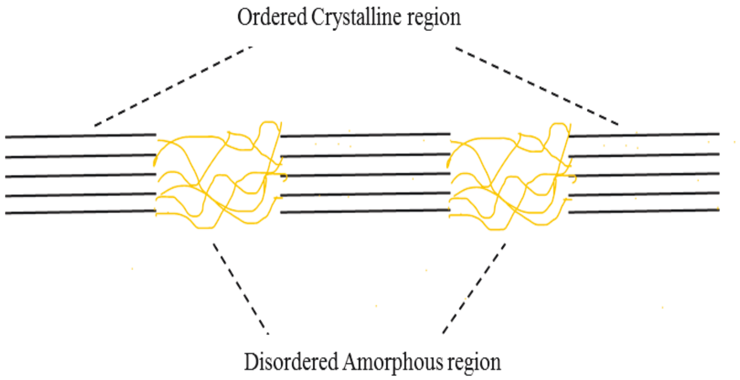

Figure 2. 3 Crystalline and amorphous regions of cellulose.

2.6 HEMICELLULOSE

Plant cell wall is mainly made up of cellulose, hemicellulose and lignin as stated before. Hemicellulose is the second major component accounting 15-30% of the cell wall.(48) They are entrenched around the microfibrils bundles as shown in figure 2.4.

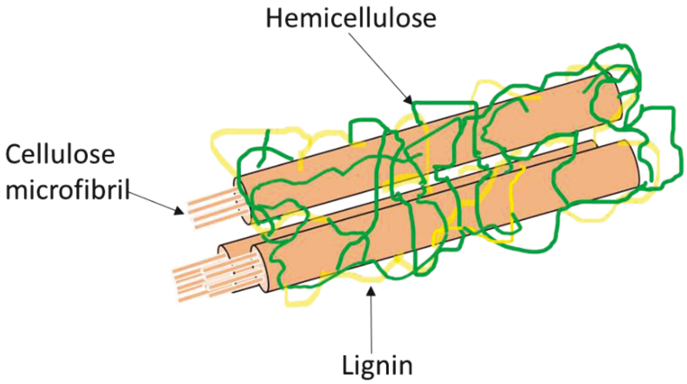

Figure 2. 4 Cellulose bundles embedded by hemicelluloses and lignin.

Hemicellulose can be divided into four different classes based on their structure as 1) Xylans, 2) Mannans, 3) β-glucans and 4) Xyloglucans. Hemicelluloses are branched polysaccharides containing β-1→4-linked backbones of glucose, mannose or xylose in equatorial configuration at C1 and C4 and the structure varies with the side chain type and the distribution of these backbones.(49) The figure 2.5 shows the structure of some backbones of hemicellulose.(50)

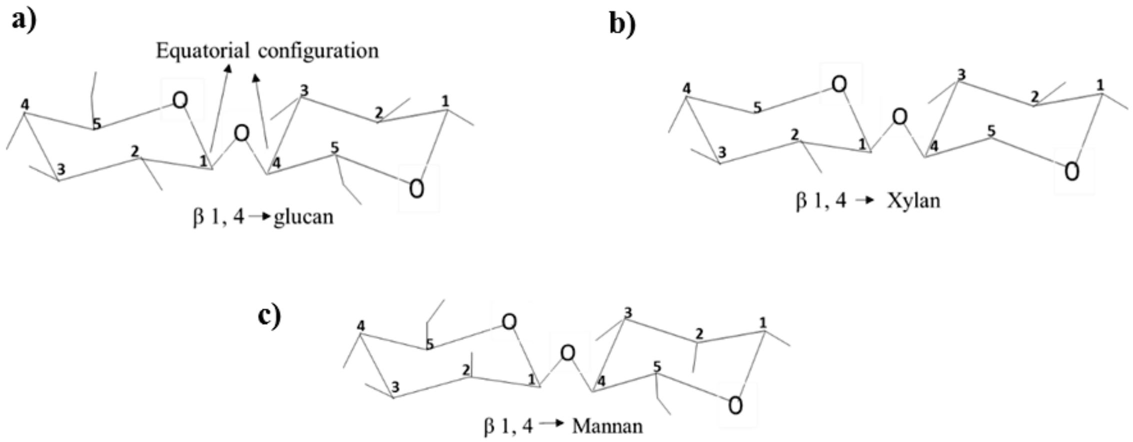

Figure 2. 5 Structural backbone of hemicellulose a) β 1,4-glucan b) β 1,4-glucan c) β 1,4-Mannan. Adopted from (50)

Few examples of xylans are glucoronoxylans and arabinoxylans and they can be found in straw, stalks, husk etc. Mannans can be classified as gluco and galactomannans which can be extracted form gaur, locust bean etc. Xyloglucans are used as thickening and gelling agent in foods and can be isolated from tamarind seeds.(51) As reported in the literature, it is known that hemicelluloses play a key role in facilitating the fibrillation process.(52,53) The reason is most likely because of the hydrogen bonding and negative charges on hemicelluloses. As realised from figure 2.4, hemicellulose surrounds cellulose microfibrils through numerous hydrogen bonding which in turn seals the gap between the microfibrils and hinders the fibrils from aggregation. Also, hemicelluloses contain glucuronic acid with carboxyl groups which enables the delamination of fibers by means of electrostatic repulsion forces. (53)

2.7 LIGNIN

Lignin is a heterogeneous and irregular cross-linked polymer of phenyl propane. It is amorphous and optically inactive material with three different monomers namely Coumaryl alcohol, Coniferyl alcohol and Sinapyl alcohol whose structure is shown in figure 2.6.(54) Lignin is derived by the enzyme mediated polymerization. The molecular weight of isolated lignin is typically in the range of 1000-20,000 g/mol, though the degree of polymerisation in nature is difficult to arrive on the account that lignin is highly fragmented during isolation and it also contains many repeating substructures in a seemingly haphazard manner.(55)

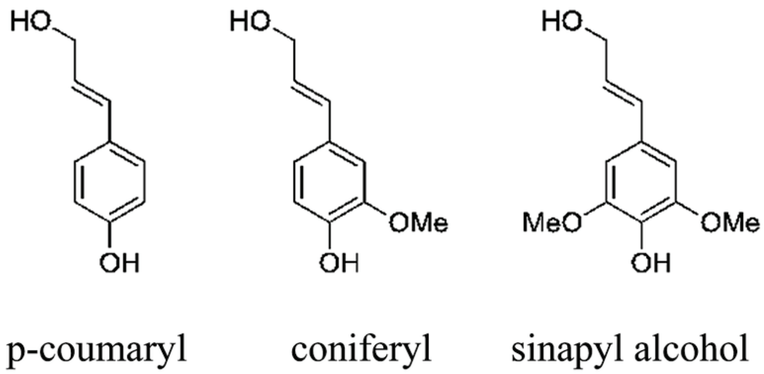

Figure 2. 6 Structural units of lignin. Reprinted with permission.(54) Copyright 2014 American Chemical Society.

Lignin is used in multiple applications as emulsifiers, dyes, synthetic flooring, binding, thermosets, paints etc. The sulfur-free and water soluble lignin is used for automotive brakes, wood panel products, bio dispersants, polyurethane foams, and epoxy resins for printed circuit boards.(56)

2.8 NANOCELLULOSE

The plant cell wall can be classified into two namely primary and secondary. The primary cell wall is the external thin layer (less than 1 µm) and the secondary cell wall chiefly contains cellulose microfibrils.(57) The Hierarchical configuration of wood to cellulose nanocrystals are shown in figure 2.7. Generally, either length or diameter of the cellulose particles are in the nano size (1-100nm) are called as NC. The plant cell wall consisting bundles of the cellulose fibrils and their diameter is in few microns. Each cellulose bundle is consisting millions of micro fibrils, these micro fibrils are composed with elementary fibrils or nano fibrils. The diameter of the nanofibrils is about 5nm, whereas in the case of the micro fibrils the diameter will vary from 10-50nm. Every nano fibers are composed of flexible amorphous and strong crystalline parts.

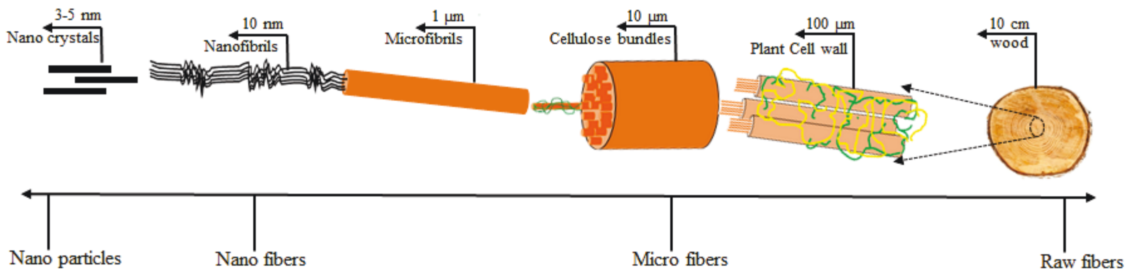

Figure 2. 7 Hierarchical structure of cellulose and its derivatives in nanoscale.

Several cellulosic derivatives are isolated from these microfibrils and depending on their isolation methods, source, dimensions they are called crystallites, NC, whiskers, nanofibrils.(11) Depending on their method of preparation, NC is classified into 1) cellulose nanocrystals (CNC) and 2) nano fibrillated cellulose (NFC). The other type of NC called bacterial cellulose (BC) and electro spun cellulose nanofibers (ECNF) can also be isolated. Nevertheless, CNC and NFC are considered as the more common and they are produced by top-down process i.e. by disintegration of cellulose fibers to nanoscale particles whereas BC and ECNF are produced by bottom-up process in which nanofibers are formed from low molecular weight sugars by bacteria or from dissolved cellulose by electrospinning respectively.(20) The morphological images of four different NC is shown in figure 2.8. (58–61)

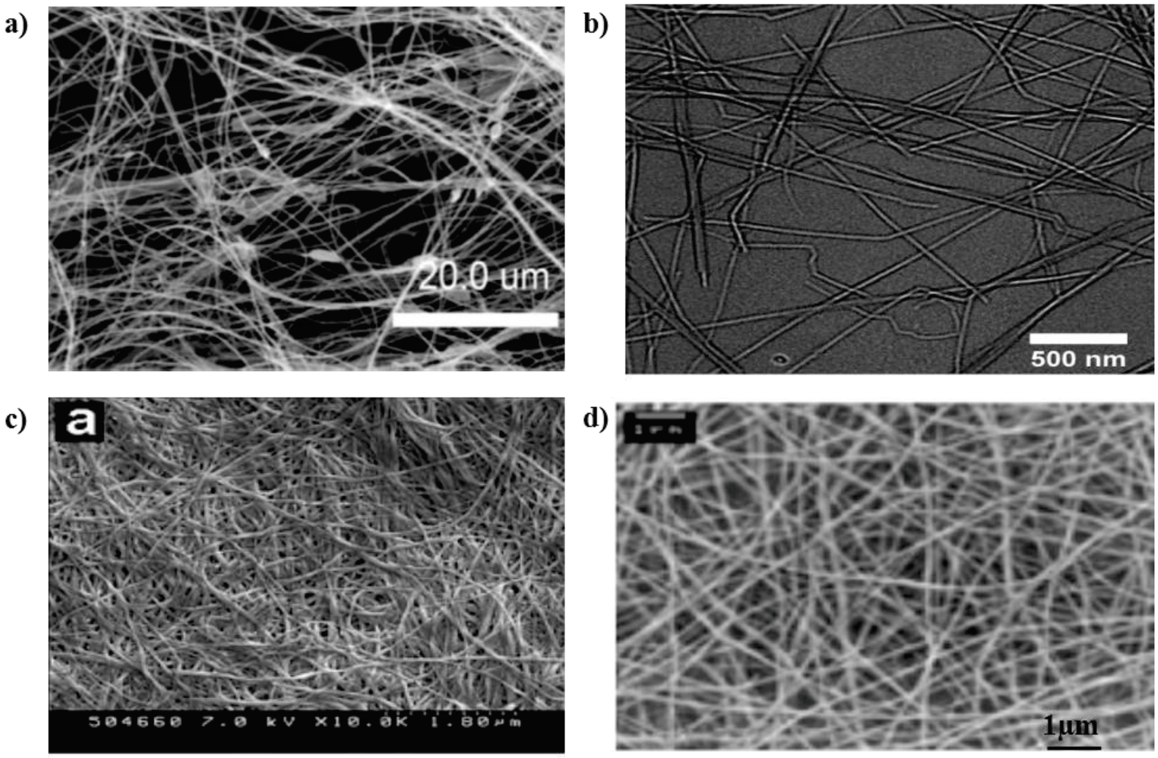

Figure 2. 8 Micrographs of NC a) NFC from corn husk. Reprinted with permission.(58) Copyright 2015 Elsevier. b) CNC from tunicate. Reprinted with permission.(59) Copyright 2014 American Chemical Society c) Bacterial cellulose. Reprinted with permission.(60) Copyright 2006 American Chemical Society and, d) electro spun cellulose nanofibers. Reprinted with permission.(61) Copyright Intech, DOI: 10.5772/8153.

2.8.1 NANOFIBRILLATED CELLULOSE

The cellulose fibers are fibrillated usually by mechanical breakdown to achieve clusters of cellulose microfibrils due to shear forces called nanofibrillated cellulose. The nomenclature can be different for these nanofibrils as a) nano fibrillated cellulose (NFC) b) micro fibrillated cellulose (MFC) c) cellulose nanofibrils (CNF) d) cellulose filaments (CF). The diameter of NFC is in nanoscale i.e. less than 100 nm and the length can be of few micrometers. The structural morphology of NFC from corn husk is shown in figure 8a. NFCs can be isolated from innumerable sources by different mechanical methods including some chemical/enzymatic pre-treatments and/or posttreatments which will be discussed in extraction methods section.

The NFC was first obtained by Turbak et al., 1983 and Herrick et al., 1983 by means of a Gaulin laboratory homogenizer.(62)' (63)The specific surface area and the number of hydrogen bonds ensuing from the surface hydroxyl groups is increased during fibrillation or delamination. Owing to this, NFCs are inclined to form gels showing increased viscosity. The major impairment of NFCs are they tend to form gels once produced, their hydrophilicity restricts the dispersion with few hydrophobic polymers. Importantly, the extraction process consumes high-energy. All these difficulties can be overcome with some pre-treatments and surface modifications. Besides the drawbacks, NFCs are commercially produced and used in plenitude applications including composites, coatings, personal care, constructions etc.(17)

2.8.2 CELLULOSE NANOCRYSTALS

Cellulose nanocrystals, also termed nano whiskers, are spherical “rod” or “needle” like highly crystalline structures with diameter of 2-25 nm and length from 100-750 nm depending on the source. The morphology of CNC from tunicate is shown in figure 2.8b. CNCs are first obtained by acid hydrolysis by Ranby in 1949.(64) As discussed in the structure of cellulose, it contains both crystalline and amorphous regions. During the acid hydrolysis, the amorphous region is removed leaving behind the crystalline particles as displayed in figure 2.9.

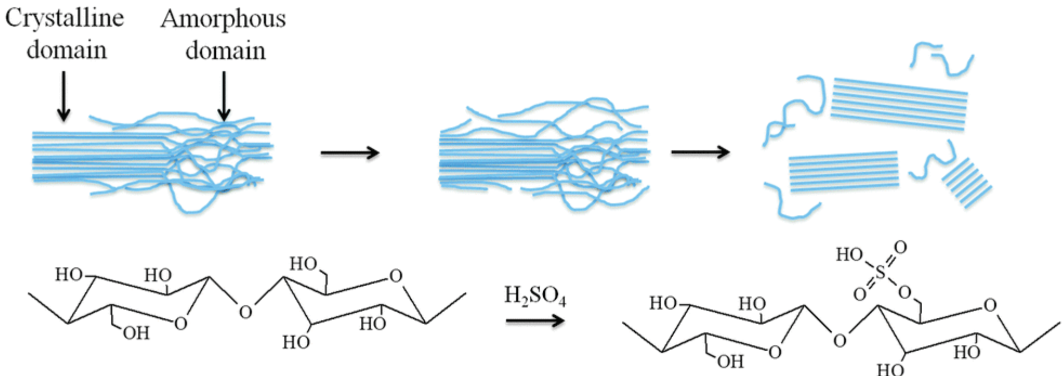

Figure 2. 9 Isolation of CNC from cellulose by sulphuric acid hydrolysis. Reprinted with permission.(65) Copyright 2017 Royal Society of Chemistry.

The amorphous regions present in the cellulose chain is the first and easily accessible to the acid for the hydrolytic action due to kinetic force and steric hindrance however the crystalline regions are more unaffected by the hydrolysis. (23,66) The size, morphology and degree of crystallinity will vary depends on the source. The acid hydrolysis can be achieved using hydrochloric acid (HCL) and sulphuric acid. However, HCL does not result in stable suspensions due to the absence of the surface charge. Whereas in the case of sulphuric acid hydrolysis, the surface of the cellulose attains the half ester sulfate groups resulting in high negative charge. (67) It was reported that the length and surface charge of CNC fibers depends on the hydrolysis period by Dong et al.(68)The length of CNC fibers decreased while increasing the hydrolysis time by increasing the surface charge.

Another interesting aspect was studied by R.H. Marchessault et al. which showed the birefringent liquid crystalline phases. (69) Revol et al. in 1992 proved that CNC formed chiral nematic phases. The authors stated that cellulose, in the form of fibrillar fragments was dispersed in water and above critical concentration, the self-organization of cellulose crystallites into chiral nematic liquid crystalline phase (parallel alignments of the anisotropic crystallites) was observed. (70)Additionally, when the water from the suspension was evaporated to yield a solid film, the chiral nematic order was retained.

2.8.3 BACTERIAL CELLULOSE

Evident from figure 2.1, cellulose is not only found in plant cell walls but also can be obtained from bacteria and are named as bacterial cellulose (BC). The bacterial cellulose is also referred as microbial cellulose, bacterial NC or bio cellulose.(11) BC can be synthesized from Acetobacter, Rhizobium, Agrobacterium, and Sarcina by aqueous culture media cultivation.(71) It is ribbon-like structure with 2-4 nm diameter. BC is having exceptional properties like higher crystallinity, water capacity and distinct degree of polymerization. The morphology of the bacterial cellulose is shown in the figure 2.8c.

2.8.4 ELECTROSPUN CELLULOSE NANOFIBERS

Cellulose in nanoscale dimension can be gained by electrospinning. In this method, cellulose is dissolved in a suitable solvent and a high voltage is applied through the solution so that the particles are charged and repulsive force is created. The network of the ECNF is shown in the figure 2.8d. At a critical voltage, the repulsive forces overcome the surface tension of the solution. When it is passed through air, the solvent evaporates resulting in fiber formation which are then collected on an electrically grounded plate.(72) ECNF is used in biomolecule immobilization, tissue engineering, bio-sensing, nutraceutical delivery, bio separation, crop protection, bioremediation and in the development of anti-counterfeiting and pH sensitive material, photocatalytic self-cleaning textile, temperature-adaptable fabric, and antimicrobial mats.(73)

2.9 IMPORTANCE OF AGRICULTURE BIOMASS

Agriculture sector is producing huge volume of wastes which is menace to the environment as they are either burnt in the fields causing air pollution or accumulated in the soil. The recovery of this waste makes it possible to protect the environment. But at the same time, it will also create new economy. Agriculture waste is the richest form of natural fiber and it is more promising and sustainable material. Towards the advancement of the materials, scientists and researchers need to elaborate new materials and new technology based on intelligent and eco-conscious materials. In other words, materials have greater impact on environment and thus choosing them reflects on the technologies they are used. On that account, materials can be an important part of solution to the problem that created by specific technology. Aforesaid solution could be developing a new material that works better based on eco-designed or bio based products.(74) Hence, interest towards sustainable materials produced using crop waste is increasing among researchers. Compared to wood in which case cellulose is present in secondary cell wall, it is more facile to isolate cellulose from agriculture fibers wherein cellulose is found in primary cell wall and the fibrillation in the latter case is done with low energy consumption.(75)

As per the OECD-FAO (Organisation for Economic Co-operation and Development and 38 the Food and Agriculture Organization) agriculture outlook, every year farmers are harvesting 39.35 million tons of natural fibres from plants.(76) Table 2 summarizes the major crop production (million tonnes) in 2014 across the world.(15)

Table 2. 2 Production of major agricultural crops (in million tons). Source: FAO 2014. Reprinted from open access. (15)

Countries	Banana	Coconut	Pineapple	Sugarcane	Rice	Oil palm fruit	Jute	kenaf	Flax	Sisal	Abaca	Kapok
Brazil	6.90	2.82	2.48	0.739	11.76	1.34	26.71	14.20	0.71	0.25	1.20	-
China	10.55	0.25	1.00	125.54	203.29	0.67	0.17	0.08	0.47	0.15	0.65	0.06
India	24.86	11.93	1.46	341.20	159.20	-	1.98	0.12	0.22	0.21	-	-
Indonesia	6.19	18.30	1.78	33.70	71.28	120.0	0.007	4.35	-	0.03	0.05	0.03
Malaysia	0.335	0.605	0.334	0.830	2.63	100.0	0.002	0.01	-	-	-	0.008
Philippine	9.23	15.35	2.40	31.87	18.44	0.473	0.002	-	0.002	-	0.08	-
Thailand	1.65	1.01	2.65	100.10	38.79	12.81	0.06	1.30	0.01	0.03	-	0.07
USA	0.008	-	0.18	27.91	8.63	-	-	-	0.004	-	-	-
Vietnam	1.56	1.31	0.54	20.08	44.04	-	0.02	8.20	-	0.01	0.01	0.003

Considering the amount of production, the waste outcome is also a lot out of which fibers can be obtained. Correspondingly, few millions of metric tons of fibers are available every year and the sum increase annually. Converting these waste materials into wealth is ongoing interest of the researchers. NC from plant origin alone or with mixture of another materials can be used in quite a lot of applications. Natural fibers serving as agri based raw material for the extraction of NC can be obtained from all parts of the plant like stem, leaves, bark, seeds. Fibers gained from the stem are called 'bast fibers' and few examples of bast fibers are flax, hemp, kenaf etc. Pineapple, banana, date palm, Sisal are examples of leaf fiber and cotton, kapok & coir falls under the seed fibers.

The quality of the fibers depends on different factors like production location, climatic conditions, plant species as presented in figure 2.10.(77) Consequently, it is a requisite to have better understanding of the properties of vegetal waste fiber.

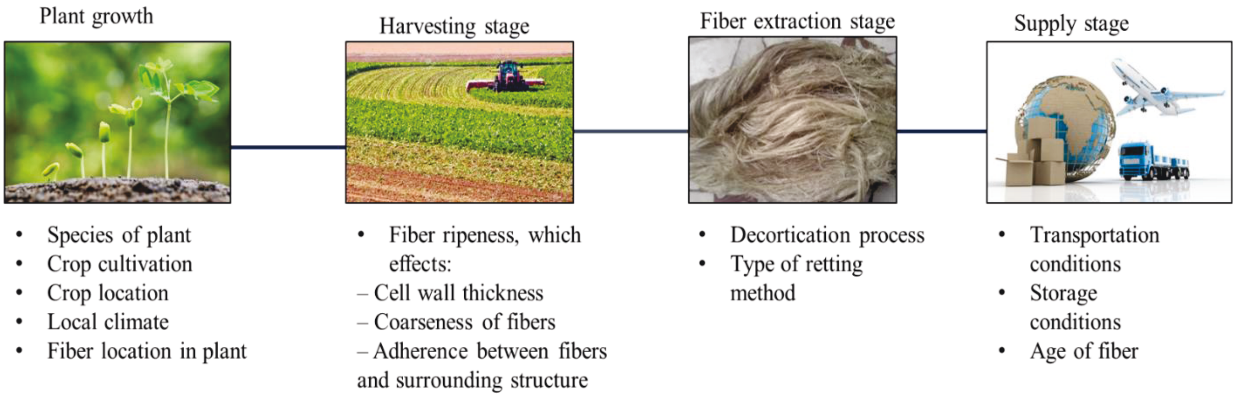

Figure 2. 10 Factors that affect the quality of the fiber at various stages of production. Adopted with permission.(77) Copyrights 2011 Elsevier.

2.10 ISOLATION OF NANOCELLULOSE FROM AGRICULTURE BIOMASS

The chemical composition of NC consists of cellulose, lignin, hemicellulose, pectins and others as discussed earlier. It is indispensable to remove lignin and other components to get pure cellulose. Figure 2.11 shows the exact picture of diverse techniques involved in the production of NC. Alkali treatment followed by delignification (bleaching) is the first process in the extraction of NC from any fiber. NC can be extracted from countless agriculture biomass by means of chemical, mechanical or enzymatic treatment. The isolation of cellulose nanocrystals can be attained by acid hydrolysis directly after the purification of biomass. Whereas nanofibrillated cellulose is produced typically by mechanical treatments like homogenization, grinding, steam explosion, Cryocrushing etc. The detailed procedures of these methods are discussed in the following sections.

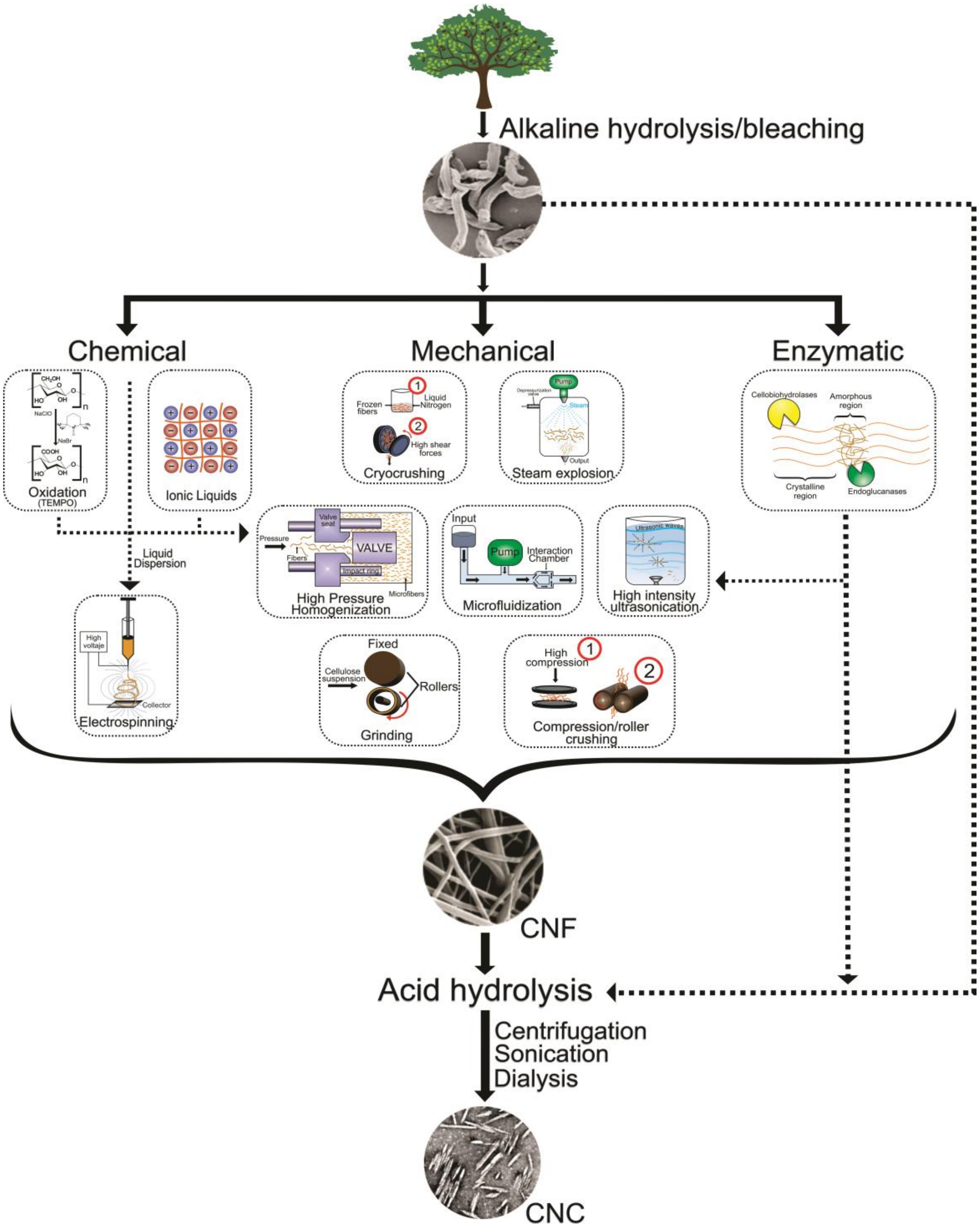

Figure 2. 11 Different methods of nanocellulose production. Reprinted with permission. © 2015 Rojas J, Bedoya M, Cito Y. Published in Intech under CC BY 3.0 license. Available from: http://dx.doi.org/10.5772/61334

Since the mechanical treatment involves high energy consumption pre-treatments like chemical/ enzymatic are carried prior mechanical treatments. Table 3 presents the extraction of NC from different crop biomass, method of purification, pre-treatments, their production methods, type of NC obtained is reported.

Table 2. 3 Agriculture biomass source, purification method, Pre-treatments, mechanical treatments, type of nanocellulose and references.

Biomass	Purification technique	Pre-treatment	Extraction method	Type of nanocellulose	References
Sugar beet pulp	Sodium hydroxide, sodium chlorite treatments	homogenization	Blending Cryocrushing,	Cellulose microfibrils	(75)
Hemp/spring flax, /rutabaga	Sodium hydroxide, hydrochloric acid treatments/kraft process	-	Cryocrushing	Cellulose nanofibers	(78)
Soybean pods	Sodium hydroxide, hydrochloric acid, chlorine dioxide treatments	Refining (PFI mill)	Homogenization	Nanofibers	(79)
Banana rachis	Sodium hydroxide, Hydrogen peroxide, Potassium hydroxide Sodium chlorite treatments	Biological retting / mechanical processing	Chemical and mechanical treatments	Cellulose microfibrils	(80)
Peel of prickly pear fruits	Bleaching Toluene, ethanol	-	Homogenization	Cellulose microfibrils	(81)
Mulberry barks	Sodium hydroxide treatment	-	Acid hydrolysis	Cellulose whiskers	(32)
Pineapple leaf	Sodium hydroxideAcetic acid, Sodium	-	Steam explosion Blending	Nanocellulose	(82)

	hypochlorite, Oxalic acid treatments				
Coconut husk fiber	Sodium hydroxide Acid hydrolysis Bleaching with Sodium chlorite and glacial acetic acid	-	Acid hydrolysis	Cellulose Nano whiskers	(83)
Cassava bagasse	-	-	Acid hydrolysis	Cellulose whiskers	(84)
Banana	Sodium hydroxide Acetic acid	-	Steam explosion, Sodium hypochlorite and oxalic acid treatments	Cellulose nanofibers	(85)
Oat straw	-	Quarterisation	Homogenisation	Nanofibrillated cellulose	(86)
Jute fibers	-	Mercerisation	Ball milling	Nanocellulose	(87)
Rice husk	Sodium hydroxide treatment, Bleaching	-	Acid hydrolysis	Cellulose nanocrystals	(88)
chardonnay grape skins	Toluene, ethanol	-	Acid hydrolysis	Cellulose nanocrystals	(89)
Sugar cane bagasse	Sodium hydroxide treatment	Ionic liquid	Homogenization	Nanocellulose	(90)
Sesame husk	Sodium hydroxide, Bleaching sodium chlorite treatments	-	Acid hydrolysis	Cellulose nanocrystals	(91)
Sugar cane bagasse	Sodium hydroxide treatment	Ionic liquid	Homogenization	Nanocellulose	(90)
Potato peel waste	Sodium hydroxide treatment, Bleaching	-	Acid hydrolysis	Cellulose nanocrystals	(92)

Raw cotton linter	-	-	Acid hydrolysis	Cellulose nanowhiskers	(93)
Bleached Eucalyptus Pulp	Bleaching	-	Grinding	Nanofibrillated cellulose	(94)
Rice straw	Toluene, ethanol, sodium chlorite, potassium hydroxide treatments	Carboxylation (TEMPO)	Blending	Cellulose nanocrystals and cellulose nanofibers	(95)
Maize straw	Soxhlet extraction using hexane, ethyl alcohol and DI water	Bleaching with H_2O_2 and TAED solution. Acetic acid and nitric acid treatment	Acid hydrolysis	Cellulose whiskers	(96)
Oil palm biomass residue	-	-	Acid hydrolysis followed by NH_4OH treatment	Microcrystalline cellulose	(97)
Pomelo (Citrus grandis) Albedo	Sodium hydroxide treatment, Bleaching	-	Acid hydrolysis	Cellulose nanocrystals	(98)
Kenaf bast fibers	Sodium hydroxide, Bleaching and anthraquinone treatment	-	Grinding	Cellulose nanofiber	(99)
Mango seed	Sodium hydroxide treatment, Bleaching	-	Acid hydrolysis	Cellulose nanocrystals	(100)
Orange waste	Sodium hydroxide, sodium chlorite treatments	-	Sonification	Nanocellulose	(101)
Alfa and sunflower	Sodium chlorite, Acetic acid Sodium hydroxide treatments	Carboxylation (TEMPO)	Blending Homogenization	Nanofibrillated cellulose	(53)

Corn cob	Sodium hydroxide Treatment, Bleaching	-	Acid hydrolysis	Cellulose nanocrystals	(102)
Wheat Straw	Hydrogen peroxide treatment	Acetic acid/formic acid, water	Grinding	Cellulose nanofibrils	(103)
Agave tequilana and barley	Sodium hydroxide, Bleaching sodium chlorite and acetic acid treatments	-	Acid hydrolysis	Cellulose nanocrystals	(104)
Garlic skin	Alkali treatment	-	Acid hydrolysis	Cellulose nanocrystals	(36)
Corn husk	Benzene, ethanol Bleaching	-	Ultra-sonication	Nanofibrillated cellulose	(58)
Chilli leftover	Sodium hydroxide, acetic acid, Bleaching	-	Acid hydrolysis	Cellulose nanocrystals	(76)
Citrus waste	Sodium hydroxide and Sodium chlorite	-	Enzymatic hydrolysis	Cellulose nanofibers	(105)
Lotus leaf stalk	Toluene, ethanol, Bleaching sodium chlorite, potassium hydroxide treatments	-	High intensity ultra-sonication	Nanocellulose	(106)
Tomato peel	Sodium hydroxide, Bleaching and Sodium chlorite	-	Acid hydrolysis	Cellulose nanocrystals	(107)
Flax fibers	Sodium hydroxide, Bleaching,sodium chlorite, potassiumhydroxide treatments	-	Ultrasonication and acid hydrolysis	Cellulose nanowhiskers	(108)
Carrot residue	Sodium hydroxide Treatment, Bleaching	-	Grinding	nanofibers	(109)

Onion skin waste	Sodium hydroxide Treatment, Bleaching	-	Acid hydrolysis	Cellulose nanocrystals	(36)
Groundnut shells	Benzene, ethanol Bleaching	-	Acid hydrolysis	Cellulose nanocrystals	(35)
Flax fibers	Sodium hydroxide Treatment, Bleaching	-	Acid hydrolysis	Cellulose nanocrystals	(110)
Miscanthus x. Giganteus	Sodium chlorite, Bleaching, Acetic acid Sodium hydroxide treatments	-	Acid hydrolysis	Cellulose nanocrystals	(111)
Citrus waste	Toluene, ethanol, Bleaching, sodium chlorite, potassium hydroxide treatments	-	Acid hydrolysis	Nanocellulose	(112)
Garlic straw	Sodium hydroxide Treatment, Bleaching	-	Acid hydrolysis	Cellulose nanocrystals	(33)

2.11 PURIFICATION OF BIOMASS

The first interest involved in the extraction of NC is purification of biomass to remove non-cellulosic (hemicellulose, lignin) to get the pure cellulose fibers. Firstly, raw materials treated with alkali(75),(113) (NaOH or KOH), organic solvents(114), Soxhlet(96) or mineral acids in order to remove the hemicellulose, lignin, pectin’s and waxes (This step also called as pulping). Secondly, delignification often called as bleaching is usually done by chemical process. The bleaching step involves single or multiple stages depending the end use applications. The most frequent bleaching agents used are sodium chlorite,(83) hydrogen peroxide, (80) oxygen or ozone. Additional process like Kraft process also called as sulfite process is also carried in the purification process.(78)

2.12 EXTRACTION OF CNC

Classical extraction of cellulose nanocrystals includes 60-65 wt.% of sulfuric acid hydrolysis (H_2SO_4) at temperature less than 50 °C followed by purification of biomass as shown in figure

2.11. Acid hydrolysis benefits to disintegrate the fibers into nanoscale and helps in preferential acid hydrolysis of the amorphous parts of cellulose leaving behind the crystalline parts of cellulose.(41) The hydrolysis is followed by repeated cycles of sonication and dialysis against ionized water yielding the pure CNC. CNC can also be produced by the acid hydrolysis using hydrochloric acid (HCL), phosphoric acid and hydrobromic acid.(115–117)Apart these, CNC was also isolated by microbial hydrolysis.(118)One of the recent study showed the isolation of CNC using catalytic ionic liquid hydrolysis.(119)The downside of producing CNC using HCL is that the suspension is unstable leading to the flocculation(120) wherein during sulfuric acid hydrolysis, the sulfate ester **($-OSO_3^-$)** are randomly spread on the surface of the nanoparticles resulting in the electrostatic layer which promotes the dispersion of CNCs in water.

Importantly, the acid hydrolysis conditions like hydrolysis time, concentration of the acid, temperature affect the properties of CNC. The influence of temperature ranging from 45 to 72 ° C on the sulfuric acid hydrolysis of cotton was studied by Elazzouzi-Hafraoui et al. The authors reported that increase in temperature resulted in shorter crystals. Though there was no clear effect on width was reported.(121)

In literature, CNCs were obtained from agriculture waste like mulberry barks, coconut husk, cassava bagasse, rice husk, onion skin waste, citrus waste etc. The dimensions and structural morphology of these CNCs are tabulated in table-4 and figure 2.13 respectively. Of vital importance in the production of CNC, the industries are trying to reuse the sulfuric acid. The cost of sulfuric acid is 4-6 times more than that of the market pulp. Hence recovering the acid by centrifugation and reusing the sulfuric acid can provide an extensive cost advantage.(122)

2.13 EXTRACTION OF NFC

Unlike the extraction of cellulose nanocrystals which could be extracted in single step after purification of the cellulose fibers. NFC is extracted in different steps like homogenization,(62) cryocrushing,(123) grinding(124) , micro fluidization (125) , and ultra-sonication.(106)Since the mechanical treatment consumes high energy, chemical and enzymatic pre-treatments have been followed prior. Chemical pre-treatment includes tempo-oxidation,(126) quarterisation, refining etc. and in the enzymatic pre-treatment, enzymes like endo and/or exoglucanase were used previously.(127) In this section, initially the pre-treatments are discussed in detail followed by the mechanical process involved in the production of NFC.

2.13.1 PRETREATMENTS

Pre-treatment is the very important step for the extraction of the NFC. Chemical or enzymatic pretreatment helps to overcome the recalcitrance of plant cell wall. Recalcitrance in other words is the resistance of the cell wall breakdown. The deconstruction of cellulose and non-cellulosic materials like lignin and hemicellulose from the cell wall is not a very simple process because the recalcitrance results from the extreme crystalline structure of cellulose surrounded with lignin and hemicellulose. An ideal cleavage of biomass to extract pure cellulose must prevent the loss of cellulose, be cost effective and consume less energy and produce less toxic wastes and hence pre-treatments should comply all these criteria.(128) Mechanical extraction of NFC consumes high energy from 20,000–30,000 kWh/ton. That being said, chemical or enzyme pre-treatments bring down the energy consumption 20times less, i.e. 1000 kWh/ton.(129)

2.13.1.1 CHEMICAL PRE-TREATMENT

The chemical pre-treatment comprises 1. Acid hydrolysis 2. Alkaline hydrolysis 3. Oxidation and 4. Organic solvents/ionic liquids. Acid hydrolysis breaks the hydronium ions in the biomass and inter and intra molecular bonding between hemicelluloses and lignin leaving behind the pure cellulose. Acids like sulfuric acid (H_2SO_4), hydrochloric acid (HCL), nitric acid (HNO_3) and phosphoric acid (H_3PO_4) are often used for the pre-treatments. Rosa et al. used H_2SO_4 acid hydrolysis to treat coconut husk fibers, Wang et al. used HCL to treat soy pods.(83,94) Strong acid hydrolysis is not eco-friendly. Moreover, it is difficult to recover the acid after the hydrolysis. On the other hand, the dilute acids at moderate temperature achieve better hydrolysis.(130)

The alkali treatment is mainly to remove the hemicellulose and it also helps in breaking the bonds between cellulose, hemicellulose and lignin. The alkali treatment involves the saponification of intermolecular ester bond between lignin and hemicelluloses. Normally, alkalis like NaOH, KOH, $Ca(OH)_2$, hydrazine and ammonium hydroxide are used. Most of the crop waste biomass like rice husk, mulberry barks, onion skin waste, and mango seed were treated with sodium hydroxide to remove lignin. The alkali treatment also causes swelling of the cellulose which leads to the increase in the surface area and decrease in the degree of crystallinity. In 2006 Saito et al. used TEMPO (2,2,6,6-tetramethylpiperidine-N-oxyl) to oxidise cellulose while extracting NFC by blending process.(126) Organic solvents like methanol, ethanol, acetone, ethylene glycol are also used in removing lignin and hemicelluloses.

2.13.1.2 ENZYMATIC PRE-TREATMENT

Biological enzymes catalyse the hydrolysis of cellulose fibers which makes the fibrillation much easier. Pääkkö et al. used endoglucanase to hydrolyse cellulose fibers and they carried out three following steps before the isolation of NFC using micro fluidizer: 1) Refining the fibers to swell the cellulose making it more available for the enzymes 2) enzymatic hydrolysis for the delamination of fibers and 3) Washing and yet again refining.(127) Mayra Mariño et al. used Xanthomonas axonopodis pv. citri (Xac 306) enzyme for the degradation of citrus waste fibers to yield cellulose nanofibers.(105)

2.13.2 MECHANICAL TREATMENT

It is worth to note that in this section authors covered the mechanical treatments used for the extraction of NFC from agriculture biomass though there are other mechanical treatments. In the literature, we can find that nanofibrillated cellulose has been extracted from number of agri biomass like alfa and sunflower, carrot, kenaf bast fibers, jute fibers, peel of prickly pear fibers, soybean pods, oats straw etc. as shown in table 2.6. Regardless of the source, NFC is produced chiefly using mechanical treatment. The mechanical treatment comprises 1. Homogenization, 2. Micro fluidization, 3. Grinding, 4. Cryocrushing and 5. Ultrasonication. All these treatments work under high shear forces cleaving the cellulose fibers resulting in the fibrillation. Following is the detailed description of these different mechanical treatments.

2.13.2.1 REFINING AND HOMOGENIZATION

Refining in most cases is performed prior homogenization. Different refiners like PFI mills, disk refiners are used to refine the pulp.(79,131) In 2011, Karande et al., extracted NFC from cotton fibers by using only disk refiner.(132) The working principle of homogenizer is shown in figure 2.12 a.

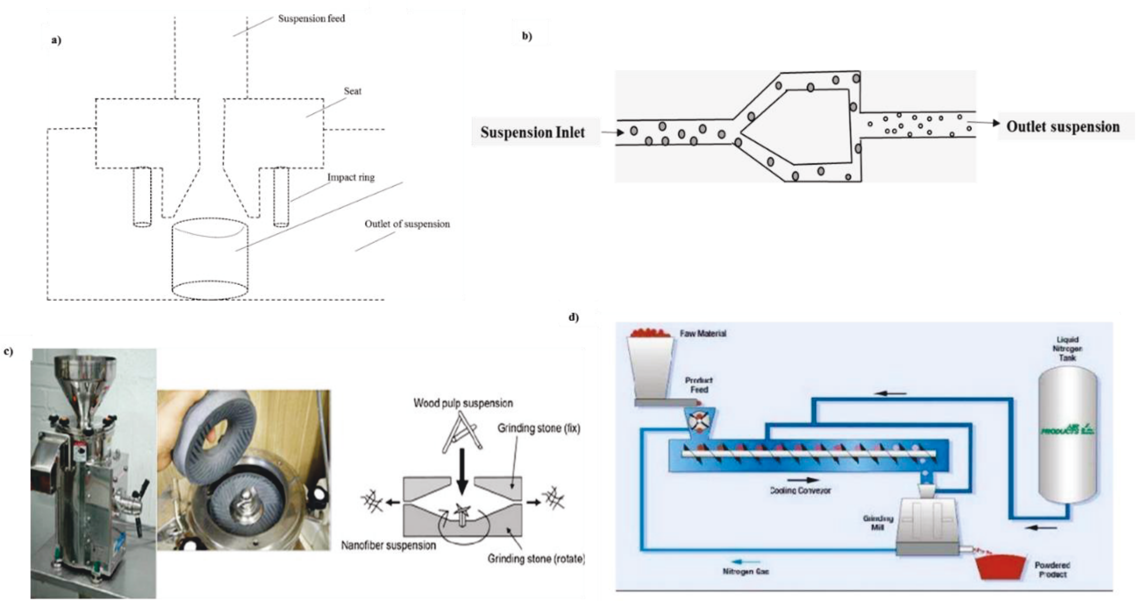

Figure 2. 12 Diagram for working principle of a) homogenizer adopted from (133)b) microfluidizer. Adopted with permission.(134)c) grinding adopted from www.masuko.com and d) Cryocrushing from (135)

In this method, the cellulose suspension is passed through a vessel between two valve seats and high pressure is applied because of which high shear forces are generated causing the fibrillation of cellulose. This procedure is repeated number of times to increase the degree of fibrillation. The isolation of micro fibrillated cellulose using homogenization was first done by Turbak et al. in 1985 using Gaulin homogenizer.(62) Dufresne et al. (1997) produced cellulose micro fibrils from sugar beet pulp using homogenization. The purified sugar beet pulp suspension was poured into the vessel and high pressure (500 bars) was applied for 0.5-3 hours resulting in the invidualization of micro fibrils.(75) In 2007, Wang and Sain used soybean pods as a raw material to produce NFC. The pre-treated soybean fibers were first beaten and refined in PFI mill at 12000 revolution which reduced the fiber length. The sample was then homogenized at high pressure (500-1000 bars) for 20 passes to delaminate the cellulose fibers into nanofibers.(79) NFC from Alfa and sunflower was extracted in 2013 by Chaker et al. using high pressure homogenization. The delignified pulp was pumped into GEA homogenizer processor. In this case, the fibrillation was done in two steps. During the first step, 1.5 wt. % of the fiber suspension was passed through the slits at 300 bars for several times to increase the viscosity of the slurry. Then the pressure was increased to 600 bars for the defibrillation process.(136) The main drawback of this method is clogging of the system and so the fiber size should be reduced before performing high pressure homogenization.(19) The other downside of this treatment is the excessive energy consumption for which few pre-treatments were developed as discussed in the previous section.

2.13.2.2 MICROFLUIDIZATION

Microfluidization is another mechanical treatment to manufacture NFC and this method was first used by Zimmermann et al. (125) In this method, the cellulosic suspension is passed through a Z or Y- shaped chamber as shown in figure 2.12b with channel sizes usually 200-400 µm and by applying high pressure through intensifier pump, the fibers are delaminated by the resulting shear forces against the colliding suspension and the channel walls. Ferrer et al. extracted NFC from empty palm fruit bunch fibers (EPFBF) using microfluidizer.(137)The clogging of fibers in homogenizer can be overcome in micro fluidization process because it has no in-line moving parts, and it can easily be resolved by reverse flow through the chamber.(138)

2.13.2.3 GRINDING

Another method to produce NFC is grinding process in which the sample slurry is passed through an ultrafine grinder as in figure 2.12c. The principle is that the fibers are ground between a static and a rotating stone (disc) rotor. The distance of the discs can be adjusted based on the type of the raw material. The cell wall structure, bonds are cleaved down by the shear forces produced during grinding causing the NFC production. In 2012, Wang et al. produced NFC for first time from bleached eucalyptus pulp using Super Mass-Colloider (Model: MKZA6-2, Disk Model: MKGA6-80#, Masuko Sangyo Co., Ltd, Japan) grinder at 1500 rpm. They used the energy input from 5 and 30 kWh/kg to study the relation between consumed energy and the fibrillation by means of crystallinity and degree of polymerisation.(94) Karimi et al., Jossel et al., Siquiera et al. extracted cellulose nanofibers from kenaf bast fibers, wheat straw and carrot residue respectively using grinding process.(34,99,103)

2.13.2.4 CRYO CRUSHING

In 1997, Dufresne et al. isolated NFC from sugar beet pulp using cryocrushing.(75) In this treatment, the cellulosic fibers are frozen in liquid nitrogen and then crushed by high shearing forces which causes the release of exert pressure of ice crystals on the cell wall breakdown leading to the nanofiber formation. Figure 2.12d shows the working principle of Cryocrushing. Bhatnagar and Sain extracted NFC from hemp, flax and rutabaga in 2005 using cryocrushing.(78)

2.13.2.5 ULTRASONICATION

Ultra-sonication is another strategy of producing NFC in which the suspension is exposed to the ultra-sonic waves. During this process, alternating low and high pressure waves are produced creating, expanding and colliding the gas bubbles. These hydrodynamic forces are used to liberate cellulose nanofibers. Junko Tsukamoto et al. isolated NFC from citrus processing waste from oranges (CPWO) using ultrasonic processor, Sonics at 750 Watt, 20 kHz and 4J. The residue from enzymatic hydrolysis of CPWO was used as a raw material here.(101)

2.13.2.6 STEAM EXPLOSION

Steam explosion is a thermomechanical process in which the heat carried by the steam penetrates sample by diffusion and the sudden release of pressure generates shear forces cleaving the glyosidic and hydrogen bonds leading to the isolation of nanofibers. This method was used by Cherian et al. to isolate NFC from pineapple leaf and by Deepa et al. in the production of NFC from banana fibers.(82,85)

2.13.2.7 BALL MILLING

In this technique, the sample is placed in a cylindrical, hollow jar partly filled with metal, ceramic or zirconia ball and when the jar rotates, the collision between fibers, ball and the walls of the container causes the fibrillation. Using ball milling Baheti et al. prepared NFC from jute fibers.(87)

2.14 CHARACTERISATION OF NANOCELLULOSE

In this section, the important characterizations of NC produced from agriculture biomass are discussed. The quality assessment of produced NC is done by studying morphology, chemical composition, crystallinity and thermal properties few of them are discussed in the following section.

2.14.1 MORPHOLOGY

Morphology is the key parameter to check the fibrillation of the NFC. It is imperative to study the morphology of the obtained NC to understand the sizes, smoothness and fibrillation. The morphology usually depends on the source and extraction methods. The size and roughness of the fibers is reduced during the production process possibly because of the removal of lignin, hemicellulose, lignin and other non-cellulosic materials during the alkali and bleaching stages.

Morphology is studied using many microscopic techniques like scanning electronic microscopy (SEM), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and Atomic force microscopy (AFM). Few of the micrographs of nano fibrillated cellulose and cellulose nanocrystals produced from different agriculture biomass sources are shown in figure 2.13.

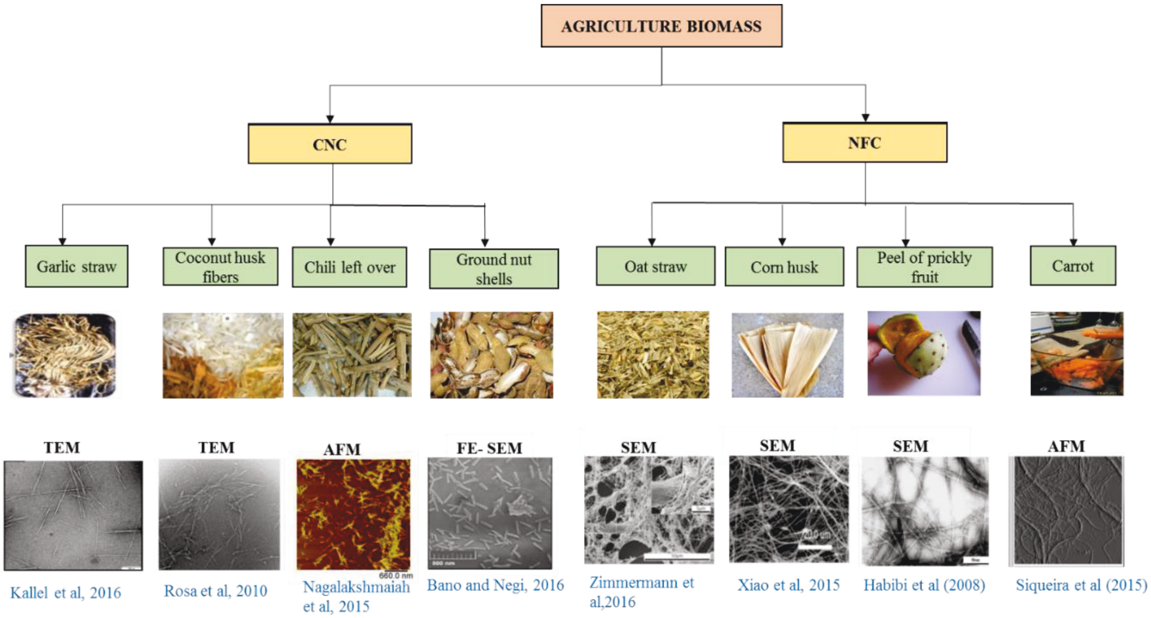

Figure 2. 13 Micrographs of nanocellulose produced from different agriculture biomass

Table 2. 4 Source, diameter and reference of NC obtained from different crop waste.

NFC		
Source	**Diameter (nm)**	**References**
Banana rachis	3–5	(80)
Prickly pear fruits	2–5	(81)
Wheat straw	10–80	(123)
Oil palm	5–40	(97)
Soy hull	20–120	(139)

CNC			
Source	**Diameter (nm)**	**length (nm)**	**References**
Coconut husk	5.5 ± 1.4	58	(83)
Chilli leftover	4-6	90-180	(140)
Garlic straw	6	480	(33)
Groundnut shells	5-18	111	(35)
Mulberry bark	25-30	400-500	(32)

It is worth noting that size and morphology of NC varies much depending on the source from which they are extracted. The sizes of NFC and CNC produced from various agri-biomass sources are listed in the table 4.

Beside source, the morphology of NFC depends on the number of passes (cycle time) and pre-treatments involved in the isolation. As stated earlier, the homogenization is repeated for different passes to get maximum fibrillation. On that note, Lee et al. in 2009 studied the effect of cycle time (1-20 passes) of homogenization on the size of NFC obtained from commercial microcrystalline cellulose. With the 1-5 passes they reported that the fibrillation was limited only to the surface as shown in figure below. However, with mechanical treatment of 10-15 passes the fibrils were split into smaller fibrils with increased aspect ratio. When passed the suspension further for 20 passes, the fibrils were more chopped into thinner fibers. Having said that, the fibers tend to aggregate due to the higher surface area and high density of hydroxyl groups. Hence the authors concluded that increasing the cycle time may result in the decreased mechanical strength.(141)

Zuluaga et al. (2009) investigated the effect of pre-treatments of banana rachis on the morphology of NFC obtained using TEM. They pre-treated the banana rachis using peroxide alkaline (PA), peroxide alkaline-HCL (PA-HCL), 5 and 18 wt.% potassium hydroxide (KOH). The PA and 5 wt.% KOH treated sample showed loose networks whereas PA-HCL treatment resulted in shorter fibrils and finally with 18 wt.% KOH the microfibrils were even shorter and interestingly part of cellulose I was changed into cellulose II.(80)

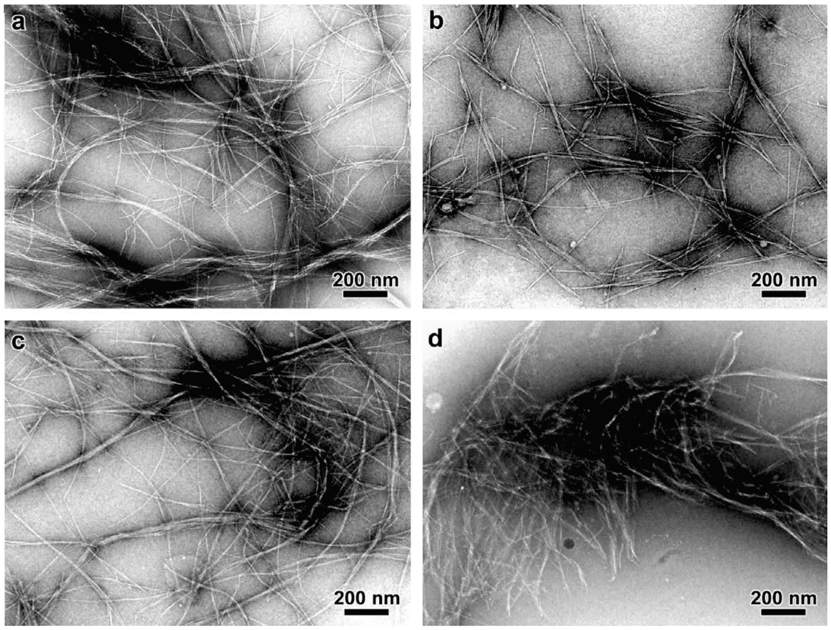

Figure 2. 14 TEM images of cellulose microfibrils after a) PA b) PA–HCl c) 5 wt.% KOH and d) 18 wt.% (KOH-18) treatments. Reprinted with permission. (80) Copyright 2017 Elsevier.

The morphology of CNC depends on source, hydrolysis time, temperature, acid concentration and different acids like hydrochloric acid, phosphoric acid or acetic acid. The effect of pre-treatments and the hydrolysis time on the morphology of CNC obtained from coconut husk fibers were inspected by Rosa et al., 2010.(83)

2.14.2 CRYSTALLINITY

The crystallinity study of produced NC is necessary to understand the effect of production methods on the crystal structure of the cellulose. The crystallinity is usually studied by X-ray diffraction (XRD) technique. It is explained elsewhere that cellulose is made of highly crystalline and disordered amorphous regions. It is believed that during extraction the disordered amorphous regions are removed resulting in the increased crystallinity. The degree of crystallinity of NFC and CNC gained from different crop waste sources is shown in the table below.

Table 2. 5 Crystallinity of raw, NFC and CNC obtained from various biomass.

NFC		
Source	**Crystallinity (%)**	**References**
Rice straw (Stem)		
Original fibres	50.9	
Purified cellulose fibers	63.8	(114)
Cellulose nanofibers	63.4	
Corn husk		
Original corn husk	35.9	(58)
Corn husk NFC	64.8	
Oil palm residue		
OPEFB-pulp	80	(97)
OPEFB-MCC	87	
Pineapple leaf		
Raw	–	(82)
Steam exploded	35.97	
Bleached	54.18	
Acid treated	73.62	
Oat straw		
Starting cellulose material	70	(142)
Non-modified CNC	64	

CNC		
Coconut husk fibers		
Untreated	38.9 ± 0.3	(83)
CNC (1B at 150 min)	62.2 ± 0.5	
Garlic straw		
Raw	37.4	(33)
Bleached	47.1	
CNC	68.8	
Chilli leftover		(140)
Alkali treated	52	
Bleached fibers	68	
CNC	78.5	
Groundnut shell		
Raw	56	(35)
Purified	68	
CNC	74	
Mulberry bark		
Original mulberry barks	46.9	(32)
Pre-treated mulberry barks	58.8	
Cellulose whiskers	73.4	

The crystallinity of NC is higher compared to that of starting material and this is due to the removal of lignin, hemicellulose, pectin or any non-cellulosic materials. In some cases, the fibers can partially contain both cellulose I and II. Normally, cellulose I can be identified at $2\theta=14.9^{\circ}$ (110), $2\theta=16.6^{\circ}$ (110), $2\theta=22.7^{\circ}$ (200) and $2\theta=34.4^{\circ}$ (004).

2.14.3 THERMAL PROPERTIES

The thermal property of NC is indispensable to use them in the composites. Cellulosic materials degrade below 400ºC (143)and the degradation temperature depends on the structure and chemical composition. The degradation starts at lower temperature owing to the decomposition of hemicellulose, lignin and then pyrolysis of cellulose occurs after which charring happens. The thermal stability of NFC in most of the cases increases due to the removal of hemicelluloses and lignin.(144) In contrast, the thermal stability of CNC decreases when compared to that of raw material because of the introduction of sulfate groups. The sulfate groups degrade at around 120ºC and they decrease the defense of cellulose pyrolysis thereby decreasing the thermal stability.

2.15 APPLICATIONS

NC is of growing interest on the grounds of innumerous applications, for example in various realm from paper industry, composites, biomedicine, textile, construction to aerospace, automotive, and sensors etc.as shown in figure 2.15.

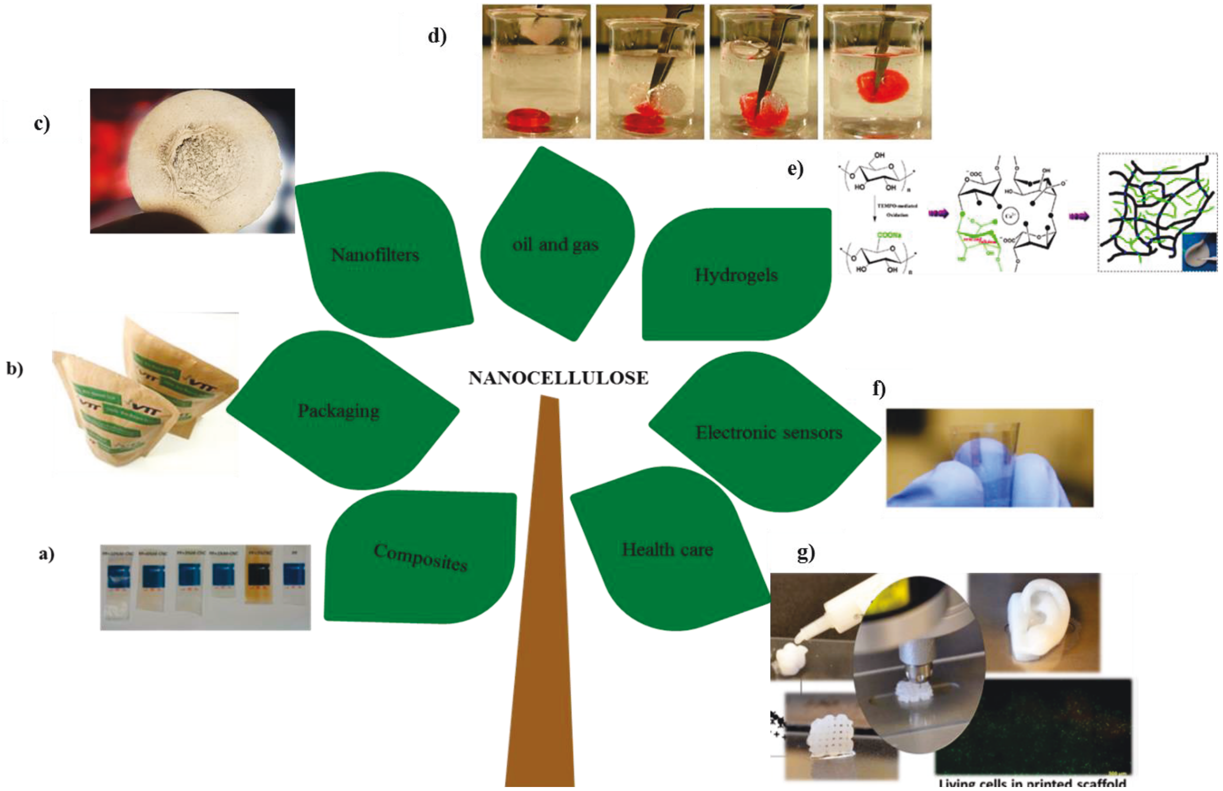

Figure 2. 15 Multitude applications of nanocellulose a) Extruded PP/CNC and M-CNC nanocomposite film. Reprinted with permission.(145) Copyright 2016 American Chemical Society b) Bio based pouches from VTT technical research.(146) c) Nanocellulose filter. Image obtained from (147). d) Cellulose nanofibril aerogels from rice straw absorbing dyed chloroform from water. Reprinted with permission.(148) Copyright 2014 Royal Chemical Society. e) Alginate-oxidized nanocellulose sponge. Reprinted with permission.(149) Copyright 2012 American chemical Society. f) Fabricated transparent and flexible Nano paper transistor. Reprinted with permission.(150) Copyright 2013 American Chemical Society. g) 3D printed small grids and human ear from NFC and alginate. Reprinted with permission.(151) Copyright 2015 American Chemical Society.

Importantly, the properties like high mechanical properties and low density with high aspect ratio facilitate to use NC in composite field for the fabrication of lightweight and high performance materials. The high water holding capacity due to the enlarged surface area enables their use as a rheology modifier mainly in paints and personal care products and this field need to be explored further for better understanding. NC has attractive optical properties this could be an added benefit in the fields of electronics, ultra-filter papers, sensors and transparent solar cells. Due to their biodegradability, compatibility NC can play vital role in biomedical field for the progress of drug delivery, artificial body parts and tissue engineering.

2.15.1 COMPOSITES

Production of high mechanical performance composites can be achieved by the reinforcement of nano fillers into polymers. In this case, NC is an appropriate candidate for composites preparation compared to the non-biodegradable nano fillers like carbon nanotubes, nano clays etc.(145) However, it is challenging to prepare nanocomposites by using NC for the reason of poor dispersion of CNC and NFC up on drying and low compatibility with hydrophobic matrices. It can be overcome by introducing hydrophobic groups through surface modification and grafting. Iwatake et al. has described the cellulose nanofiber reinforcement on polylactic acid (PLA). The goal of this study was to prepare green composites. The nanofiber reinforcement increased the Young's modulus and tensile strength of PLA by 40% and 25% respectively.(152)Recently, high dispersion and thermal stability was achieved for the quaternary salt modified CNC reinforced with polypropylene. (145)The first application of NC in composite reinforcement was done by Favier and group wherein poly(S-co-BuA) was reinforced by using cellulose whiskers. The authors found that the mechanical properties were increased.(153)

2.15.2 PACKAGING

In the modern world, usage of packaged food is increased. Most of the food is packed in the petro based polymers. Therefore, industries are very keen to develop biodegradable and lightweight food-packaging materials. This kind of materials can preserve the quality in terms of freshness and taste. Moreover, the shelf life of the food also will increase which is important for both consumers and industries.(154)

Previously, paper substrate was coated with mixture of microfibrillarted cellulose and chlorhexidine digluconate (anti bacterial molecule) and quality of the food packed with these materials also reported.(155)Elsewhere reported the antimicrobial activity of the nisin grafted CNF has shown promising anti bacterial activity against Bacillus subtilis and Staphylococcus aureus bacteria.(156)NC materials increases the fiber-fiber bond strength resulting in the increase of the reinforcement effect on paper materials. Even with only less amount of cellulose pulp as a filler, NC materials can be used the lightweight packaging because of this bond strength.

2.15.3 PAINTS AND COATINGS

NC is an ideal material to use in the paint and coating industry. Thanks to its high surface area which helps to hold the water hence acting as a highly viscous material. It is used in improving the durability of paints and protects paints and varnishes from wear and tear caused by UV rays. They can alter the viscosity of paints and coatings. The VTT group, Finland used NC in polyurethane varnishes and paints as additives, which increased the durability of coatings of paints.(157) Some other company called Cellu Comp from United Kingdom claimed, the NC extracted from carrot improved the hardness, flexibility and crack resistance of the paints.(158)

2.15.4 OPTICAL MATERIALS

Nanofibrillated cellulose possess great optical properties considering the size of the NFC is less than the wavelength of the visible light. Hence the paper prepared with nanofibrils are more transparent.(159) This can be added benefit to the different applications like electronics, sensors and solar panels. Adequate research results have been reported in the literature. Jia Huang and team reported the flexible field effect transistors printing on the nano paper for the green electronic transistor applications.(150) The other research group studied the deposition of tin-doped indium oxide along with silver nano wires and carbon nanotubes for solar cell applications.(159)

2.15.5 BIOMEDICINE

NC has ample application in biomedicine as excipients, in drug delivery, for enzyme/protein immobilization, implants, skin and bone tissue repair and others. The competence of NC in drug delivery was studied by Letchford et al. (142). This study proved that nanocrystalline cellulose could bind the significant amount of ionizable water soluble antibiotics tetracycline and doxorubicin by surface modification using cationic surfactant called CTAB (cetyl trimethylammonium bromide). In other study reported by Alain dufresne and his group the cross-linking between the alginate and oxidised nano fibrillated cellulose hydrogels for the drug delivery system was produced.(149) Same group also reported the double membrane hydrogels using cationic cellulose nanocrystals and alginate for quick and slow drug release from first layer and second layer respectively.(160) Nanomaterials have wide applications as hydrogels in tissue engineering. In 2015, Markstedt et al. reported the 3D bioprinting with living cells. They combined nanofibrillated cellulose with alginate for the 3D bioprinting of living soft tissue with cells.(151)

2.16 NANOCELLULOSE TOWARDS INDUSTRIALIZATION

The scientific abilities of the NC were progressed from last six decades. The attractive properties of the tiny fibers and particles play vital role for the creation of the new bio economy. Few decades ago, microcrystalline cellulose (MCC) emerged as new material, which is widely used in pharma, composites and chemical fields. Subsequently, NC is emerging as a key material in industrialization. According to the global market outlook for NC, by 2022, the annual turnover can reach 808.29 million dollars. The significant mechanical, optical and rheological properties of these materials attracted the both researchers and industries. The journey of the NC from last seven decades is shown in figure 2.16 along with the major research findings.

The enticements for the NC industries are because it is a new source with wide range of applications that need to be established. Hence producing new products resulting in new business breakthroughs. In addition, they can be extracted from easily available sources and are bearable and renewable. The first pilot plant to produce NC was started in 2011 by Innventia at Sweden.(161)The industrialization of NC can be parted into three main segments viz. products, applications and areas where there are produced. The products of NC are cellulose nanocrystals, nanofibrillated cellulose, bacterial cellulose and electro spun cellulose nanofibers. Applications of NC includes paper industry, composites, personal care, biomedical, electronics, paints etc. Figure 2.16 shows the journey of NC towards industrialization.

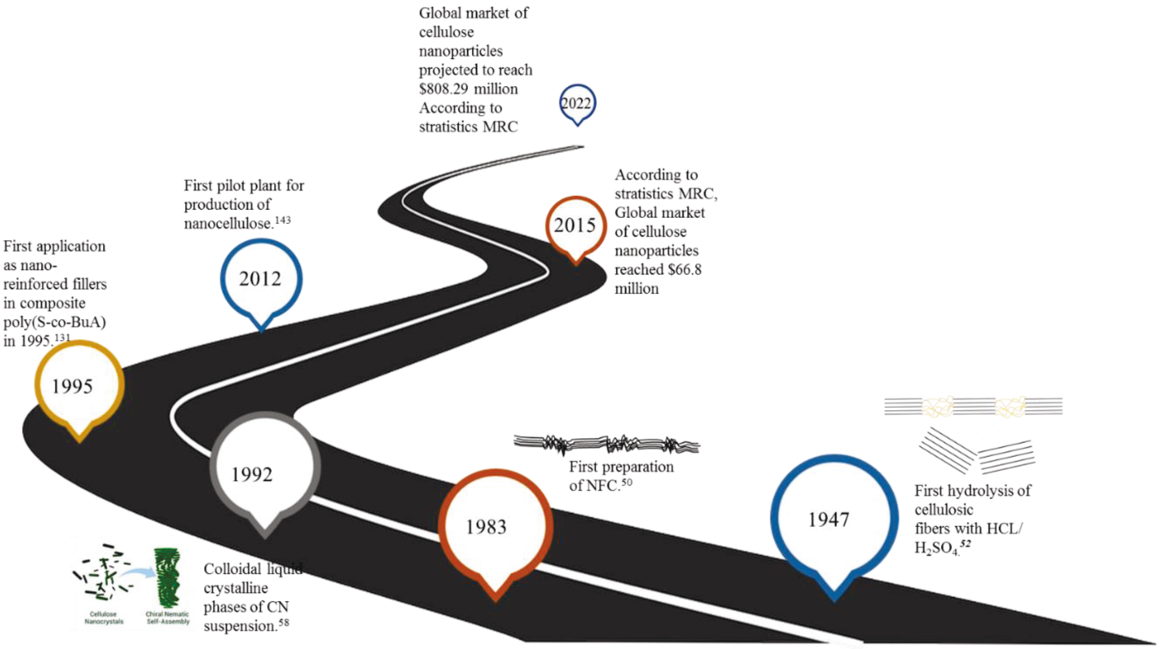

Figure 2. 16 Road map of nanocellulose towards 2022

The pronounced market of NC is seen in areas of North America, Europe, middle East. Table 6 indicates the company producing NC across the world with the quantity produced and the type of the product based on the TAPPI NANO outlook 2015.(18) Industries collaborate with other universities or institutes to develop new Nano cellulosic materials. The detailed study of industrial turnover and industrial methods is discussed in the following section.

Table 2. 6 Company producing nanocellulose, product type and the production capacity/day in kilograms.

Production unit	Production capacity/day (Kg)	Product type
CelluForce-CANADA	1000	CNC
Paper logic -USA	2000	NFC and CNC
University of Maine-USA	1000	NFC and CNC (dry &wet)
Borregaard-NORWAY	1000	NFC
American process-USA	500 to 1000	NFC, CNC
Nippon paper-JAPAN	150-500	Tempo- CNC, NFC and CNC
Innventia-SWEDEN	100	NFC
CTP/ FCBA - FRANCE	100	Enzi. NFC, T-CNF
OHI paper- JAPAN	100	NFC

Stora Enso-FINLAND	unknown	NFC
UPM- FINLAND	unknown	NFC
SAPPI- NETHERLANDS	unknown	NFC
Lulea university- SWEDEN	unknown	NFC
Holmen - SWEDEN	100	CNC
Alberta innovates - CANADA	20	CNC
India council for Ag. research	10	CNC
Melodea - Israel	unknown	CNC
FP-Innovations - CANADA	unknown	CNC, NFC
Blue goose refineries-CANADA	10	CNC

2.16.1 INDUSTRIAL TURNOVER AND METHODS

Every material invention starts at research table and it will take decades to commercialize. Similarly, commercial NC production was started in 2012, nearly six decades after first invention. From thereon, focus on the biomaterials increased due to the awareness of the biodegradable and renewable materials for the betterment of the society. This might be the main reason behind the production activities of the NC. All over the world more than 40 companies was established with their allied organizations to produce the NC. However, the potential application was not yet established. Industries are currently under research to find the key advancements in the fields of the concretes, paints, composites and packaging. Authors attempted to shortlist all the production sites of NC, nature of material manufactured, their production capacity and methods of the preparation in table-7 based on the TAPPI NANO, 2015 ISO/TC 6/TG 1 study.(162)

Table 2. 7 Industries producing nanocellulose, product type, their production capacity and method of production across the world. Reproduced with permission.(162) TAPPI NANO, 2015 ISO/TC 6/TG 1 study.

Cellulose Nanocrystals (CNCs)

Production activities

Country	Company	Product/ Trade name	Production Capacity	Source/Method
CANADA	CelluForce*	NCCTM	1 ton/day	**Bleached kraft pulp** Sulfuric acid hydrolysis
	Alberta Innovates (AITF)	CNCs	20 kg/day	**MCC, bleached kraft pulps (softwood and hardwood),dissolving pulp** Sulfuric acid hydrolysis
	Blue Goose Biorefineries Inc.	CNCs	10 kg/day	**Lignocellulosic feedstocks including wood, grasses and cereal straws** Oxidative, nanocatalytic process
	FPInnovations	CNCs	2 kg/day	**Bleached chemical pulp and others** Sulfuric acid hydrolysis
USA	American Process Inc.**	Nanocellulose BioPlusTM CNCs Lignin-coated hydrophobic CNCs	0.5 ton/day (est.)	**Wood chips ,Agricultural residues Bamboo, grasses** **USA** Sulfur dioxide and ethanol pretreatment (Patented AVAP® technology)
	USDA-Forest Service-Forest Products Laboratory (FPL)	Aqueous suspensions Freeze-dried CNCs	50 kg/week	**Wood pulp ,** Sulfuric acid hydrolysis
SWEDEN	MoRe Research backed by Holmen Pulp and Paper and SP Technical Research Institute of Sweden	Nanocrystalline cellulose	0.1 ton/day pilot plant in place during first half of 2016	**Paper industry sludge** Controlled sulfuric acid hydrolysis + washing, sonication Based on technology by Melodea
ISRAEL	Melodea Ltd. backed by Holmen Pulp and Paper, Sweden	Nanocrystalline cellulose (NCC) NCC foam	--	**Paper industry sludge** **Bleached pulp** **Flax, Hemp** Hydrolysis + washing, sonication
IRAN	Nano Novin Polymer Co	Bacterial nanocellulose	--	**Bacterial cellulose** Production of cellulose nanofibers using bottom-up approach of bacterial synthesis Provide nanocellulose and other bio-based nanopolymers using top-down approaches
CHINA	Tianjin Haojia Cellulose Co., Ltd.	CNCs Suspension Spray-dried Freeze-dried Chemically modified?	--	**Dissolving pulp** **Cotton** **Bleached kraft pulp (softwood, hardwood)** Mechanical shearing + combined enzymatic and acidic hydrolysis
INDIA	Indian Council of Agricultural Research - Central Institute for Research on Cotton Technology (ICAR-CIRCOT)	CNCs and CNFs	10 kg/day	**Cotton linters** **MCC from short staple cotton fibers** **Sugarcane bagasse, other agro-biomass** Novel microbial, enzymatic and chemo-mechanical processes, e.g. in membrane reactor for continuous hydrolysis and removal of nanocellulose without substrate inhibition

Nanofibrillated cellulose(NFCs)
Production activities

Country	**Company**	**Product/ Trade name**	**Production Capacity**	**Source/Method**
CANADA	Kruger Bioproducts Inc.** FILOCELL	Cellulose filaments	5 tons/day	**Bleached kraft pulp or TMP** Mechanical treatment
	Performance BioFilaments Inc.**	Cellulose filaments Wet fluff form or rolls of dried film	--	**Bleached kraft pulp or TMP** Mechanical treatment
	GreenCore Composites Inc.**	NCellTM Natural fiber-reinforced thermoplastics	--	**Wood or agricultural fibers** "In-situ generation of lignocellulosic microfibers" PP or PE matrix reinforced with up to 40% natural cellulosic microfibers
USA	American Process Inc. (AVAPCO)**	Nanocellulose BioPlusTM CNFs Lignin-coated hydrophobic CNFs	0.5 ton/day (est.)	**Wood chips** **Agricultural residues** SO2/ethanol pulping Mechanical treatment
	USDA-Forest Service-Forest Products Laboratory (FPL)	CNFs Aqueous suspensions Freeze-dried	1 kg/week	**Wood pulp** TEMPO oxidation and mechanical treatment
	UMaine	CNFs Aqueous suspensions	1 ton/week	**Wood pulp** Mass colloider grinder
	paperlogic	CNFs Planned for first half of 2015	--	**Wood pulp** Mechanical treatment
NORWAY	Borregaard	CMFs "Exilva MFC"	~3 ton/day planned for mid-2016	**"Specialty cellulose"** Mechanical treatment
	Norske Skog Saugbrugs	CMFs/ nanocellulose	Pilot plant planned as of Dec 2013	**Thermomechanical pulp** High pressure treatment
SWEDEN	Innventia AB	CMFs	100 kg/day pilot plant Mobile demo plant July 2014, planned with BillerudKorsnäs	**Wood fibers** Chemical and/or enzyme pre-treatment, Mechanical treatment (homogenization)
FINLAND	UPM-Kymmene Ltd.*	BiofibrilsTM	Pilot-scale demo plant "For trials at UPM mills"	**Wood fibers** Mechanical treatment
	VTT* collaboration with Aalto U, UPM	CNFs Roll-to-roll film	Pilot scale	**Birch fibril pulp** Mechanical treatment
	Stora Enso Ltd.	CMFs "Microcellulose"	Pilot plant started up end 2011	**Wood fibers** Mechanical treatment

Country	**Company**	**Product/ Trade name**	**Production Capacity**	**Source/Method**
UK	Zelfo Technology GmbH	MFC	--	**Cellulose fibres, fibre-based waste (recycled)** CORE technology enables modification of cellulose fibres using minimum energy BASF SE owns exclusive rights to industrialise Zelfo MFC fibre technology within pulp, paper and board industries
	CelluComp 11 partners in 5 countries, supported by Strathclyde U and Reading U, coordinated by Institute of Nanotechnology UK	CNFs Curran® Paste/slurry Powder Thin sheets Composites	Small plant running	**Waste streams of root vegetables** **"Proprietary technology"**
	Imerys	FibreLean MFC combination of kaolin or calcium carbonate with MFCs	1000 to > 10,000 tons/year	**Range of (wood) pulp species** No fiber pretreatment; co-grinding mineral with fiber On trial by Imerys customers in a wide range of papers
FRANCE	CTP/FCBA InTechFibres partnership (to summer 2014)	CMFs/CNFs	~ 0.1 ton/day capacity 100 g to 80 kg CMF/CNF	**Lignocellulosics** TEMPO-catalyzed oxidation Meca-enzymatic pre-treatments Other pre-treatments Ariete NS3075H 1000 L/h, 55 kW motor, 1500 bars maxi Semi-industrial production For research applications: Panther homogenizer 50 L/h and lab microfluidizer
	InoFib LGP2 start-up	CMFs Modified CMFs	unavailable	**Cellulosic fibres** Mechanical treatment
SWITZERLAND	Swiss Federal Laboratories for Materials Science and Technology Empa	CNFs	15 kg/day	**Wood and other lignocellulosic fiber sources** Enzymatic pre-treatment Microfluidizer
GERMANY	J. Rettenmaier & Söhne GmbH	CMFs (maybe)	--	--
NETHERLANDS/UK	Sappi in partnership with Edinburgh Napier University, on Brightlands Chemelot Campus in Sittard-Geleen, the Netherlands	CNFs dry powder readily re-dispersed in water	8 tons/year target (pilot plant) planned for early 2016	**Wood fibres** "New low-cost process" CNFs with unique morphology, specifically modified for either hydrophobic or hydrophilic applications

Country	**Company**	**Product/ Trade name**	**Production Capacity**	**Source/Method**
IRAN	Nano Novin Polymer Co	Industry	--	**Bacterial cellulose** Production of cellulose nanofibers using bottom-up approach of bacterial synthesis Provide nanocellulose and other bio-based nanopolymers using top-down approaches
CHINA	Tianjin Haojia Cellulose Co., Ltd.	CNFs Modified CNFs TEMPO-oxidized, cationized, carboxymethylated, polymer grafted	--	**Dissolving cotton pulp** **Bleached sulfate pulp (soft- and hardwood)** High pressure homogenizer -or- Super micro-grinder
INDIA	Indian Council of Agricultural Research - Central Institute for Research on Cotton Technology (ICAR-CIRCOT)	CNFs and CNCs	10 kg/day Pilot plant	**Cotton linters** **MCC from short staple cotton fibers** **Sugarcane bagasse** **Other agro-biomass** Novel microbial, enzymatic and chemo-mechanical processes, e.g. in membrane reactor for continuous hydrolysis and simultaneous removal of nano-cellulose without substrate inhibition
JAPAN	Daicel**	Nano CelishTM filtration/food/industrial grades	-- 10-35% solids	**Purified pulp** Mechanical treatment
	Dai-ichi Kogyo Seiyaku Co., Ltd.	"Cellulose single nanofiber": RheocrystaTM	50 ton/year 2% solids	**NO INFO** TEMPO oxidation
	Daio Paper	CNFs	--	**NO INFO** Mechanical treatment, etc.
	Sugino Machine	BiNFi-s Biomass nanofiber	-- 2, 5, 10% solids	**NO INFO** Ultra-high pressure water jet
	Chuetsu Pulp & Paper	CNFs CNF/plastic composites	--	**Bleached kraft pulp:** **Bamboo, Softwood/Hardwood** Aqueous counter collision
	Nippon Paper Industries*	CNFs CellenpiaTM	> 30 ton/year (> 0.1 ton/day)	**Wood pulp** TEMPO oxidation Carboxymethylation Mechanical treatment
	Oji Holdings	CNFs	--	Chemical modification Mechanical treatment
	Asahi Kasei**	PreciséTM (non-woven containing CNFs)	--	--
	Seiko PMC	CNF nanocomposites Mentioned in slide from TAPPI Nano conference, holds patent with DIC Products	--	**Wood pulp** Mechanical treatment + Hydrophobization
	DIC Corporation	CNF/plastic nanocomposites	--	--
	Tokushu Tokai Paper	Absorbent products (SAP and CNF)	--	No information on company website

CHAPTER 3

HOMOGENOUS AND TRANSPARENT NANOCELLULOSIC FILMS FROM CARROT

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Accepted date: February 24, 2018
Current status: Published
Journal: Industrial crops and products
Citation: (9)

DOI: https://doi.org/10.1016/j.indcrop.2018.02.076

3.1 RÉSUMÉ

La nanofibre fibrillée (NFC) et la cellulose nanocristalline (NCC) ont été extraites de la pulpe de carotte en utilisant des procédés non conventionnels de broyage à billes et d'hydrolyse acide. Initialement, les fibres brutes de carottes lavées à l'eau chaude et traitées au peroxyde d'hydrogène menaient à l'obtention de fibres riches en cellulose en absence de β-carotène et de lignine. Les observations des fibres brutes et blanchies au microscope électronique à balayage (MEB) ont montré que la carotte était constituée de fibres classiques et inhabituelles en forme de ressort. Les fibres purifiées ainsi obtenues ont été fibrillées par un procédé de broyage à billes à trois différents temps de broyage pour obtenir des NFC. L'effet du temps de broyage sur la fibrillation et la morphologie des NFC obtenues a été étudié par MEB. En parallèle, des fibres de carottes pures traitées aux alcalis ont été utilisées pour extraire les NCC par hydrolyse acide. Les propriétés structurelles, fonctionnelles, cristallines et thermiques des NFC et des NCC ainsi obtenus ont été caractérisées au moyen de la microscopie électronique à transmission (MET), de la microscopie à force atomique (AFM), de la spectroscopie infrarouge à transformée de Fourier (FT-IR), de la diffraction aux rayons X (XRD) et par analyse thermogravimétrique (TGA). La longueur et le diamètre de la NCC préparée à partir de carottes étaient compris entre 54 et 610 nm. Une amélioration significative de la cristallinité a été observée pour NFC (69 %) et NCC (78 %) par rapport à celle des fibres brutes (36 %). Les suspensions de NFC et NCC obtenues ont servies à couler différents films nanocellulosiques (NCF). Les propriétés optiques et morphologiques des films résultants ont été systématiquement analysées en spectrophotométrie ultraviolet et visible (UV-vis) suivie d'une analyse en MEB. Une amélioration significative de la transparence et de l'homogénéité de la NCF a été montrée avec l'augmentation du temps de broyage. De plus, les propriétés mécaniques de la NCF issue de la carotte ont été étudiées à l'aide d'essais de traction.

3.2 ABSTRACT

Nano fibrillated cellulose (NFC) and nanocrystalline cellulose (NCC) have been extracted from carrot pulp by using non-conventional ball milling and acid hydrolysis process respectively. Initially, hot water washed carrot raw fibers treated with hydrogen peroxide, yielded the cellulose rich fibers in the absence of β-carotene and lignin. The scanning electron microscopy (SEM) of raw and bleached fibers showed that carrot consisting of both classical and unusual spring shaped fibers. The purified fibers were fibrillated by ball milling process at three different grinding time to obtain NFC. The consequence of grinding time on fibrillation and

morphology of the resulted NFC was investigated by SEM. In parallel, alkali treated pure carrot fibers were used to extract the NCC by acid hydrolysis process. The structural, functional, crystalline and thermal properties of resulted NFC and NCC was characterized by means of transmission electron microscopy (TEM), atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The length and the diameter of the NCC prepared from carrot was in the range of 54-610nm. Significant improvement in crystallinity was observed for 5NFC (69%) and NCC (78%) compared to that of raw fibers (36%). The obtained NFC and NCC suspensions were separately cast into nanocellulosic films (NCF). The optical and morphological properties of the resulted films were analyzed systematically by ultraviolet-visible spectrophotometry (UV-vis) and SEM respectively. NCF exhibited the significant improvement in the transparency and homogeneity with increase in the grinding time. Furthermore, the mechanical properties of the carrot NCF were studied by using the tensile test.

3.3 INTRODUCTION

Over the last few years, interest on the extraction of nanocellulose from vegetal biomass is increasing due to social, environmental and economical facets. As reported by United Nations Environmental Programme (UNEP), every year 1.3 billion tonnes of the food are going to waste bins, which is nearly equal to one third of the food production in the entire world.(163) However, it is not a mere economical issue but also ecologically, food waste ends in landfills, which subsequently leads to global warming. Such produced wastes raise threat to the environment. Despite part of this food waste is used to feed the livestock in some parts of the world, food waste management is still a big issue. In order to overcome these issues and to create new economy, industries and researchers are focussing to generate new products out of agriculture wastes.

The major contribution of the food waste is from vegetables. The foremost vegetable waste is coming from tomato, potato, carrots etc. The perishable wastes are produced during various stages like damage during pre-and post-harvesting, lack of storage facilities, rejected from buyers and super market waste after use by date. Nevertheless, some vegetables like potatoes are used to extract the starch.(164) Carrot is one of the hidden source of cellulose containing 80% on dry mass.(165,166) Carrot is a root vegetable and the scientific name is "*Daucus carota*". In accordance with food and agriculture organization (FAO) every year farmers are harvesting 37 million tonnes of carrots. Carrot is widely used in the industries for the juice production yet the residues of pulp remained huge problem even though part of them is used as feed stocks for the animals.(34)

The residue of carrot comprises the minimal amount of alpha and beta carotene, lipids, proteins, pectin's and some minerals like Ca, Fe and Mg. It has the low lignin and hemicellulose content 2.5 and 9 % respectively.(34) Upon delignification process, pure cellulose can be valorized. Cellulose is a nature derived polymer, consisting the glucose as a monomer. Cellulose is present in the plant cell wall in bundles of the rigid microfibers surrounded with the hemicelluloses, lignin and pectin.(167,168) The nano sized cellulose fibers resulting from biomass, demonstrate the excellent optical, mechanical, barrier properties and they are completely biodegradable in the end use. These materials are the best choice to replace the inorganic materials like glass, hydroxyapatite,(169) nano clays (170–174) and carbon nano tubes.(175)

Nanocellulose (NC) is a remarkable material given by nature. If either length or diameter of the cellulose is in nanoscale, then it is called NC. It can be classified as microfibrillated cellulose (MFC)/nanofibrillated cellulose (NFC)/cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC). NC has great attention from academic researchers and industries.(176) According to the market experts, by 2019 the NC turnover may exceed $250 million dollars. Several methods were previously reported to prepare micro and nano fibrillated cellulose like mechanical disintegration with homogenizer,(62,177) Cryo-crushing,(75) ball milling(178) and steam explosion.(82)

In some other studies, to avoid the high energy consumption for the production of the NFC, different pre-treatments like enzymatic and chemical treatment were carried, for example, TEMPO oxidation,(179) Per-iodate oxidation(180,181) with subsequent mechanical treatment. Recently, extraction of NFC from carrot fibers was reported by using two different mechanical process (grinding and homogenization).(34)

In the present study, authors reported the isolation of the NFC and NCC from carrot pulp. To the best of authors knowledge NCC was extracted from carrot pulp for the first time thus far. Firstly, the raw carrot fibers were washed with hot water and bleached using hydrogen peroxide. The bleached fibers were characterised by using FT-IR, XRD, TGA and SEM to understand the functional, crystalline, thermal and morphological properties. The NFC and NCC were then prepared by ball milling (mechanical) and acid hydrolysis (chemical treatment) process respectively. The size, morphology and surface analysis of the derived NC were investigated.

Finally, transparent nanocellulosic films of NFC and NCC were prepared by casting. Optical, tensile and morphological properties of the NCFs were investigated by means of UV-visible spectra photometer, tensile test and SEM respectively.

3.4 EXPERIMENTAL SECTION

3.4.1 MATERIALS

Damaged carrots were collected from the local farmer and were used in this study. Firstly, juice was extracted and the remained raw pulp was used for the extraction of NFC and NCC. 30% Hydrogen peroxide solution was obtained from VWR Anachemia. Sodium hydroxide (99% pure) used for alkaline treatment, was purchased from sigma Aldrich.

3.4.2 METHODS

3.4.2.1 PREPARATION OF NANOCELLULOSIC FILMS

The nanocellulosic films (NCFs) were prepared by simple casting evaporation. The raw, hot water washed and bleached carrot fibers were dispersed and then allowed to the evaporation of water under room temperature (R.T) in hood for 72 hrs. Whereas in the case of the NFC at different ball grinding time (1.5, 3, 5 min) and NCC was dispersed in water to 0.5 wt. % and then casted at R.T for 3 days.

3.4.2.2 SCANNING ELECTRON MICROSCOPY (SEM)

Scanning electron microscopy (SEM) was used to analyse the morphology of the carrot fibers before and after different stages of treatment. The fibrillation of obtained NFC was also monitored. The surface and cross-sectional morphology of nano films were observed. The samples were coated with gold to avoid the charring due to the electron bombardment. The SEM images were captured by using S-4700 scanning electron microscope (Hitachi, Japan).

3.4.2.3 ATOMIC FORCE MICROSCOPY (AFM)

AFM was used to study the size and structural morphology of NFC and NCC using a Veeco Nanoscope IIIa digital instruments. Previously NFC and NCC samples were diluted at 0.01wt% and a drop was deposited onto silica vapour on mica substrates and dried under room temperature by applying external air for 15minutes. Each sample was characterized in both topographical and phase images at different randomly selected locations.

3.4.2.4 TRANSMISSION ELECTRON MICROSCOPY (TEM)

The length and diameter of the individual NCC and the structural morphology of the NFC was analyzed by using TEM. Initially, one drop of diluted samples of NFC and NCC was placed on the copper grid (400mesh with a film of formvar-carbon), dried for one hour at room temperature, and analysed at 80KV. H-7500 transmission electron microscope (Hitachi, Japan) at 80Kv was used.

3.4.2.5 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FT-IR)

Fourier-transform infrared spectroscopy (FTIR) was performed on the raw, hot water washed (H.W washed), bleached and air-dried NFC and NCC of carrot fibers to understand the functional groups present in the carrot fibers in terms of wavenumber (cm^{-1}). JASCO 4600 Spectrometer (Japan) equipped with an ATR PRO ONE reflection accessory was used. Spectra were recorded with a resolution of $4cm^{-1}$ in the range of 4000 to 600 cm^{-1}.

3.4.2.6 THERMOGRAVIMETRIC ANALYSIS (TGA)

The thermal degradation of all the samples was monitored by thermogravimetric analysis (TGA) with TA instruments-Q500. The weight loss was recorded for 10-20mg of sample as a function of temperature. At a heating rate of 10ºC/min in the temperature range of 20–900ºC under oxidizing atmosphere.

3.4.2.7 X-RAY DIFFRACTION (XRD)

X-ray diffraction (XRD) was performed on all the samples after each stage of the treatment. The fibers were ground by using ball miller and the resultant powder were analysed by using the A Philips X'Pert diffractometer equipped with a general area detector diffraction system with Copper Kα radiation ($\lambda = 1.542$ Aº), 2θ (Braggs angle) was from 8 to 40º. The Crystallinity index, Ic, was evaluated using the Buschle-Diller And Zeronian Equation.(182)

$$Ic = 1 - I_1 / I_2$$

where, I_1 is the intensity at the minimum ($2\theta = 18.5^{\circ}$) and I_2 Is the intensity associated with the crystalline region of cellulose ($2\theta = 22^{\circ}$).

3.4.2.8 BALL MILLER

Never dried carrot pulp (4 wt.%) was defibrillated by using RESTCH ball mill mixer MM 400 with zirconium ball at the rate of 2400RPM at room temperature. The fibrillation was performed for samples at three different grinding time namely 1.5, 3 and 5min and are referred to as 1.5NFC, 3NFC and 5NFC respectively.

3.4.2.9 NANO ZETA SIZER

Malvern Zetasizer Nano ZS was used to determine the zeta potential of the NCC separately. Each sample was measured 12 times to check the reproducibility.

3.4.2.10 ULTRAVIOLET-VISIBLE (UV-VIS)SPECTROPHOTOMETRY

Spectra max plus 384 UV vis spectrometers (from molecular devices, Canada) was used to investigate the transmittance of the NFC and NCC nano films separately within the range of the 200-800nm. Each sample was inserted in cuvette and measured. The transmittance spectra were attained by means of cuvette as background.

3.4.2.11 TENSILE TEST

Tensile properties of the nanocellulosic films were measured according to ASTM D-638 by using a Zwick/Roell z050 machine equipped with 5N load cell. The tensile tests were conducted at crosshead speed of 2 mm/min, at relative humidity of 35% and room temperature (25ºC). The samples were prepared by cutting 10 mm length strips of the nanocellulosic films.

3.5 RESULTS AND DISCUSSION

3.5.1 ISOLATION AND CHARACTERIZATION OF FIBERS FROM CARROT PULP

As shown in figure 3.1, carrots were directly passed through the juicer and remained pulp was used as raw material. Initially, pulp was dried at 60ºC for 12h to quantify the dry content. Further raw pulp was washed with plenty of pre-boiled hot water (boiled at 80ºC). The hot water washed (H.W) pulp was dried before bleaching step. In order to remove the lignin, carotene and pectins 7.5% hydrogen peroxide solution was added to 10g of dry pulp and stirred at 65ºC for 8h. The reaction mixture colour changed from orange to white as shown in the S1 in the supporting information. After, the purified pulp was cooled to room temperature and washed with plenty of water, filtered and stored in refrigerator at 8ºC before preparing NFC and NCC. Hemicelluloses present in the

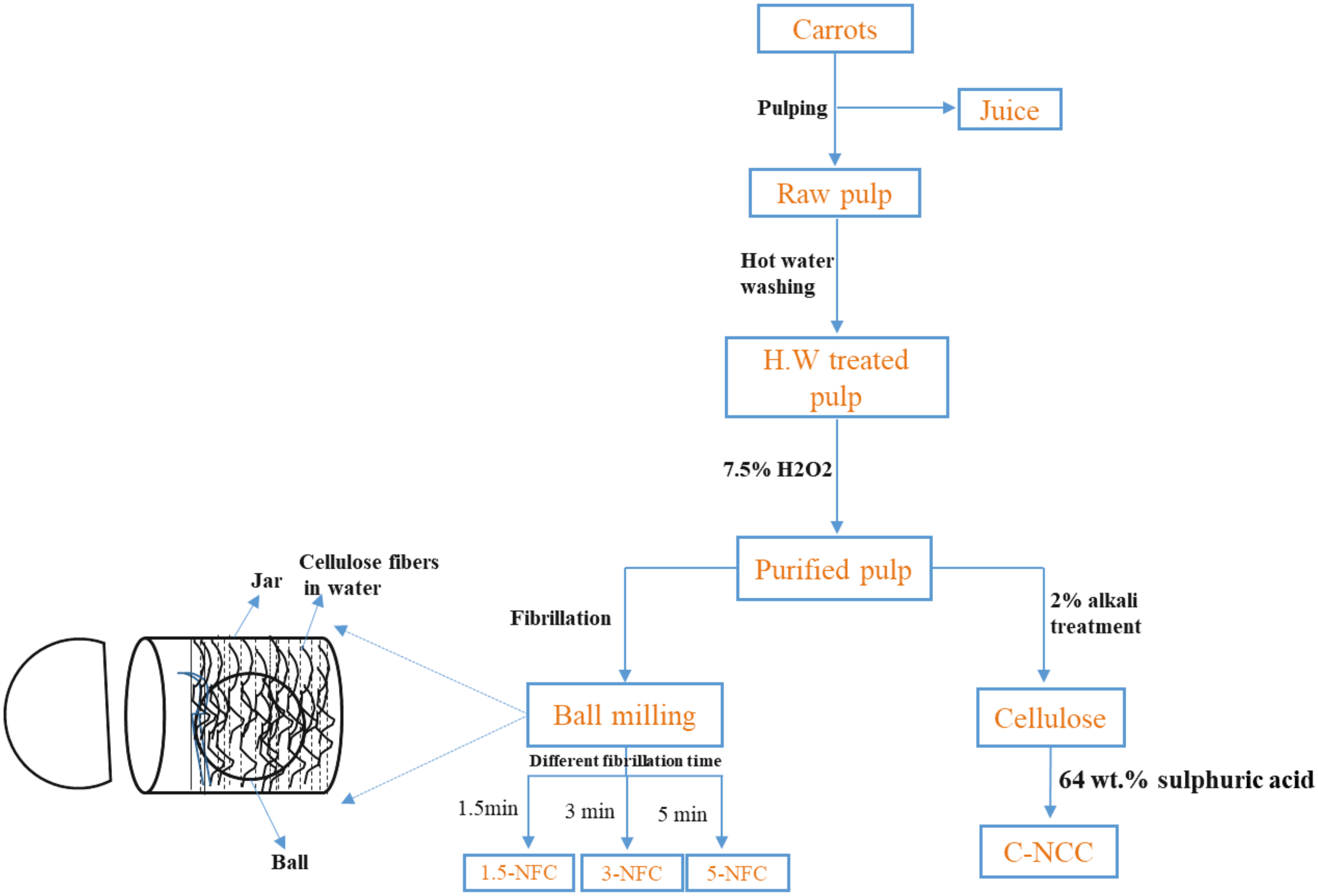


Figure 3. 1 Detailed schematic diagram for the preparation of NFC and NCC

bleached pulp was quantified (4.6% on dry content) and detailed procedure is explained in the supporting information. (9)

3.5.1.1 FIBRILLATION PROCESS BY BALL MILLING

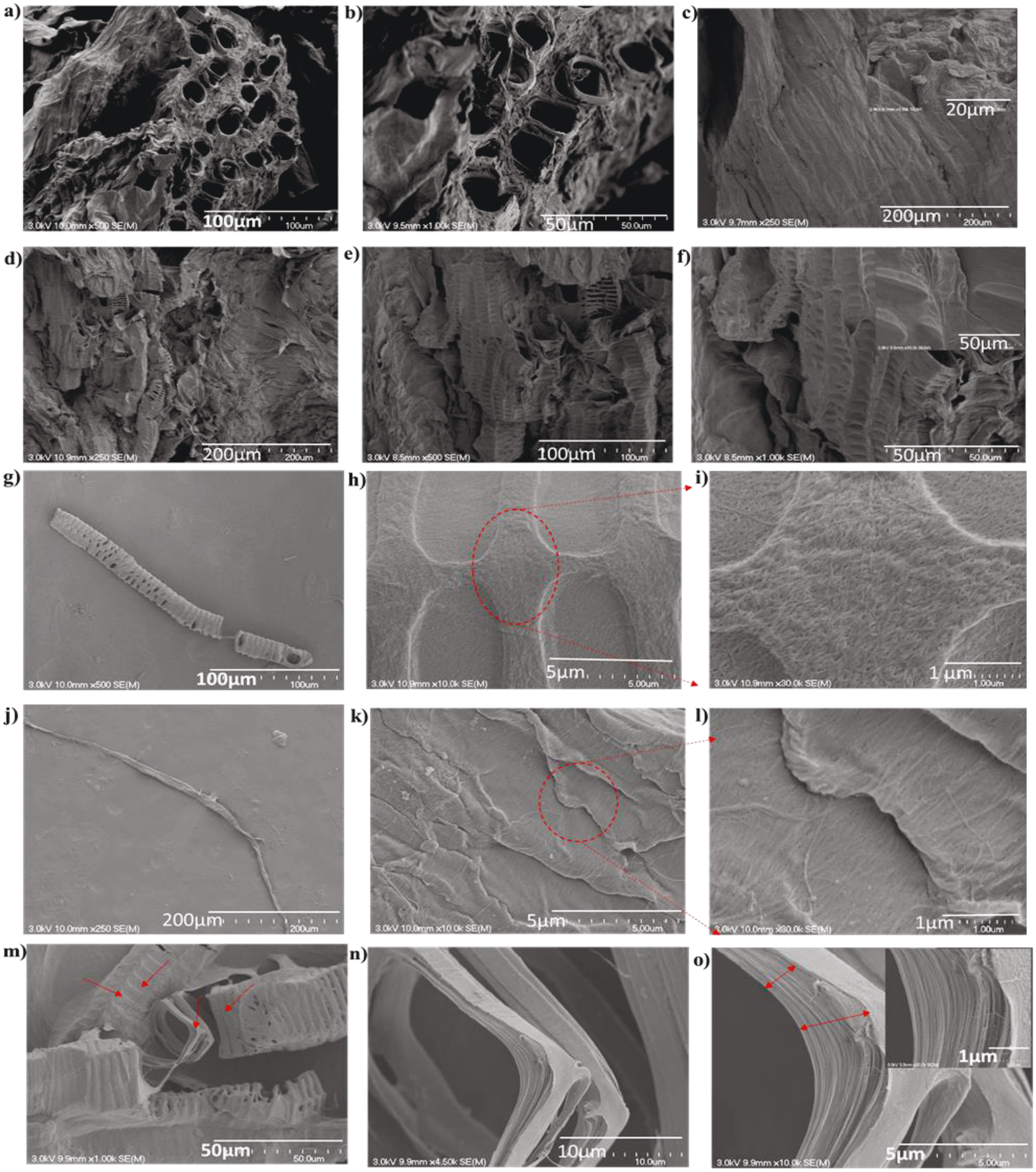
The final concentration of the obtained NFC was 2wt.%. While increasing the fibrillation time homogeneity of the nanofibrils was increased. It is note worthy that the fibrillation was done in the presence of the hemicelluloses (HC). Elsewhere reported that HC can play vital role to facilitate the fibrillation due to the hydrogen bonding and negative charges on HC.(52,136) In detail, HC surrounds cellulose microfibrils through abundant hydrogen bonding which in turn seals the gap between the microfibrils and protect the fibrils from aggregation. In addition, hemicelluloses contain glucuronic acid with carboxyl groups, which enables the delamination of fibers by means of electrostatic repulsion forces.(136) The HC present in the NFC suspension was difficult to measure since the full recovery of the NFC was not possible by the ball grinding process. It is worth to note that this work is containing of preliminary study, future research will be conducted on the influence of the HC on the fibrillation, dispersion up on drying and mechanical properties at different concentrations of the HC will be studied.

3.5.1.2 ACID HYDROLYSIS

Initially, carrot pulp was treated with 2% NaOH at 50°C to remove the hemicelluloses and further the pulp was washed and filtered with plenty of water to remove the unreacted sodium hydroxide and stored in refrigerator. 5g of this pulp was dispersed in water and treated with 64 wt.% sulphuric acid solutions for 1.30h at 50ºC. Then the reaction was stopped by quenching with cold water. The resulted solution was centrifuged few cycles to remove the unreacted acid and further nano crystalline cellulose (NCC) was dialyzed for one week, until the pH of the solution was close to 5-6 and then few drops of chloroform was added to the solution of NCC (to avoid fungal development) and refrigerated.

3.5.1.3 MORPHOLOGY OF CARROT FIBERS BEFORE AND AFTER TREATMENT

Figure 3.2 shows the scanning electron micrographs of the carrot fibers before and after hot water treatment and delignification. Before hot water wash (H.W) the raw material showed the unusual spring and classical fibers (can be seen in figures a, b and c). Fibers were completely cemented with lignin, hemicelluloses (HC) and carotene. Importantly, the surface of the fibers was completely rough probably due to the presence of lignin (can be seen in the inserted image of figure 3.2c)). However, after H.W the fibers were loosened up and more visible (as shown in figures 3.2d), e) and f)), this can be attributed to the partial removal of carotene. Elsewhere reported



hot

Figure 3. 2 a), b) and c SEM images of carrot fibers: raw, d), e) and f) H.W treated; g), h) and i) bleached spring fibers; j), k) and l) bleached classical fibers and m), n) and o) cross section of the spring fibers

water wash can also dissolve the fractions of HC.(183) Nevertheless, the surface of the fibers was still rough due to the presence of lignin.

After hydrogen peroxide treatment, the spring and classical fibers were individualized, (as seen in the figures 3.2g) and j)) due to the delignification process, which prompted the separation of the fibers from the bundles. The micrographs from figures 3.2g), 2n) and 2m), have two different kinds of spring fibers i) window oval spring ii) continuous oval spring fibers (can be seen in marked places in figure 3.2m)). Irrespective of the fiber, cell wall was poised with millions of thin micro fibers. The cross section of the spring fibers is shown in figures 3.2n) and 2o), the diameter was in the range of 2-4µm (seen in marked places). The cross section was composed with very thin microfibers. Collectively, cellulose rich carrot has different kind of fibers. The surface and cross section have the nature knitted microfibers regardless of the fiber. The length and diameter of the individual fibers was determined by SEM. The length and diameter of the spring and classical fibers were in the range of the 200-215, 400-415µm and 10-14 and 2-10µm respectively.

3.5.1.4 ASSESSMENT OF FIBRILLATION

The fibrillation of NFC was assessed by using SEM. The fibrillation was studied at different ball milling times. The fibrillation was monitored at different time intervals and was started at 1.5 mins. With respect to the SEM study, the fibrillation time of 3 and 5 mins was effective. Hence, to optimize the fibrillation of carrot fibers, different ball grinding times (i.e. 1.5, 3 and 5min) were tried at constant frequency. Figure 3.3 shows the micrographs of the NFC after 1.5min (a and d), 3min (b and e) and 5min (c and f) of grinding time at low and high magnification. While increasing the ball grinding time, the nanofibers were individualized and thus homogeneity is also increased. The partially fibrillated bundles of nanofibers can be seen after 1.5 min of fibrillation (1.5NFC), the fibrils were not homogeneous in size. However, after 3min (3NFC) of grinding time the fibers morphology was changed. Several individual nanofibrils started to peel off from the bundles with increasing time, though few of them remained partially attached to the bundles. The 5NFC exhibited the classical mesh like entangled network structure was observed as seen in the figure3.3 (c and f). This can be explained that with the increase in grinding time, it is possible that fibrillation occurred through the mechanisms of splitting the larger nanofibers into smaller fibers and the peeling away of nanofibers from the surface of these large fibers.

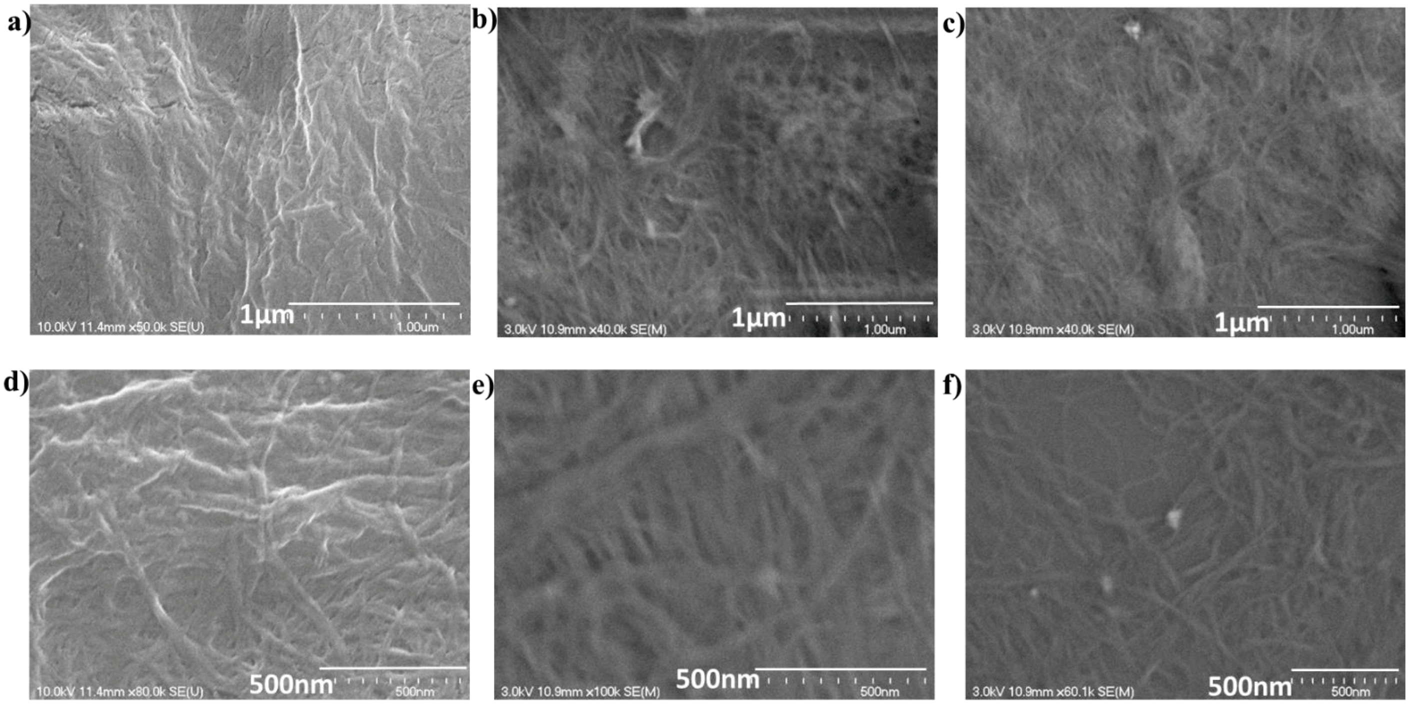


Figure 3. 3 SEM images of NFC at low and high magnification: a) and d) 1.5 NFC, b) and e) 3 NFC, c) and f) 5NFC.

3.5.2 STRUCTURAL MORPHOLOGY OF NFC AND NCC

3.5.2.1 TRANSMISSION ELECTRON MICROSCOPY (TEM)

TEM was used to study the size and structural morphology of the 5NFC and NCC. Figures 3.4a) and 4b) show the TEM images of 5NFC at low and high magnification. After 5minutes of oscillatory grinding process, the fibers completely disintegrated and formed web-like nano-fibrous network. The distinct nanofibrils width varied from 2-18nm and the length exceeded two micrometers.

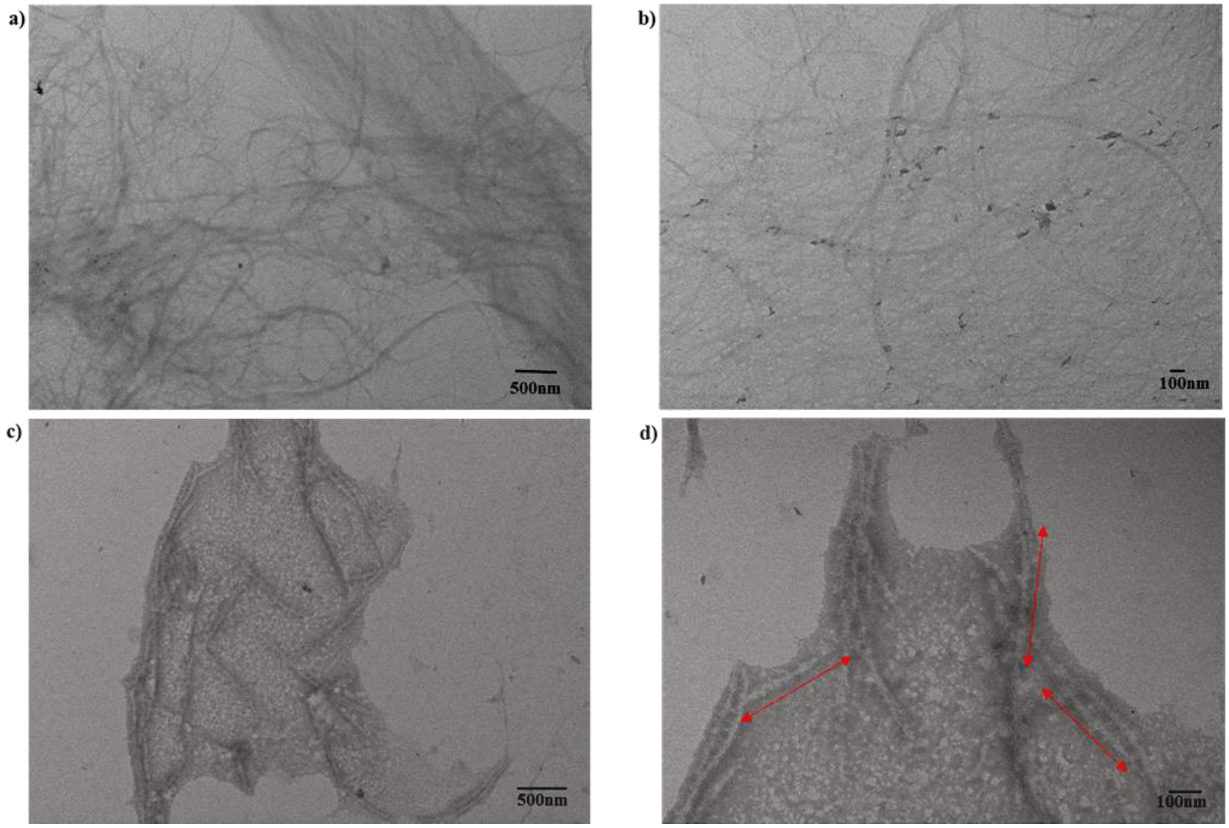


Figure 3. 4 TEM images for a) and b) 5 NFC; c) and d) NCC at low and high magnification.

It is worth to note that fibrillation process by ball milling was easier, compared to the birch kraft pulp disintegration in literature.(184) This might be due to the presence of the elementary fibers in the thin cell wall of the both spring and classical fibers that can be seen in the SEM images after delignification step.

Generally, NCC is isolated by acid hydrolysis. During the hydrolysis, the amorphous part of the cellulose is hydrolysed leaving behind the crystalline parts of cellulose.(140) Figures 3.4c) and 4d) show the NCC images of the carrot fibers. The length (L) was in between 84-590nm and diameter (D) varied between 10-36nm and the relative aspect ratio (L/D) was in the range of 8-19.

3.5.2.2 ATOMIC FORCE MICROSCOPY (AFM)

The structural morphology of the 5NFC and NCC was also observed by using AFM. Figures 3.5a) and 5b) show the AFM images of 5NFC. the width of the NFC was in the nano scale in the range of the 8-24nm and the length was in few microns. The lateral sizes were measured by using the height profile images. The dimensions of the carrot NCC was measured by using the AFM by air drying the sample on mica plate and images are shown in Figures 3.5c) and 5d). The rod like nano particles can be seen in different magnitudes. The length and diameter of the nanoparticles varied from 56-588nm and 6-42nm respectively. Hence, the aspect ratio of the NCC was in the range of the 9-18. The results agreed with that of TEM.

The comparison of the dimensions and structural morphology of carrot NCC with literature was not possible since authors reported for first time. Nevertheless, NCC extracted from tunicate were in the same range of carrot NCC in length.(185)

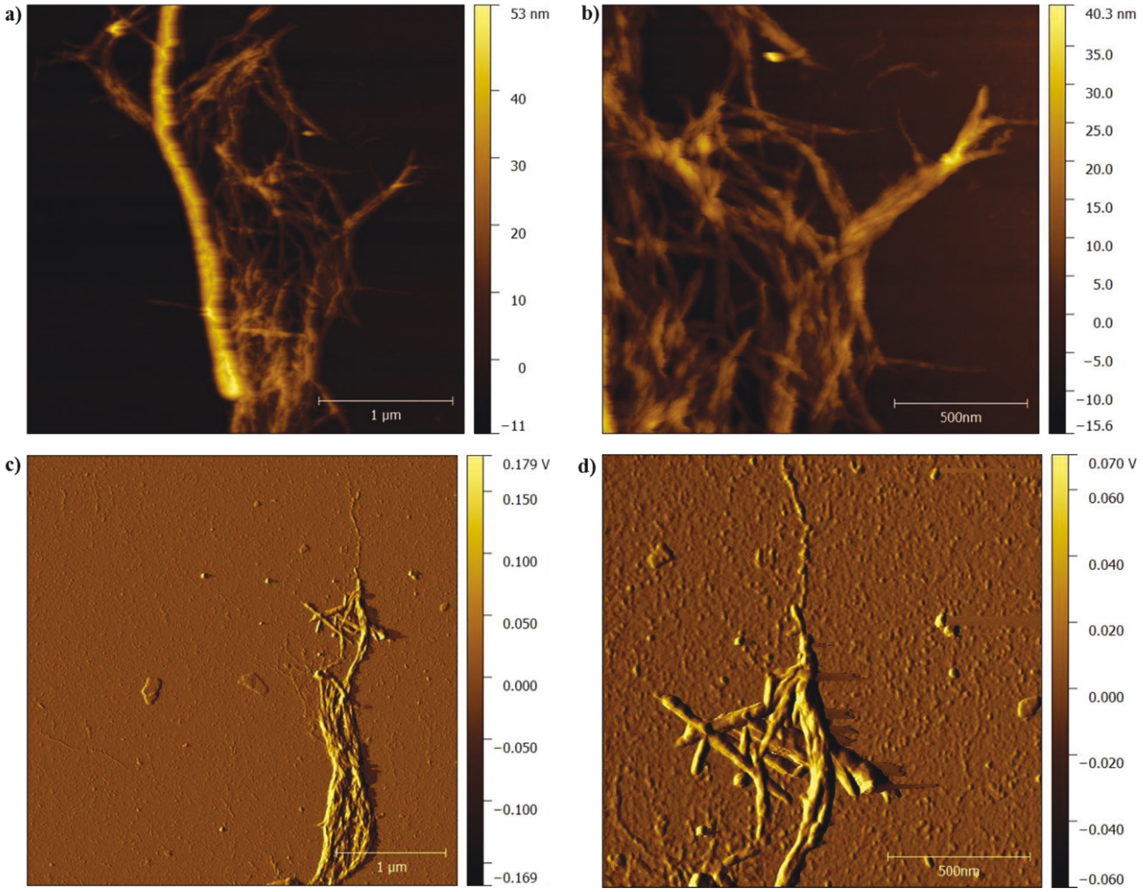


Figure 3. 5 AFM images for a) & b) 5 NFC, c) & d) NCC at low and high magnification.

3.5.2.3 ZETA SIZER

The surface charge of the NCC extracted from carrot was measured by using zeta sizer. The surface charge of NCC is a very important parameter. Since, the negatively charged half-ester sulfate groups formed during acid hydrolysis process will help to form more stable and dispersed suspension. This can be attributed to the electrostatic repulsion between the NCC particles. The zeta potential of the obtained NCC is -25.8mV at pH 5-6. Previously, the zeta potential of NCC at different pH was measured (65) and the results from the present study are in the similar range with the literature. The zeta potential and electrophoretic mobility values of the NCC from carrot is reported in table-1.

3.5.3 CRYSTALLINE, FUNCTIONAL AND THERMAL PROPERTIES

3.5.3.1 XRD

The degree of crystallinity of the carrot fibers before and after each treatment was studied by using XRD. The diffraction peaks for raw, HW, bleached, 5NFC and NCC is shown in figure 3.6. The typical peaks appeared at 16.4, 22.6 and 34.4° were related to cellulose I and are the reflections of 101 to 020 lattice planes respectively.(145,186) The results show that the chemical or ball milling treatment does not affect the crystallinity of the carrot fibers.

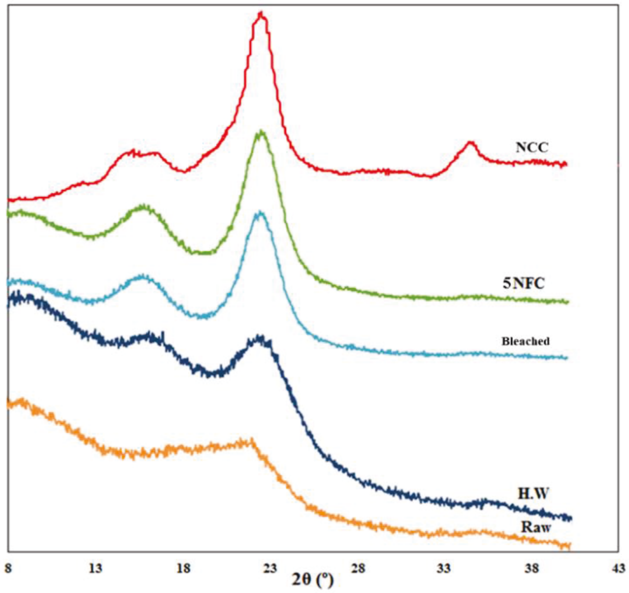


Figure 3. 6 XRD patterns for raw, bleached, 5NFC and acid hydrolysed cellulose from carrot pulp.

It is remarkable that the raw fibers show single diffraction at 22.5 and this might be due to the presence of the lignin, HC and carotene. However, after H.W treatment the diffraction peaks at 16.4 and 22.6 were more visible possibly due to the partial removal of some non-cellulosic materials by hot water washing. Also, after hydrogen peroxide treatment and ball grinding the fore mentioned diffraction peaks intensity significantly increased in evident to the removal of the other constituents present in carrot fibers. It is also evident from the SEM results shown in the morphology section.

Table 3. 1 Dimensions, surface properties and crystallinity of carrot NCC.

NCC size from AFM/TEM	Electrophoretic mobility (µm.cm. V^{-1}. S^{-1})	ζ-potential (mV)	Crystallinity index (%)
L :54-610 nm D: 8-46 nm L/D: 10-18	-2.028	-25.8	78

Importantly, NCC has shown all the typical diffraction peaks at 14.8, 16.8, 22.6 and 34.4° for cellulose I. This can be attributed to the evolution of the crystalline cellulose after acid hydrolysis. The crystallinity index (C.I) of the raw, H.W, bleached, 5NFC and NCC was 36, 43, 61, 69 and 78% respectively. C.I was determined by using the method mentioned in the methods section. The significant improvement in crystallinity for 5NFC, NCC can be fully attributed to the removal of the amorphous materials (like lignin, carotene and HC) after hydrogen peroxide and alkali treatment respectively.(186)

3.5.3.2 FT-IR

The changes before and after each treatment (hot water, hydrogen peroxide, ball milling and acid hydrolysis) in chemical composition was studied by using FT-IR and results are presented in figure 3.7.

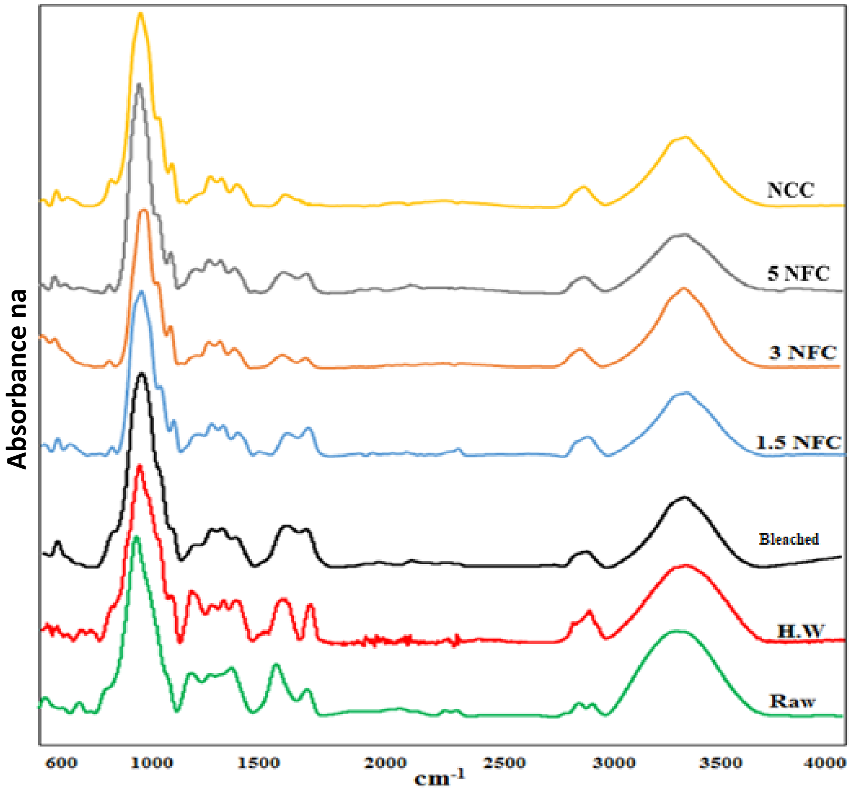
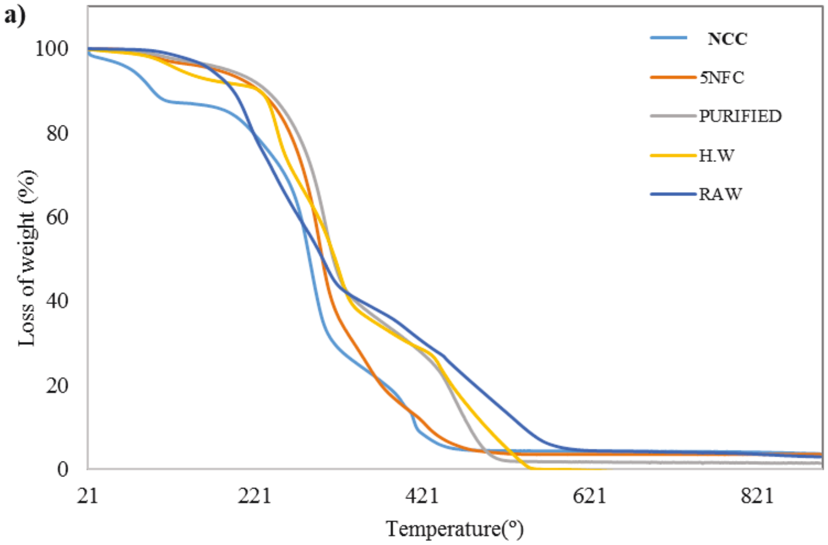


Figure 3. 7 FTIR peaks for raw, H.W treated, purified, NFC and NCC from Carrot.

Irrespective of the sample, the absorbance band appeared at 3400 cm^{-1} related to the stretching and bending vibrations of the OH groups present in cellulose. Slight spilt in 3400cm^{-1} have been observed (3250, 3300cm^{-1}) in the case of CNC this is mainly due to the rearrangement of the intramolecular hydrogen bonding between. Elsewhere reported the rearrangement is due to the removal of water (187). In the present study, this effect can be partially attributed to the removal of water prior to the FT-IR characterization. The asymmetric and symmetric stretching of C-H can be seen around 2900 cm^{-1}. The absorption band observed between 2950-3000cm^{-1} correspond to the trans-CH=CH- of beta carotene.(188) The intensity of the carotene band was higher in the case of the raw carrot fibers. Whereas, it completely disappeared after bleaching stage. This can be ascribed complete removal of the carotene during bleaching stage. Regardless of the sample, the band at 1638cm^{-1} was linked with O-H bending vibrations of the absorbed water.(140) The peak appeared at 1250cm^{-1} was related to the C-O stretching of aryl group present in lignin. It is noteworthy that this peak was completely absent after bleaching with hydrogen peroxide. This indicates after bleaching most of the lignin and carotene were removed. The peak projecting at 1730 cm^{-1} represent the stretching of C-O present in acetyl group and uranic ester groups in HC or ester groups present in the carboxylic group of ferulic and p-coumaric acids of lignin and/or hemicellulose.(189) Nevertheless, absence of this peak can be seen after alkali or prior to the acid hydrolysis owing to the removal of HC.

3.5.3.3 TGA

Thermogravimetric analysis was used to understand the thermal stability of the raw, chemically and mechanically treated carrot fibers. The results were shown in weight loss as a function of temperature in figure 3.8a and their corresponding DTG curves are shown in figure 3.8b. Irrespective of the sample an initial loss of weight of fibers was observed under 100°C, due to the presence of moisture. Raw carrot fibers have three different degradation temperatures at 200-210°C this can be attributed to the release of the non-polymeric materials like carotene and some aromatic hydrocarbons.(190) The second (250-260°C) peak associated with degradation of HC, pectin and lignin.(191) The third peak (300-310°C) correspond to the cellulose degradation.(191,192)



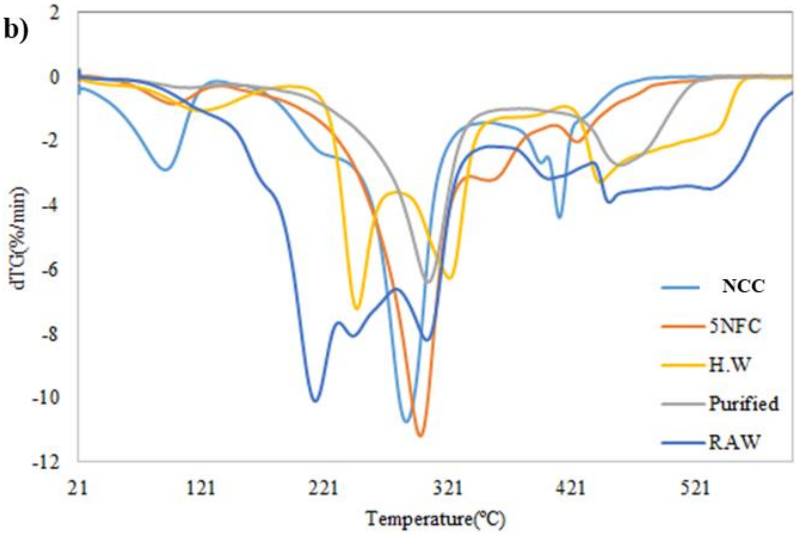


Figure 3. 8 a) TGA curves b) dTG curves for raw, H.W treated, purified, NFC and NCC from Carrot.

However, the first peak observed at 200°C was diminished for hot water washed carrot fibers. This revealed that hot water wash could remove carotene and the results were also in agreement with that of FT-IR. But in the case of the bleached and 5NFC fibers the first (200°C) and second (250°C) degradation peak were disappeared. This can be ascribed to the significant removal of the lignin, HC and pectins. The results can be clearly seen in the DTG curves shown in figure 3.8b). It is interesting to note that the main cellulose degradation temperature for 5NFC is less compared to raw, H.W and bleached. This might be due to the ball milling process; elsewhere reported fibrillation process can decrease the thermal stability partially.(193) Whereas in the case of the NCC the onset degradation started from 160-200°C due to the sulfate groups present in the NCC prepared by sulphuric acid hydrolysis.(194) Certainly, these results revealed that the non-cellulosic materials exhibit the lower thermal stability compared to cellulose.(195)

Regardless of the sample the degradation temperature starting from 350-730°C, correspond to the residue char. Though, this char residue is higher in the case of the raw fibers compared to the H.W and bleached carrot fibers. The existence of the ash and lignin in the raw carrot fibers was the reason behind the increased residue amount or char fraction at higher temperatures.(196) In fact, due to the pyrolysis lignin produces more residual char than cellulose. Importantly, ash does not degrade at high temperatures due to this the residual weight is higher. This residual weight is the characteristic of the carbon containing fibers.(140,197) Additionally, the char fraction of NCC is slightly high compared to the raw, H.W and bleached fibers this might be due to the flame-retardant sulphate groups.(194) This char fraction is very less in the case of the 5NFC since there is no sulfate groups and lignin, which is the source for the high char residue.

3.6 PREPARATION OF NANOCELLULOSIC FILMS

The nanocellulosic films (NCFs) were prepared by simple casting evaporation. Generally, NFC flocculates due to the strong hydrophilic interactions however, in the present study authors prepared NFC along with hemicelluloses, which helped to improve the dispersion. Whereas in the case of NCC, the suspension was homogenously dispersed due to the electrostatic repulsion between the nanocrystals, which was endorsed by the sulphuric acid hydrolysis. After casting, the visual appearance of the films was shown in the figure 3.9. The thickness of the films was in between the 20-40µm.

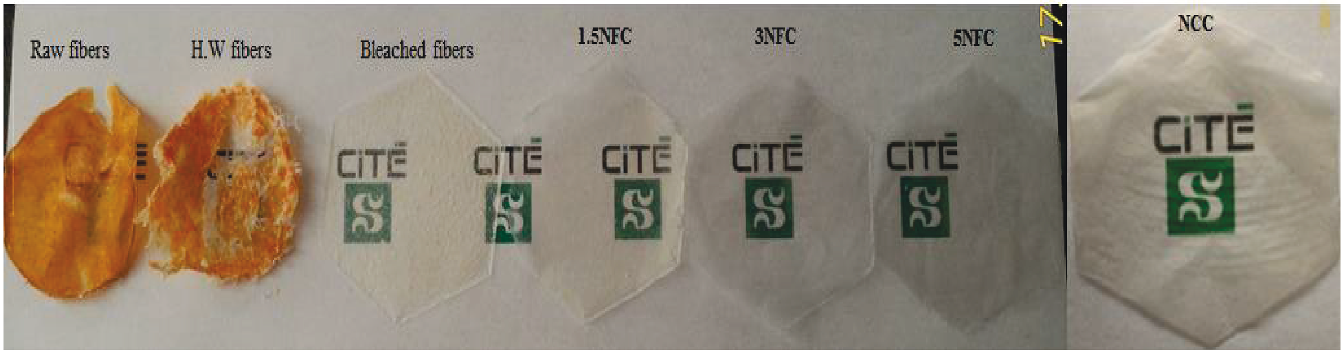


Figure 3. 9 Visual aspect of the films prepared with raw, H.W, bleached, 1.5NFC, 3NFC, 5NFC and NCC (from left to right).

The NCFs prepared with raw and H.W carrot fibers were not transparent. However, the film formed by bleached sample was hazy. Nonetheless after ball grinding process the films were transparent and the transparency increased while increasing the ball milling time as seen in figure 3.10. The NCC film was the most transparent owing to the higher crystallinity. The flexibility of the NCFs of NFC was more than that of NCC film which can ascribed to the fact that NFC has flexible fibril structure whereas NCC contains only rigid crystalline structure.

3.6.1 OPTICAL PROPERTIES OF NANOCELLULOSIC FILMS

The transparency of the films was studied using UV-visible spectrophotometer. As mentioned in literature review, the degree of fibrillation can be assessed by the capacity of the films to scatter the visible light. In fact, the more the light scattering the less is the transparency. After ball milling process the transparency increased. Indeed, the film surface became smoother with increasing fibrillation time. Thus, the light reflection caused by the rough surface was reduced and the transparency increased from 1.5 to 5 NFC. The transparency of 5NFC was increased by 25% than the raw film. The CNC film was highly transparent as seen in the figure 3.10. The transparency in this case is close to 50% which is 20% higher than the 5NFC film. This could be attributed the highly crystalline property of CNC.

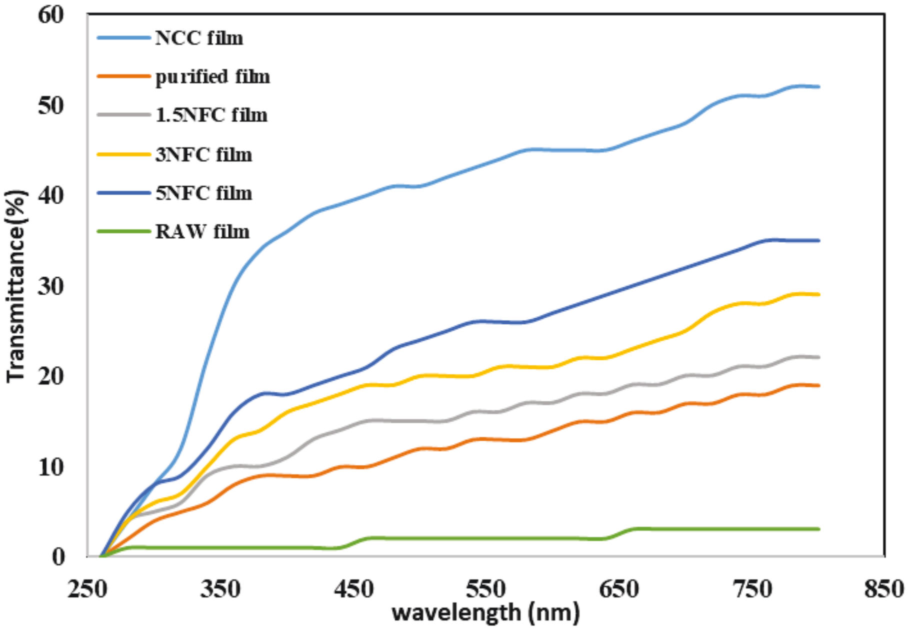


Figure 3. 10 UV transmittance spectra for Nano films of NFC and NCC from Carrot.

3.6.2 MORPHOLOGY OF NANOCELLULOSIC FILMS

Figure3.11 shows the SEM images of the NCFs of NFC (a, b and c) and CNC (d). The cross-section of the corresponding films was also investigated and the micrographs are shown in figure3. 11e-h. The surface morphology of the raw and bleached films is shown in S2 in the supporting information. The figure shows the random distribution of nanofiber network and they illustrate the porosity in the network for 1.5 and 3 NFC. While in the 5NFC the porosity was very less, which showed the highly dense network due to high fibrillation time as explained in the fibrillation assessment section. Whereas in the case of the CNC film, the vastly thick network can be seen due to the presence of the rod like structured nanocrystals and it can be seen in the inserted image in figure 3.11d. The neat arrangement of ordered chiral nematic structure can be seen in the case of CNC films. Irrespective of the sample, the cross-sectional micrographs indicate the lamellar organization of the nano fibers and nano crystals. Such NCF can be used in different applications like electronics, packaging and advanced materials.

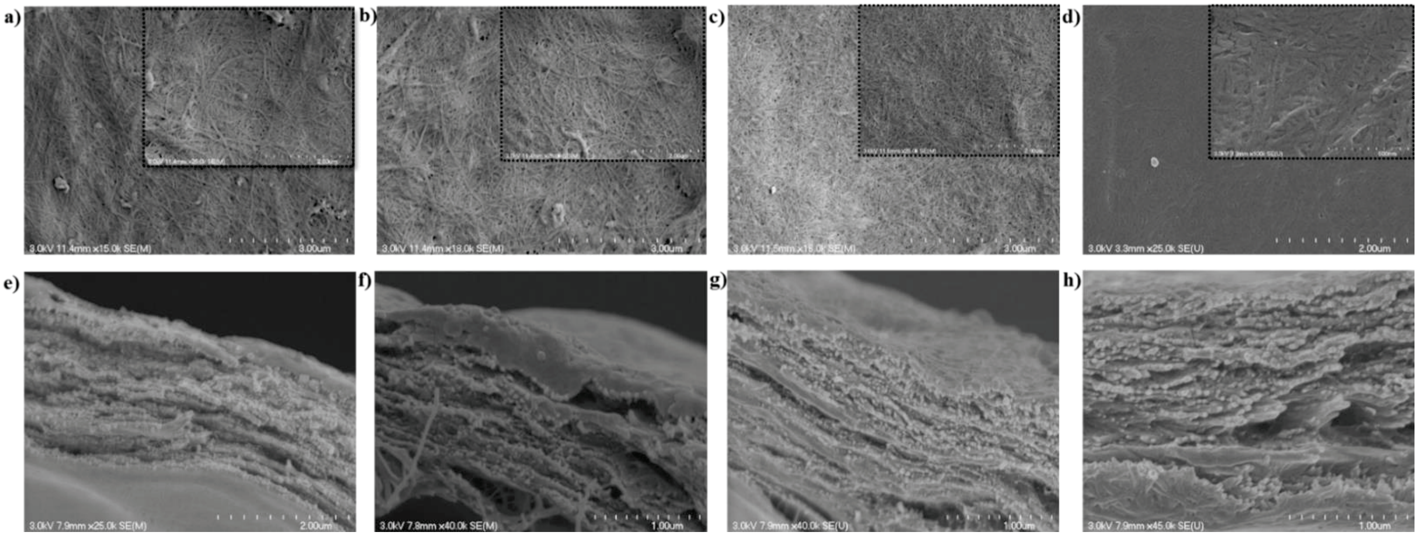


Figure 3. 11 SEM images of surface and cross section of a) and e) 1.5 NFC b) and f) 3NFC c) and g) 5NFC d) and h) NCC Nano films respectively.

3.6.3 TENSILE PROPERTIES OF NANOCELLULOSIC FILMS

The mechanical properties of the carrot nanocellulosic films prepared with 5NFC was measured and compared with previously reported values. The young's modulus and tensile strength of the nanocellulosic films prepared from carrot 5NFC was 1.2 GPa and 23.6 MPa respectively. The results obtained from previous studies and carrot NCF was reported in table 3.2. The previously reported values were higher than that of carrot NCF from current study. This might be due to several reasons like preparation method, source of the nanofibers and type of the nano fibers used in the preparation of the films. Elsewhere reported the quick drying process can enhance the mechanical properties of the nanocellulosic films.(198) Kristin Syverud et al. reported the preparation method of the films could also influence the mechanical behaviour of the films.(199)

Table 3. 2 Mechanical properties of various nanocellulosic films and comparison with carrot nano film

Sample name	**Preparation process**	**Young's modulus (GPa)**	**Ultimate Tensile strength (MPa)**	**Elongation at break (%)**	**Reference**
Carrot NFC film	Casting	1.02 ± 0.2	23.6 ± 6.2	2.7 ± 0.6	Present study
Carrot NFC film	Filtration + Pressing	12.2 ± 1.3	243 ± 28	8.7 ± 0.7	(34)
Hardwood-NFC film	Filtration + hot press	8.1 ± 0.7	121 ± 16	7.9 ± 0.8	(198)
Wood flour NFC film	Filtration + hot press	13	223	-	(Nogi et al. 2009)
Spruce MFC film	Filtration + Casting	15.7 ± 1.3	104	5.3 ± 1	Syverud and Stenius 2009)

3.7 CONCLUSION

In this study, residue of the carrot pulp was used to produce the nanocellulose. Simple and effective bleaching process (hydrogen peroxide) was used to purify the carrot pulp. The purified carrot pulp has shown unusual spring and classical fibers. Effective removal of the non-cellulosic materials was verified by the FT-IR and TGA results. Bleached pulp was used to extract the nano fibrillated and nano crystalline cellulose by mechanical and chemical process. The diameter of prepared NFC and NCC was in the range of 2-18 nm and 8-46 nm respectively as evidenced by the AFM and TEM. The resulted NCC aspect ratio was in between 9-18. The crystalline properties of the NFC (69%) and NCC (78%) has shown high in crystallinity. Nanocellulosic films prepared with carrot NFC and NCC demonstrated high transparency. The morphology of the nanocellulosic films shown the lamellar (helical) arrangement of the nanofibrils and crystals. The mechanical properties of the nanocellulosic films was low compared to the literature this might be due to the different preparation method of the nanocellulosic films.

CHAPTER 4

ENHANCEMENT OF SURFACE PROPERTIES OF THE NANOCELLULOSIC FILMS BY TiO_2 SOL-GEL COATING

4.1 RÉSUMÉ

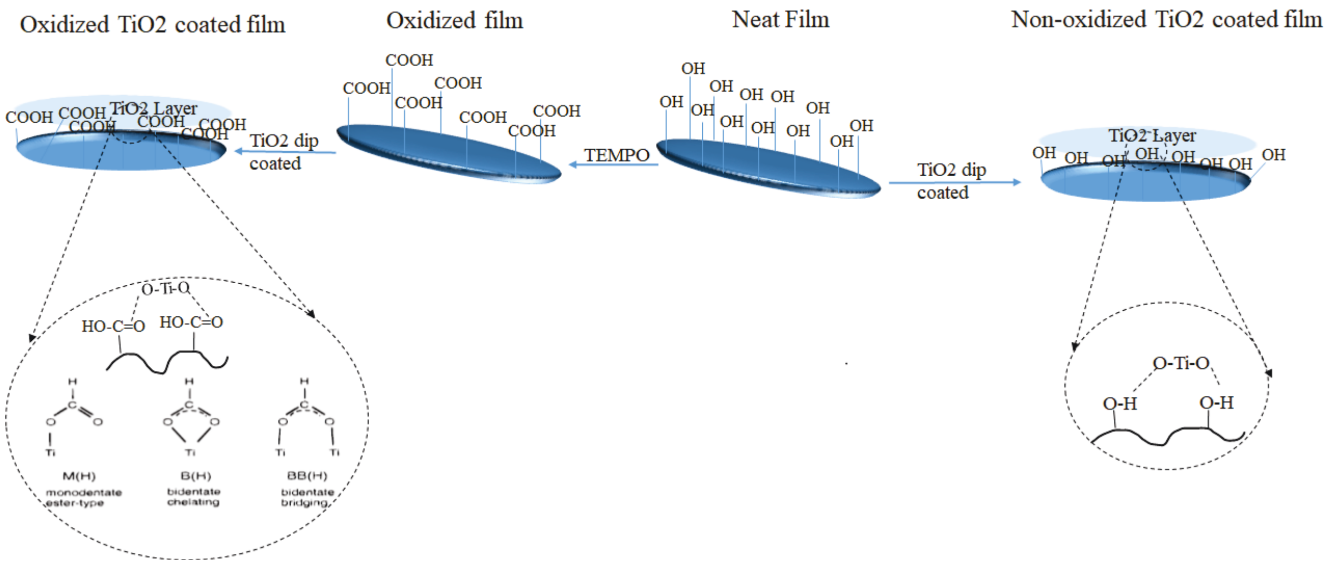
L’intérêt mondial pour la recherche sur les biomatériaux s’intensifie en raison de leurs propriétés mécaniques, physiques, barrières et leur biodégradabilité. Dans ce contexte, des films de nanocellulose (NCF) hautement percolés ont été préparés par filtration et procédé de pressage à chaud. En outre, la surface non-modifiée des NCF préparés a été oxydée en utilisant du 2, 2, 6, 6-tétraméthylpipéridine-N-oxyle (TEMPO). Les NCF non-modifiés puis oxydées ont été revêtues de dioxyde de titane (TiO_2) par technique sol-gel par revêtement par immersion. Le NCF revêtu de TiO_2 a été séché à 65 °C pendant deux heures, puis traité à 95 ° C pendant une heure pour former une couche de TiO_2 à la surface des films. L’effet du revêtement de TiO_2 sur le NCF non-modifié puis oxydé a été caractérisé par microscopie électronique à balayage (MEB), ultraviolet (UV), spectroscopie infrarouge à transformée de Fourier (FT-IR), taux de transmission de l’oxygène (OTR) pour comprendre les propriétés optiques, fonctionnelles et barrière des NCF. La mesure de l'angle de contact a montré que la nature hydrophobe des films revêtus de TiO_2 non oxydé et revêtus de TiO_2 oxydé augmentait considérablement, avec un angle de contact passant de 89 ° à respectivement 41 ° et 29 °. En particulier, les propriétés barrières et les propriétés optiques des films revêtus de TiO_2 ont été considérablement améliorées par rapport à celles des films NCF purs non-modifiés. Il est aussi important de noter que la résistance à la traction et l'élasticité des films NCF revêtus de TiO_2 ont été considérablement améliorées par rapport aux films NCF purs non-modifiés. Idéalement, ces films revêtus peuvent être des alternatives valables pour les applications dans l’emballage.

4.2 ABSTRACT

The global research interest towards biomaterials is growing due to their mechanical, physical, barrier and biodegradable properties. In this context, highly percolated nanocellulose films (NCF) were prepared by filtration and hot pressing process. Further, the prepared neat NCF surface were oxidized using 2, 2, 6, 6-tetramethylpiperidine-N-oxyl (TEMPO). The neat and oxidized NCF were coated with Titanium dioxide sol-gel (TiO_2) by dip coating. The TiO_2 coated NCF was dried at 65ºC for two hours and then treated at 95ºC for one hour to form the TiO_2 on the surface of the films. The effect of TiO_2 coating on neat and oxidized NCF was characterized by means of scanning electron microscopy (SEM), ultra violet (UV), Fourier transform infra-red spectroscopy (FT-IR), Oxygen transmission rate (OTR) to understand the morphological, optical, functional, and barrier properties. The contact angle measurement showed that the hydrophobic nature of the non-oxidized TiO_2 coated and oxidized TiO_2 coated films were increased drastically from 89° to 41° and 29° respectively. Notably, the barrier and optical properties of the coated films were significantly improved compared to that of the neat NCF films. Importantly, the tensile strength and elasticity of the TiO_2 coated NCF films were improved considerably compared to neat NCF. Ideally, these coated films can be validated for the packaging applications.

Keywords: Nanocellulosic films, Barrier properties, TiO_2 coating, surface properties and TEMPO oxidation.

4.3 GRAPHICAL ABSTRACT



4.4 INTRODUCTION

With eternally growing quest towards the sustainability, scientists and industries are looking to replace the plastic materials by the renewable materials (200). In this framework, Cellulose is an ideal candidate due to their abundance, low cost, mechanical and biodegradable properties (10). Cellulose is a natural material exist in plant cell wall. There are two remarkable nanomaterials which can be produced from cellulose and are classified as nanofibrillated cellulose (NFC) and cellulose nanocrystals (CNC) (201). The nanofibrillated cellulose can be prepared by different methods i) pre-chemical treatment followed by mechanical treatment ii) chemical treatment iii) mechanical treatment. CNC can be obtained by the acid hydrolysis of the cellulose fibers (10). NFC holds long fibrils with the combination of both amorphous and crystalline regions of cellulose. While CNC contains the solid crystalline regions of the cellulose.

Of late, the industrial production of NFC is predominantly increased all over the world due to its commendable properties like high mechanical properties, low density, low cost and biodegradable nature. Hence, the researchers and industries are concentrating more on this remarkable nanomaterial. NFC exists in different forms like suspension, hydrogels, aerogels, films and powder (20). NFC is suitable for vast range of applications and not limited to packaging, building, paints, personal care products, polymer nanocomposites and electronics (202). This is mainly due to their remarkable optical and barrier properties thanks to their web like network (127). The films prepared with NFC are translucent and express great flexibility along with better barrier properties compared to the regular petro-based polymers. Hence NFC based materials are ideal for food packaging application (203). NFC films can be prepared in different methods such as casting evaporation, filtration followed by hot press etc.(199).

Nanocellulosic films (NCF) are considered as the rival for petroleum based polymers and NCFs are the best replacement for the plastics for example, those used in packaging, thin films etc. In this context, there are some extensive studies to improve the barrier and anti-microbial properties of NCFs such as surface modification, chemical grafting with some anti-microbial active molecules (204).

Recently, nanocellulose films with inorganic materials coating or blending made a huge impact on the mechanical and barrier properties (205). Few interesting strategies were used to improve the barrier properties. CNC reinforced with carboxymethyl cellulose (CMC) films plasticized with glycerine (206) claimed considerable progress of mechanical properties. In some other study nanocellulose- inorganic talc hybrid films were prepared by vacuum filtration method. The results shown remarkable improvement in tensile strength and Young’s modulus. The films possessed with good oxygen barrier properties nevertheless films are not resistant to high moisture content (207). Elsewhere reported that NC/nanoclay (montmorillonite (MTM)) composite films were developed and shown significant improvement in transparency and oxygen barrier properties (208). In some other work self-standing nanocellulose films were produced by three different regioselective oxidation along with further derivatization treatments and films shown enhancement of transparency (209). NC films interface was coated with residual lignin and improved mechanical and barrier properties were reported (210). Interesting study on NFC/titania nanoparticles hybrids formation in aqueous media was studied. However, the results shown the mechanical and optical properties were diminished due to an inhomogeneous and agglomeration cross nanostructure formation (211).

The objective of the present study is to understand the influence of the TiO_2 coating on the surface of nanocellulose films before and after TEMPO oxidation. The films were prepared by filtration followed by hot pressing for the evaporation of water. The neat films were oxidized with TEMPO and coated with TiO_2 sol-gel. For comparison neat and non-oxidized TiO_2 coated films were also characterized to understand the mechanical properties, water absorption, morphological, optical and barrier properties.

4.5 MATERIALS AND METHODS

4.5.1 MATERIALS

Commercial NFC was obtained from University of Maine, USA as 3.5 wt. % suspension. TEMPO, Sodium bromide (NaBr), Sodium perchlorate (NaClO) and hydrochloric acid (HCL) were procured from Sigma Aldrich. Titanium isopropoxide, isopropanol, glacial acetic acid used for TiO_2 coating were also purchased from Sigma Aldrich.

4.5.2 METHODS

4.5.2.1 PREPARATION OF THE NANOCELLULOSIC FILMS

The commercial NFC suspension (3.5 wt. %) was diluted to 0.5 wt. % with distilled water and then filtered using Buckner funnel/flask set up and then filtered nanocellulose wet cake was hot pressed at 90°C for 30 minutes.

4.5.2.2 TEMPO OXIDATION OF THE FILMS

The oxidation of the films was done by using TEMPO. For 1g of the NCF, 20 mg of TEMPO is dissolved in 100 mL distilled water and 483 mg of NaBr is added under stirring and 495 mg of NaClO is added to the solution. HCl is used to adjust pH to 10. The films were then immersed in this solution for 10 seconds and washed with plenty of distilled water to stop the oxidation on the surface of the NCFs. The oxidised films were then dried at room temperature before characterization.

4.5.2.3 TIO$_2$ SOL-GEL PREPARATION

In order to the coat the NCFs, TiO$_2$ sol-gel was prepared in two stages as described below and the entire process was completed under inert atmosphere of argon purging.

Step-1:

In order to prepare the TiO$_2$ sol-gel, Titanium isopropoxide (TIP) was used as precursor. In a three neck round bottomed flask, 0.02 mol of TIP was added to 50 ml of 2-isoproponal under constant stirring. Then, 0.01 mol of trimethylamine was added and stirred for 5min.

Step-2:

In a beaker, 200 ml of 2-isopropanol was taken and to this 0.3 mol of glacial acetic acid and 2.88 ml of distilled water were added. The solution was stirred well for 10 minutes. The solution 2 was slowly introduced to the solution 1, mixed well under vigorous stirring and the argon gas was purged until a stable solution was obtained. The mechanism of TiO$_2$ sol-gel (212) was shown in figure 4.1.

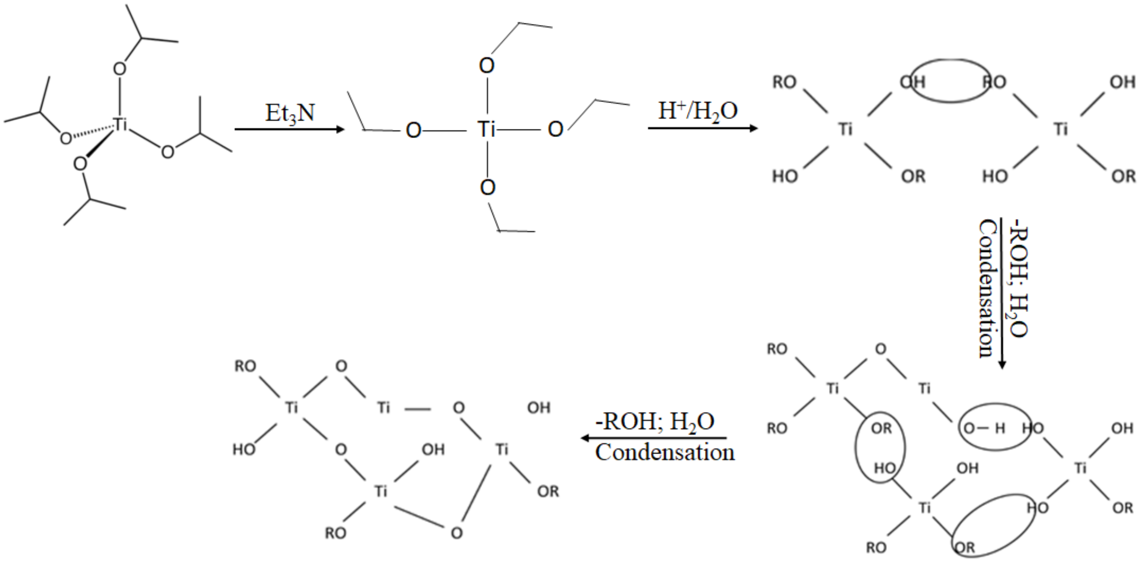


Figure 4. 1 Mechanism of TiO$_2$ Sol-gel

4.5.2.4 DIP COATING OF THE FILMS

The prepared Nanocellulosic films were coated with TiO_2 sol-gel by machine dip coating.

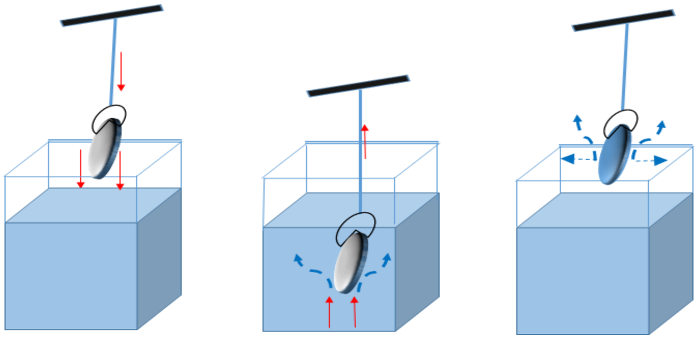


Figure 4. 2 Machine dip coating mechanism of nanocellulose films

During the Machine coating films were cut into 4x4 cm (Maximum size limit for machine coating) then dip coated by the sol-gel with the average withdrawn speed of 10 mm/min. The films were then oven dried at 65°C to remove the excess solvents and heated to 95°C to form titanium dioxide layer on the surface.

4.5.2.5 FOURIER TRANSFORM INFRA-RED SPECTROSCOPY (FTIR)

Fourier-transform infrared spectroscopy (FTIR) was used to understand the surface functionalization of NCF before and after oxidation with TEMPO. JASCO 4600 Spectrometer (Japan) equipped with an ATR PRO ONE reflection accessory was used. Spectra were recorded with a resolution of $4cm^{-1}$ in the range of $4000–600cm^{-1}$.

4.5.2.6 SCANNING ELECTRON MICROSCOPE (SEM)

The surface and cross sectional morphology of the neat and coated films were observed by using the SEM. Prior to that the samples were coated with gold to avoid charring due to electron bombardment. S-4700 scanning electron microscope (Hitachi, Japan) was used to capture the micrographs.

4.5.2.7 TENSILE TEST

Tensile properties of the nanocellulose films such as neat, oxidised coated and non-oxidised coated NCFs were measured according to ASTM D-638 by using a Zwick/Roell z050 machine equipped with 100N load cell. For each condition, at least 10 specimens were tested. The tensile tests were conducted at crosshead speed of 2mm/min, at relative humidity of 35% and room temperature (25°C). The samples were prepared by cutting 10mm length strips of the nanocellulosic films.

4.5.2.8 WATER ABSORPTION STUDY

The water absorption capacity of the films for neat, TEMPO oxidized, and non-oxidised coated films were checked. Throughout the study ASTM D570 regulations was followed. 10-mm-long specimens were cut, dried, and weighed prior to immersion in water at ambient laboratory conditions. The samples were immersed in water and removed from the water after every 1 hour, the dripped water was removed, and weighed during 76 hours. The water content at saturation in weight percentage (Ws) was calculated using the following equation:

$Ws = (P_S - P_d) / Pd \, X100 \, (\%)$

Where P_S and P_d are the sample weights in saturated and dry states, respectively.

4.5.2.9 WETTABILITY OF NCF

The coated NCFs hydrophobic nature was observed by using contact angle. Neat films contact angle was also measured for comparison of the end results. The films were immersed in water and studied using dynamic contact angle measurement.

4.5.2.10 LIGHT TRANSMITTANCE

The optical properties of the neat, oxidised and non-oxidised coated films were studied by means of UV-VIS spectrometer (Spectra max plus 384 from molecular devices, Canada). Each film was inserted into the cuvette and the light transmittance was checked with the cuvette as a background.

4.5.2.11 OXYGEN PERMEABILITY

The oxygen permeability of NCF was measured by using MOCON OX-TRAN (model 2/21) at 0% relative humidity at 23ºC. The surface area of the films was $1cm^2$ and prior to each measurement the films thickness was measured.

4.6 RESULTS AND DISCUSSIONS

Firstly, the films were characterized by FT-IR to understand the surface functionalization by using TEMPO. Secondly, the neat, non-oxidised and oxidised TiO_2 coated films were characterized to determine the influence of the coating on the surface properties. Often surface properties (such as wettability, water absorption study, OTR and optical properties) of films play vital role to govern the material suitability for the packaging applications. Further the morphological and mechanical properties of all the films were also studied and discussed in the following sections. The physical appearance of the TiO_2 coated films can be seen in Figure 4.3 a. The flexibility of the coated films remained the same like the neat film can be seen in Figure 4.3b.

Figure 4. 3 a) The physical appearance of non-oxidized and oxidized TiO_2 coated films (from left to right respectively) b) flexibility of the film after coating

4.6.1 SURFACE PROPERTIES OF NANOCELLULOSE FILMS

4.6.1.1 FTIR

Figure-4 shown the FT-IR of the Nanocellulose films (NCF) before and after oxidation in order to understand the surface functionalization. Neat Nanocellulose contains the primary hydroxyl groups and were oxidized by using TEMPO to obtain carboxylic groups on the surface of NCF. It is worth to note that after oxidation the FT-IR spectra shown significant change. Particularly, after oxidation new band is observed at 1735cm^{-1} (marked in figure-4) which is corresponding to the –C=O present in the –COOH (149). It is evident that the surface of the NCF was successfully oxidized by TEMPO. Irrespective of the sample different bands can be observed in marked place in figure-4.4 at 3350 cm−1 (O−H) and 2868 and 2970 cm−1 (C− H from −CH2−) (213). These peaks are attributed to hydroxyl groups and symmetric, asymmetric bands of the cellulose respectively. Regardless of the oxidation a peak can be observed at 1640cm^{-1} which is corresponding to the absorbed water, as it is certain that cellulose materials absorb water due to the presence of the hydroxyl groups (213).

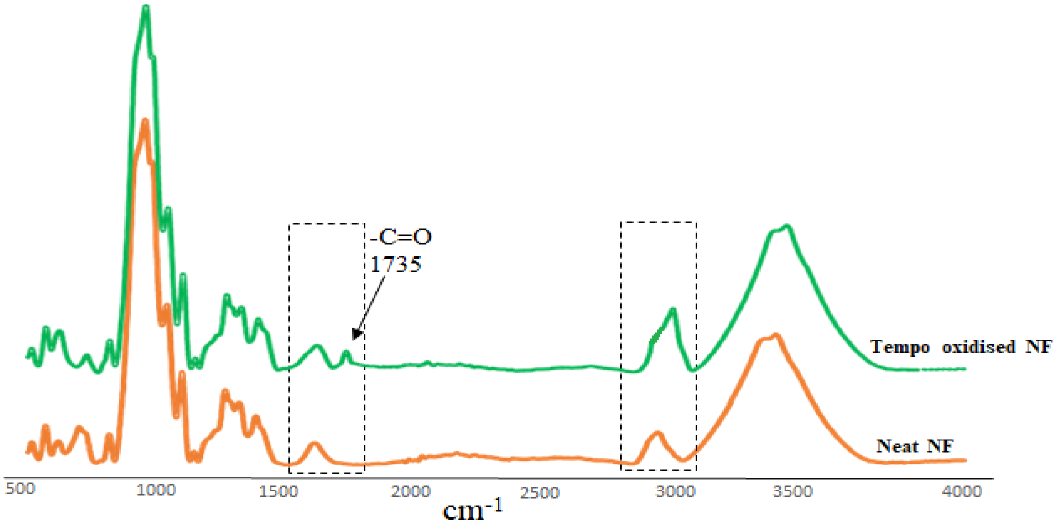


Figure 4. 4 FTIR spectra for neat (NCF-OH) and oxidized Nanocellulose films (NCF-COOH)

4.6.1.2 SCANNING ELECTRON MICROSCOPY

The surface morphology and cross sectional morphology of neat, NCF-OH TiO_2 coated and NCF-COOH TiO_2 coated films was studied by means of SEM. The results were shown in figure 4.5 and figure 4.6 respectively. Figure 4.5a showing the distinctive morphology of the neat nanocellulose film. The cellulose nanofibrils were entangled and formed dense web like network. The individual nanofibrils diameter was in between 50-200nm and their length was in few microns. The results can be seen from figure 4.5b. The NCF-OH TiO_2 coated films were shown in figure 4.5c & d. It is evident that the TiO_2 coated films were rough and TiO_2 layer completely concealed the surface of the cellulose nanofibrils network. Importantly, the TiO_2 layer was uneven and plenty of cracks can be seen (can be seen in marked places in figure 4.5c) this might be due to the lack of the covalent or non-covalent interactions between TiO_2 sol-gel and hydroxyls groups of the nanocellulose. Figure 4.5d showing the higher magnification of the NCF-OH TiO_2 coated film. The results showing the significant cracks and those cracks are exposing the nanocellulose network. Due to this poor layer formation on the surface these films are not stable at hydro conditions and it also evident from contact angle and water absorption study. Whereas in the case of NCF-COOH TiO_2 coated film (Figure 4.5e) the morphology was completely different to the fore mentioned sample.

The TiO_2 layer formation was homogeneous and there were no major cracks on the surface of the coated films. This might be mainly due to the Ti-Complexation such as bridging-linkage between TiO_2 and ester linkage (214). The mechanism shown in graphical abstract. However, the surface was rough and uneven due to the excess of the unreacted TiO_2 on the surface of the film. Figure 4.5f micrograph displays the high magnification of NCF-COOH TiO_2 coated film. It is worth to note that the surface was uniform and smooth. However, few cracks can be observed which might be due to the high electron bombardment on the surface of the film at high magnification.

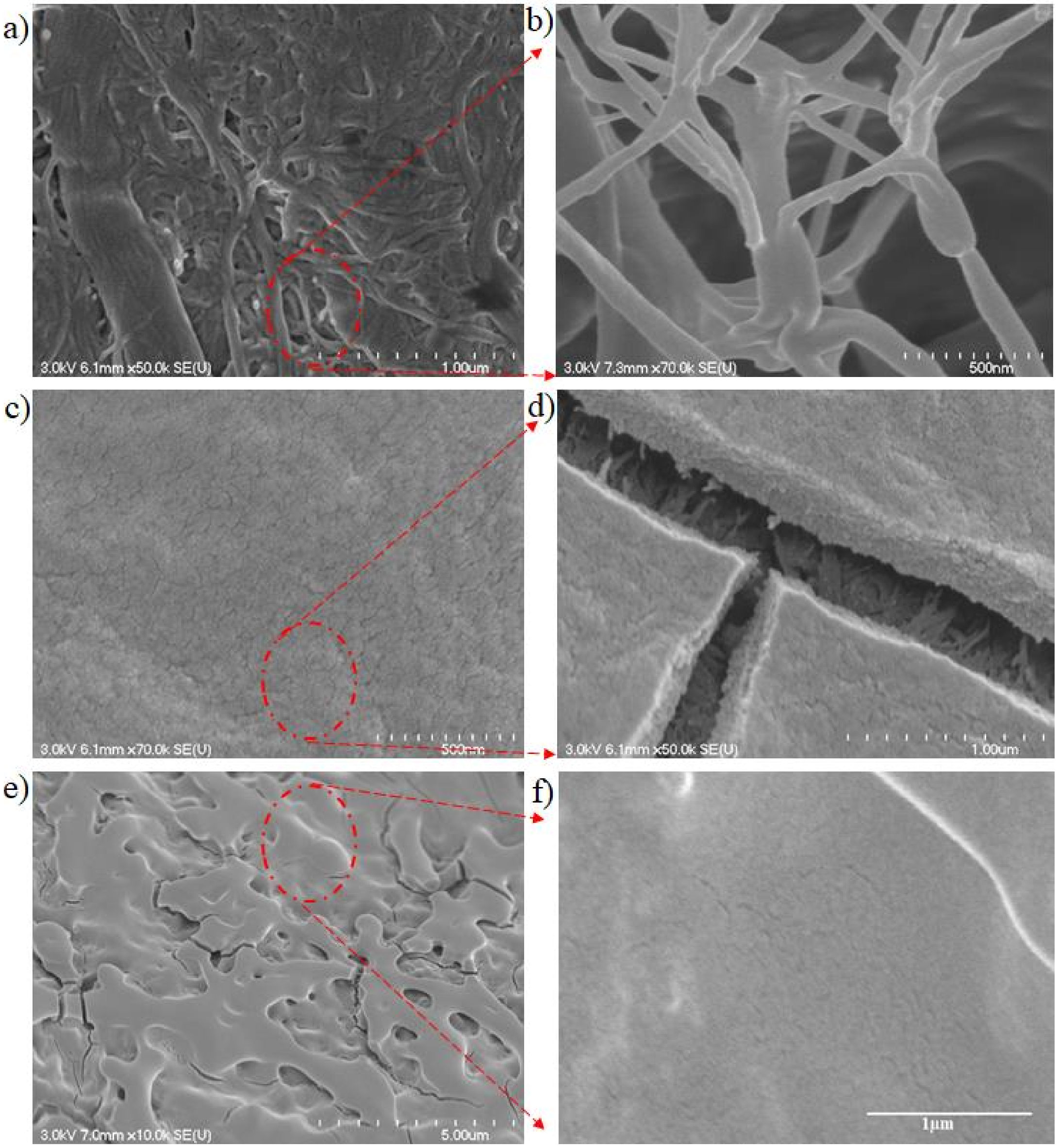


Figure 4. 5 SEM images of the a) and b) Neat nanocellulose film, c) and d) Non-oxidised TiO_2 coated film e) and f) Oxidised and TiO_2 coated nanocellulose film.

The cross-sectional morphology of the neat and TiO_2 coated nanocellulose film before and after oxidation was analyzed and the results are shown in figure 4.6. The results revealed that the nanofibrils were arranged in lamellar form regardless of the sample. This phenomenon can be attributed to the slow evaporation of water during the casting process. However, the TiO_2 coating for non-oxidised film was irregular that can be seen from figure 4.6b in the marked areas. Unlike the TiO_2 layer was uniform and continuous for oxidised TiO_2 coated film which can be seen in the marked places in top and bottom of the figure 4.6c.

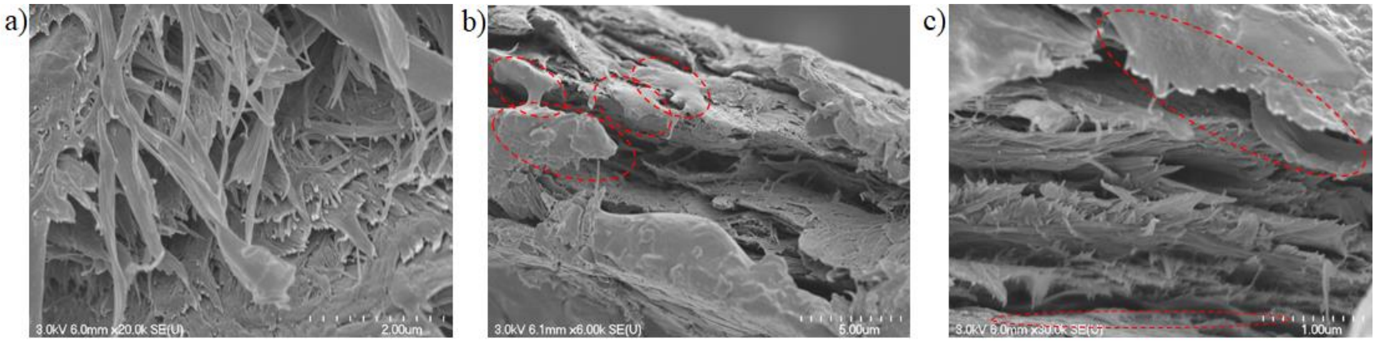


Figure 4. 6 SEM images for the cross-section of the a) Neat, b) Non-oxidized TiO_2 coated film and c) Oxidized TiO_2 coated nanocellulose film.

It is also evident from the surface morphology images, the TiO_2 was discontinuous. Whereas the oxidised coated films surface formed bridging linkage between the TiO_2 and the carboxylic groups (214) present on the surface of the nanocellulose film. It is worth to note that, irrespective of the coating the thickness of the coating was measured using SEM and the value was ranging from 175 nm- 200 nm.

4.6.1.3 WATER ABSORPTION AND BARRIER PROPERTIES

In order to understand the stability of the films water absorption study was done at room temperature. It is clearly evident from the results the water absorption capacity of the neat film was higher compared to that of non-oxidized and oxidized TiO_2 coated films. This behaviour is due to the hydrophilic nature of hydroxyl groups present in the nanocellulose. Initially the films water absorption capacity was gradually increased with respected to time during first 11h and then it was constant w.r.t time and regardless of the sample.

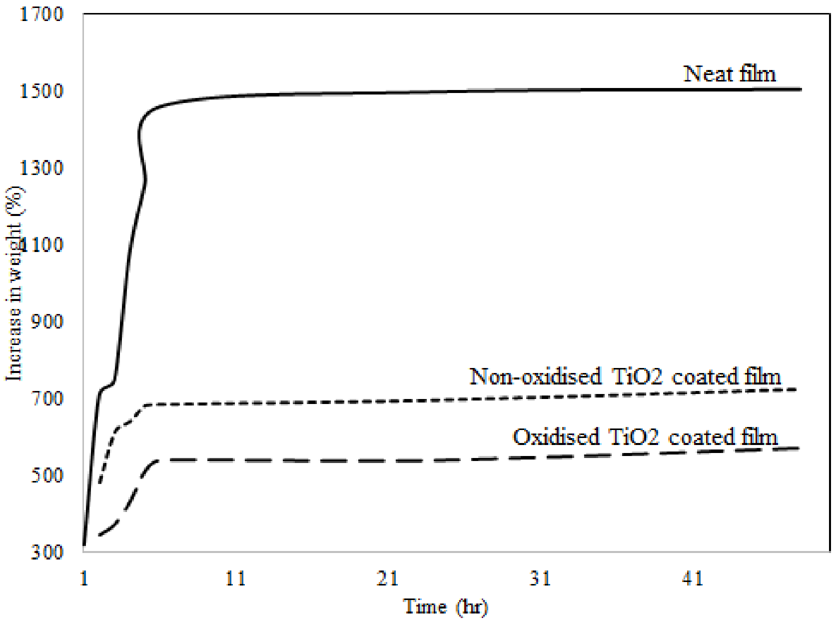


Figure 4. 7 Water absorption of Neat, non-oxidized and oxidized TiO2 coated nanocellulose films time (hr) with respect to the weight increase (%).

Whereas in the case of the TiO_2 coated non-oxidized film the weight was 750% less compared to the neat film this might be due to the influence of the TiO_2 coating on the surface of the film. Considerably 250% higher compared to TiO_2 coated oxidized film. This is mainly due to the discontinuous and irregular cracks present on the surface of the film. The water is passed through the cracks and fully absorbed by the nanocellulose. It is evident from the morphological observation by SEM. Predominantly, the oxidized TiO_2 coated film water absorption capacity was dropped 1000% and 250% compared to neat and non-oxidised TiO_2 coated film respectively. This phenomenon demonstrates the cohesion between the TiO_2 and the outer layer of the oxidized film. Thanks to homogeneous layer formation of TiO_2 on the surface of the nanocellulose film. Hence the hydrophobic nature of the TiO_2 coated oxidised film was increased compared to that of rest of the samples.

4.6.1.4 OXYGEN TRANSMISSION RATE (OTR)

In order to assess the gas barrier properties of the TiO_2 coated and neat films preliminary test of oxygen transmission rate (OTR) was conducted at relative humidity (RH) 0%. The neat film was shown around 375 cm^3.micron/m^2/day. For the TiO_2 coated non-oxidized and oxidized films the OTR value was significantly decreased to 56 and 52 cm^3.micron/m^2/day respectively.

Predominantly this is due to the laminar structure formation of the TiO_2 layer on the surface of the nanocellulose film. Interestingly the oxidized coated film barrier properties were improved compared to non-oxidized coated film this describes the strong bridging complexation between the nanocellulose and TiO_2. Further study on barrier properties of the TiO_2 coated films will be done at different relative humidity (RH) w. r. to oxidation time to understand the steadiness of the films.

4.6.1.5 CONTACT ANGLE MEASUREMENT

In order to understand the wettability of neat, non-oxidized TiO_2 coated and oxidized TiO_2 coated films were studied by dynamic contact angle measurement. The measurements were made using Wilhelmy method. The results in terms of advancing and receding contact angle was tabulated in Table 4.1. It is obvious that the neat film wettability is high (the θa-89° to θr-64°) compared to coated films due to the highly hydrophilic nature of the nanocellulose. Whereas in the case of the non-oxidized TiO_2 coated film advancing contact angle was decreased compared to that of the neat film. However, the receding contact angle was 41°. Significant change of contact angle was observed for oxidized TiO_2 coated film from 45° to 29°. This is mainly due to TiO_2 coating which concealed the hydroxyl groups on the surface of the nanocellulose film. The dynamic contact angle results agree with water absorption study.

Table 4. 1 The average contact angle (θ_a and θ_r) measurements of the films.

Name of the sample	Advancing contact angle (θ_a)	Receding contact angle (θ_r)
Neat film	89	64
TiO_2 coated non-oxidized film	53	41
TiO_2 coated oxidized film	45	29

4.6.2 OPTICAL PROPERTIES OF THE FILMS

The optical properties of the films are key for the packaging applications. In order to understand the transparency of the films UV-Visible spectrometry was used. It is well known that the nanofibrillated cellulose films are translucent due to the presence of the amorphous parts of cellulose (201). This will also lead to the high scattering of the nano fibrillated cellulose with visible light (201). The transmittance of the visible light for the neat film was less compared to coated films.

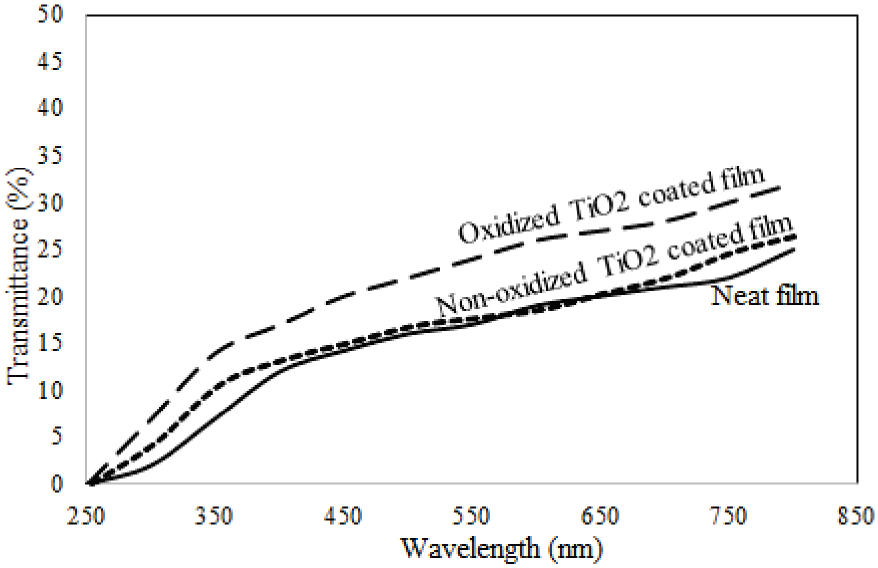


Figure 4. 8 Transmittance of the nanocellulose films in the UV-Visible region

However, the oxidized coated TiO_2 film transparency was high. This is mainly due to the TEMPO oxidation. During the oxidation process the surface hydroxyl groups were converted into carboxyl groups thus increasing the transparency (179). It is worth to note that the transparency of the oxidized TiO_2 coated film was 10% higher compared to neat and TiO_2 coated film due to TEMPO oxidation.

4.6.3 MECHANICAL PROPERTIES

The mechanical performance of the films for non-oxidized and oxidized TiO_2 coated films was investigated to understand the effective action of coating on the films and neat films also verified for comparison and the results are tabulated in Table 4.2. The primary goal of the coating of nanocellulosic film using TiO_2 was to improve its mechanical properties inorder to make it a suitable for packaging applications. The effect of TEMPO oxidation and the carboxylic acid groups and the TiO_2 coating on the mechanical properties was also an argument of interest. The tensile strength and the elasticity of the non-oxidized TiO_2 coated film was increased significantly when compared to that of the neat film. This can be attributed to the increased external strength provided by the coating. The elasticity might have increased because the force applied had to stretch the TiO_2 coated surface and since the fibers were covered by the thin coating the elongation time to reach the fiber was more when compared to the neat film, wherein the fibers were stretched immediately when force was applied. High mechanical performance was anticipated from oxidised TiO_2 coated film compared to that of the neat and TiO_2 coated film. In contrary, the mechanical properties were diminished compared to neat and TiO_2 coated films. This might be due to the fact that the TEMPO oxidation could have loosened and/or damaged the fibrous network of the nanofibrillated cellulose. Elsewhere reported that during the oxidation amorphous cellulose parts will dissolve and lead to untied network (179). This can be also an important factor for the diminishing the mechanical performance. It is worth to note that this is our preliminary study to understand the TiO_2 coating at different conditions. Owing to this, the oxidation time of Nanocellulosic films will be reduced by performing at different duration (2, 4, 6 and 8 seconds) for the comparison in our next study.

Table 4. 2 Mechanical properties of the nanocellulose films before and after TiO_2 coating

Name of the sample	**Young modulus (GPa)**	**Standard deviation**	**Tensilestrength (MPa)**	**Standard deviation**	**Elongation at break (%)**	**Standard deviation**
Neat film	1.66	0.28	117	10.4	9.3	7.1
TiO_2 coated non-oxidized film	1.56	0.39	123	8.66	12	3.0
TiO_2 coated oxidized film	1.32	0.45	103	4.59	9.4	1.1

4.7 CONCLUSION

Highly entangled nanocellulose films were prepared by filtration followed by hot press. Further, the neat films surface was functionalized to obtain carboxylic groups by using TEMPO. It is evident from FT-IR results that the surface was successfully oxidized. The oxidized NCF were coated with TiO_2 sol-gel to understand the surface properties and non-oxidized TiO_2 coated films were also checked for the comparison. Substantially, the surface properties were improved compared to neat and non-oxidized coated films. The surface and cross-sectional morphology of the oxidized TiO_2 coated films was homogeneous compared to non-oxidized, thanks to the bridging complexation between carboxylic groups and TiO_2. Importantly, the hydrophobic nature of the coated NCF was improved significantly and it is evident from the wettability and water absorption study. Ultimately, the oxygen transmission rate was considerably less for the oxidized TiO_2 coated compared to neat and non-oxidized TiO_2 coated films. Apart of this the optical properties of the TiO_2 coated films were increased associated to neat films. Despite of poor mechanical behaviour these films can be progressive approach for the development of the nanocellulose based materials for food packaging. In order to improve the mechanical performance few new strategies were excelled as follow up work for our current work.

CHAPTER-5

SINGLE STAGE PURIFICATION OF FLAX, HEMP AND MILK WEED STEM FIBERS AND THEIR PHYSICAL AND MORPHOLOGICAL PROPERTIES

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Accepted date: September 30, 2017

Current status: Published

Journal: International journal of polymer analysis and characterization

Citation: (8)

DOI : https://doi.org/10.1080/1023666X.2017.1387688

5.1 RÉSUMÉ

La biomasse agricole est une solution alternative aux bois tendres et durs classiques pour l'extraction de cellulose. Cependant, la valorisation de la cellulose est un défi pour les chercheurs car elle comporte plusieurs étapes. Dans la présente étude, des fibres brutes de lin, de chanvre et de tiges d‘asclépiade ont été purifiées en une seule étape en utilisant du peroxyde d'hydrogène dans l'eau. Par cette méthode, les auteurs ont réussi à extraire les fibres de cellulose purifiées sans endommager la longueur des fibres. Les fibres purifiées ont été caractérisées pour comprendre leurs propriétés thermiques, fonctionnelles, cristallines et morphologiques par analyse thermogravimétrique (TGA), spectroscopie infrarouge à transformée de Fourier (FT-IR), diffraction des rayons X (X-RD) et microscopie électronique à balayage (MEB). Les résultats en FT-IR ont montré une élimination efficace de la lignine. Une amélioration significative de la stabilité thermique a été observée par TGA. En parallèle, les observations au MEB ont montré une amélioration significative de la morphologie par rapport à celle des fibres brutes. Les résultats X-RD ont montré que le traitement n’affecte pas la cristallinité des fibres.

5.2 ABSTRACT

Agriculture biomass is an alternative possible solution for the extraction of cellulose, compared to the classical soft and hard wood. However, the valorization of cellulose is challenging for the researchers as it involves multiple steps. In the present study, the raw fibers of flax, hemp and milk weed stem fibers were purified in single step using hydrogen peroxide in water. By this method authors successfully extracted the purified cellulose fibers without damaging the fiber length. The purified fibers were characterized to understand the thermal, functional, crystalline and morphological properties by means of thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (X-RD) and scanning electron microscopy (SEM). The FT-IR results showed the effective removal of lignin and significant improvement in thermal stability was observed by TGA. Evidently, the SEM results showed significant improvement in the morphology compared to that of the raw fibers. X-RD results showed that the treatment does not affect the crystallinity of the fibers.

Keywords: Agriculture biomass, scanning electron microscopy, thermo gravimetric analysis, Crystallinity and morphology.

5.3 INTRODUCTION

According to the agriculture and agri-food Canada (AAFC), every year farmers are harvesting 11 million metric tons of biomass in Canada.(6) Mainly, this biomass is coming from different crops like wheat, flax, hemp, corn, durum, oats, barley, rye, canola, soybeans and rice. However, these crops are mainly cultivated for the food grains, oil and bioenergy production. The leftover of all these crops remained a huge problem for the farmers before moving to next cultivation. Some of these harvested stems are widely used in various low value applications like fabrics, ropes and twines. Only 42% of the biomass is used and remaining are simply burnt in the fields. Therefore, farmers, manufacturers, researchers and entrepreneurs are keenly looking for high value added products from this biomass.

The main composition of the agriculture biomass is cellulose, hemicellulose, lignin and others (pectins, ash, minerals, fat and waxes). However, cellulose is the major component in the crop biomass (like flax, hemp, rice, wheat, etc.) varying from 50-72%.(215) From the last decade the interest in annual plants is increasing due to the ecological values and renewable materials. These annual plant fibers are widely used in the thermal insulation, bio-composites and packaging application as an alternative for the regular fillers like glass and carbon fibers.(215) Though, the valorization of pure fibers is challenging.

Certainly, improving the purification methods of these annual plants will open the gateways for multitude applications. The pure cellulose from annual plants will allow the extraction of nanocellulose (micro fibrillated (MFC), nano fibrillated (NFC) and nanocrystalline cellulose (NCC)). These materials are remarkable in mechanical properties, which in turn will permit to develop the high value added application. Nowadays, nanocellulose is used in many applications like packaging, paints, concretes, nanocomposites and biomedical applications.

In this study authors used flax, hemp and milk weed stem fibers based in Canada to extract the pure cellulose by aiming the nanocellulose as end product. Nevertheless, this study is restricted to the purification of the annual plant fibers. Flax fibers used was industrially processed raw fibers from Biolin research, Canada. Typically, it is called as *Linum usitatissimum* (L. Usitatissimum) means ‘most useful’. In general, Flax is a self-fertilized crop and it can adopt to any kind of climates in the world. According to flax council of Canada, every year flax crop is cultivated from

400,000 to 800,000 hectares. It is well known that Flax seeds are widely used in food and feedstock.(216)

Hemp is classified as *Cannabis sativa L.* and it is widely cultivated in Canada under certain regulations for the seed and fiber purpose. Hemp fibers are robust, durable and long from 15-50 microns and the cellulose content is about 70% and importantly low lignin content.(2,215) Another annual plant used here is milkweed and it is often called as *Asclepias Syriaca L*. This crop is cultivated twice a year mainly for the floss.(217,218) The density of the floss is very low (0.9 g/cm3) contrasting to any other plant fiber and it has great demand as a filling material in jackets and for nonwovens.(219–221) There is no information on the usage of the milkweed stems for the production of cellulose fibers. Previously, Yang group from USA attempt to characterize the fibers from bark of milkweed.(3) Nevertheless, the aim of this study is completely different from the above.

Previously reported research articles on flax, hemp and milkweed fibers show that they were purified by multiple steps. The most frequent methods to purify the plant fibre is acid and alkali treatment to eliminate the pectins and hemicelluloses. Further bleaching process was used to remove the lignin to obtain pure white fibers. Elsewhere, Kaushik et al. reported the extraction of cellulose fibers from wheat straw by means of both chemical and steam explosion.(4) Previously, Mohini sain et al. reported the purification of cellulose fibers from flax and hemp. The method involves multiple steps like i) refining fibers were treated with 0.05M hydrochloric acid at 70ºC for 2h. The fibers were cooled and then neutralized with ammonium hydroxide. ii) the fibers were bleached by using the sodium chlorite and acitic acid at pH 3-5 for 4h at 75ºC.(2) In another study, milkweed stem was treated with 0.5M alkaline solution at 80ºC for 30 min and further washed fibers were dipped for 5min at 60ºC with 10% (w/ w) nitric acid and 10% (w/w) chromic acid solutions after initiating the reaction for one 24h.(3,5)

In the current study, the authors purified the stem fibers of flax, hemp and milkweed in single stage using hydrogen peroxide. Further, the purified fibers were characterized to understand the functional, crystalline and morphological properties by means of FT-IR, X-RD and SEM.

5.4 EXPERIMENTAL

5.4.1MATERIALS

Refined raw flax (*Linum usitatissimum)* fibers used in this study was supplied by Biolin Research Saskatoon, Canada. Hemp (*Cannabis sativa L)* fibers was supplied from Biolin Research (Saskatchewan, Canada). Milkweed (*Asclepias Syriaca L)* fibers used were picked from Montérégie agriculture fields in Canada. Before using, the milkweed stem bark was removed and retted for three months to attain the dry fibers. Hydrogen peroxide, 30% solution was procured from VWR Anachemia.

5.4.1.1 PURIFICATION OF RAW FIBERS

The residual fibers were placed in the solution of 7.5 % Hydrogen peroxide (H_2O_2) in DI water. The fibers were cooked at 65ºC without stirring for 4h. The fibers were then washed with plenty of water and dried in oven for 24h at 50^{o}C before characterization. In general, hydrogen peroxide is widely used for bleaching process to remove the lignin. Elsewhere reported, high concentration of hydrogen peroxide can lead to the oxidation of the cellulose(222) hence reducing the degree of polymerization of cellulosic chains. For this reason, in the present study authors optimized the concentration of H_2O_2 7.5%. The initial and final weight of the fibers is reported in table 5.1.

Table 5. 1 Initial and final weight of the flax, hemp and milkweed fibers

Name of the source	Initial weight (g)	Yield (g)	Yield Percentage %
Flax	1	0.72	72
Hemp	1	0.88	88
Milkweed	1	0.76	76

Hydrogen peroxide directly oxidizes the lignin and then dissolve in the water.(223) It is worth to note that the residual fibers used in this study were refined through industrial process due to their huge demand for different applications. Whereas in the case of milkweed stem, was broken into small pieces as it is not refined fibers. The visual appearance of flax, hemp and milkweed fibers can be seen in the figure 5.1a. The raw residual fibers were in brown and yellow color. However, after treating the fibers with hydrogen peroxide significant transformation in color was observed as shown in the figure 5.1b. The fibers were completely white due to the delignification of the fibers. The inserted images shown in figure 5.1a & b is the powder of the milkweed stem for better visual appearance before and after treatment. It clearly shows that, the treatment of hydrogen peroxide with milkweed stem was not only on the surface it also penetrated the inner cell walls and removed the lignin. The possible reaction mechanism of hydrogen peroxide with lignin is shown in figure 5.2.

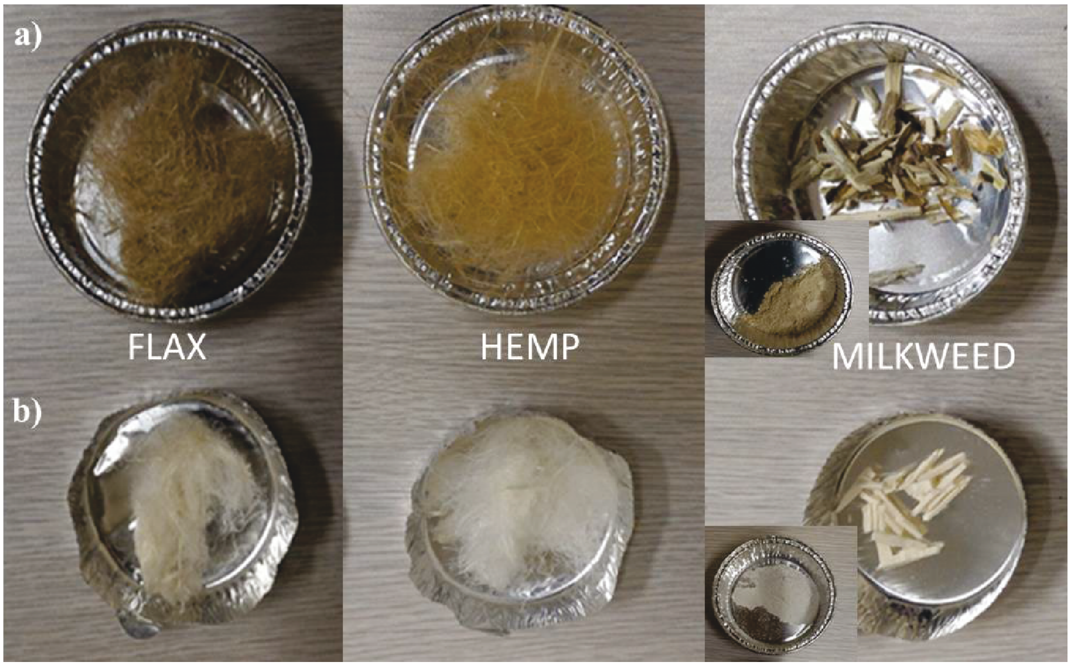

Figure 5. 1 Visual impression of flax, hemp and milkweed fibers respectively a) before b) after treatment.

$$H202 + HO_2^- \longrightarrow {}^{\bullet}OH + H2O + {}^{\bullet}O_2^-$$

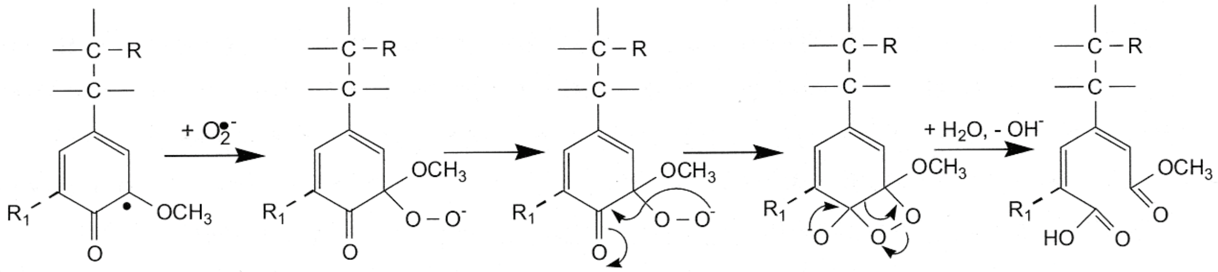

Figure 5. 2 Reaction mechanism between hydrogen peroxide and lignin

5.4.2 METHODS

5.4.2.1 SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy (SEM) was used to characterize the fibers before and after purification to understand the morphology. The samples were coated with gold to avoid the charring caused by electron bombardment. The SEM images were captured by using S-4700 scanning electron microscope (Hitachi, Japan).

5.4.2.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY

Fourier-transform infrared spectroscopy (FTIR) was performed on flax, hemp and milkweed fibers before and after purification to understand the functional properties of the fibers. The samples were characterized by using a JASCO 4600 Spectrometer (Japan) equipped with an ATR PRO ONE reflection accessories. Spectra were recorded with a resolution of 4cm^{-1} in the range of 4000 to 600 cm^{-1}.

5.4.2.3 THERMOGRAVIMETRIC ANALYSIS

The thermal degradation of the fibers was monitored by thermogravimetric analysis (TGA) with TA instruments-Q500. The loss of weight and differential thermogravimetric as a function of temperature was recorded at a heating rate of 10^{o}C/min in the temperature range of 20–900^{o}C under oxidizing atmosphere.

5.4.2.4 X-RAY DIFFRACTION

X-ray diffraction (XRD) was performed on flax, hemp and milkweed fibers before and after treatment. The fibers were grounded by using ball miller and the resultant powder were analysed by using the A Philips X’Pert diffractometer equipped with a general area detector diffraction system with Copper Kα radiation (λ = 1.542 A^{o}), 2θ (Braggs angle) was from 7 to 40^{o}. Each sample was measured twice to check the repeatability.

5.5 RESULTS AND DISCUSSION

5.5.1 MORPHOLOGICAL PROPERTIES OF THE FIBERS

Scanning electron microscopy was used to understand the morphology of the flax, hemp and milkweed fibers before and after treatment. The resulted images can be seen in the figure 5.3, 4 &5. Henceforth, before and after treated fibers will be termed as BT (before treatment) and AT (after treatment) with respect to source. In the case of flax fibers, before treatment the bundles of the fibers were assembled together and it can be seen in the figure 5.3a. The surface of the fibers was completely rough because of the lignin. Importantly, lignin and hemicelluloses were acting as non-covalent binding agent between the cellulose fibers(224) and it can be seen clearly in marked place in the figure 5.3b. The individual fibers of BT-flax are shown in figure 5.3c, the fibers are completely irregular and not smooth (can be seen in inserted image). Remarkably, AT-flax fibers have significant difference. It reveals that the hydrogen peroxide process can remove the lignin. The fibers were detached as seen in figure 5.3d. The marked places in the figure 5.3e shows that the surface of the detached fibers was smooth compared to BT-flax fibers. The individual cells of the cellulosic fibers can be seen clearly in figure 5.3f and the inserted image shows that the AT-flax fibers are clean compared to BT-flax.

It is worth to note that the diameter of the AT-flax fibers was between 8-10µm as seen in the marked place in figure 5.3f. The results are matching with previously reported.(225) This results show that the hydrogen peroxide treatment can be very significant in delignification process.

Figure 5.4(a-f) shows the SEM images of the hemp fibers. The micrographs of BT-hemp fibers shown rough and uneven bundles of fibers due to lignin. The results can be seen in the arrow marked places from figure 5.4(a-c). The inserted image in figure-4c shown the impact of the lignin at higher magnification. The hydrogen peroxide treated hemp fibers can be seen from figure 5.4(d-f). The lignin content was completely reduced and AT-hemp fibers roughness was not observed. The bundles of the fibers were broken up to individual fibers. The diameter of the hemp fibers was between 12-15µm. These results are in agreement with previous reported values.(114,226)

Figure 5(a-f) shows the morphological images of the milkweed stem before and after treatment. The untreated milkweed stem surface was covered with lignin, hemicellulose and other non-cellulosic constituents of the plant. The results can be seen in the figure 5a&b. The bundles of the milkweed fibers can be seen in the figure 5c the surface was serrated before the treatment. However, after treating with hydrogen peroxide morphology of the stem was completely transformed. The treatment removed most of the substances present on the surface. Interestingly, the individual cells of the milkweed stem cell wall can be seen clearly in marked areas from figure 5 d-e.

The individual fibers of the milkweed stem were separated after the treatment that can be seen in the figure 5f. The inserted image shows the surface of the individual fiber is clean and uniform results can be seen in figure-5f. The diameter of the individual fiber was between 10-14µm. The results are matching with previously reported.(3)

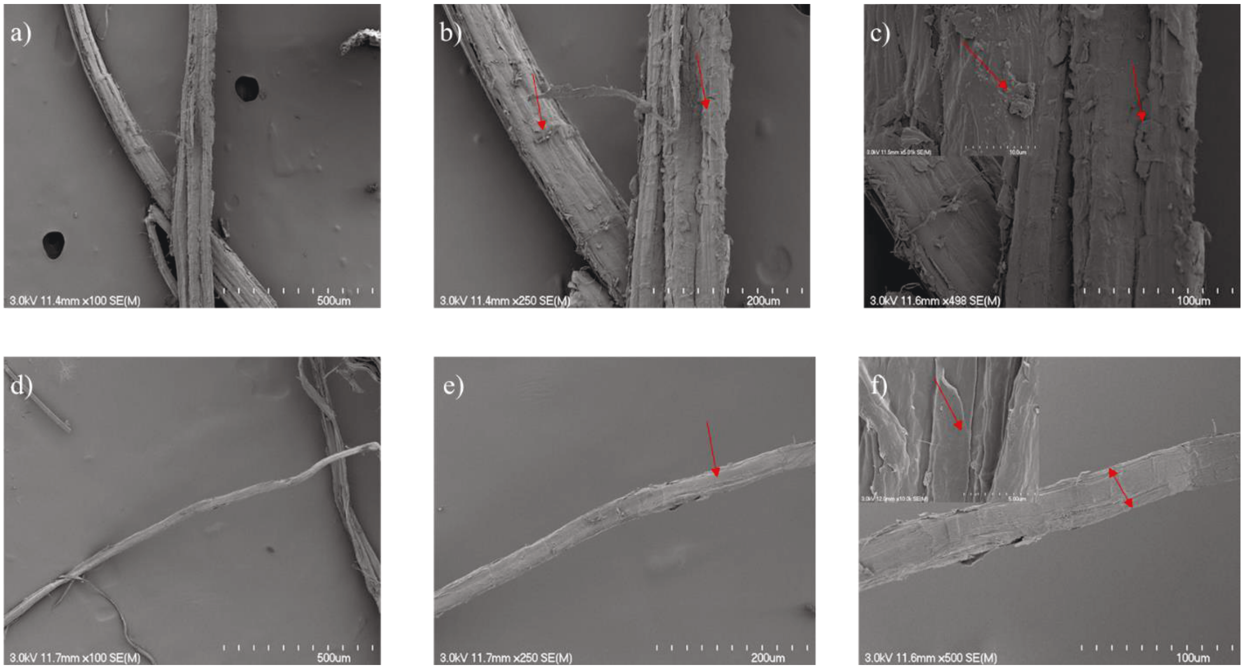

Figure 5. 3 SEM images of flax fibers a) Bundles of untreated fibers b) surface of untreated fibers c) Individual untreated fibers d) Bundles of the fiber after treatment e) surface of treated fibers f) individual fibers after treatment.

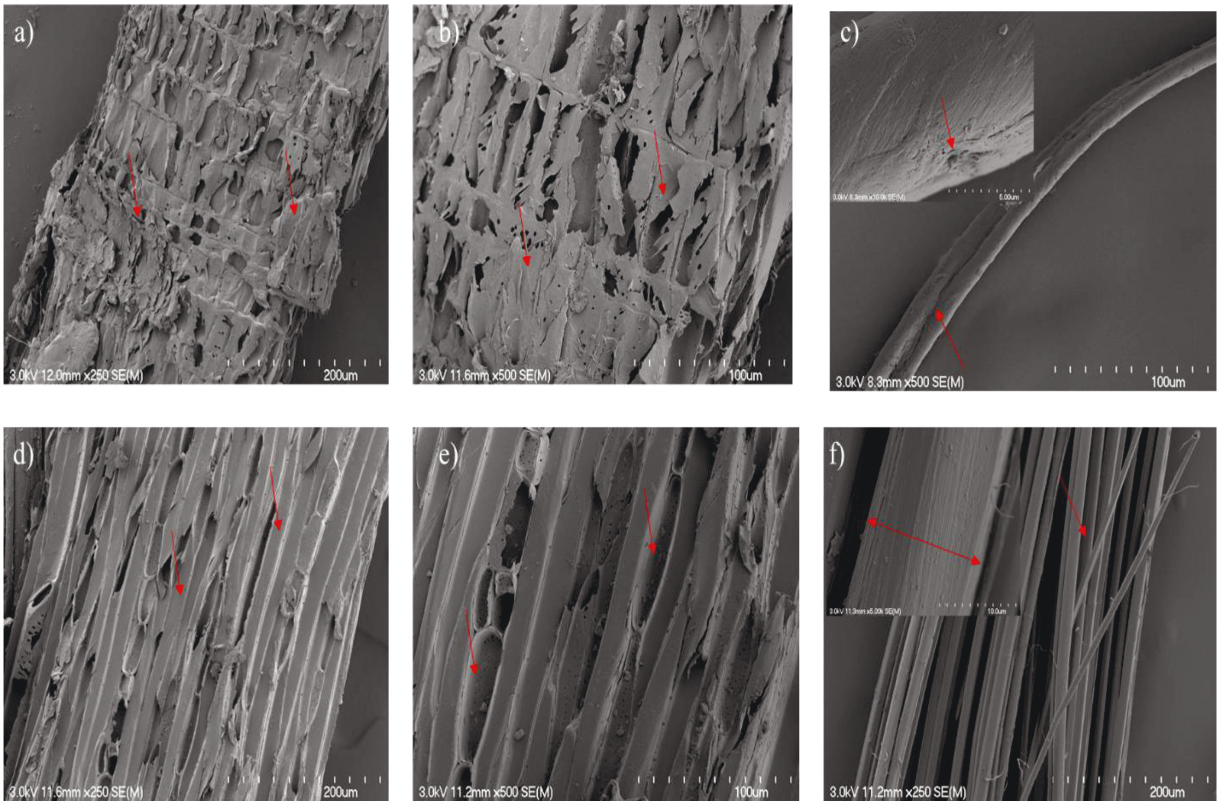

Figure 5. 4 SEM images of hemp fibers a) Bundles of untreated fibers b) surface of untreated fibers c) Individual untreated fibers d) Bundles of the fiber after treatment e) surface of treated fibers f) individual fibers after treatment

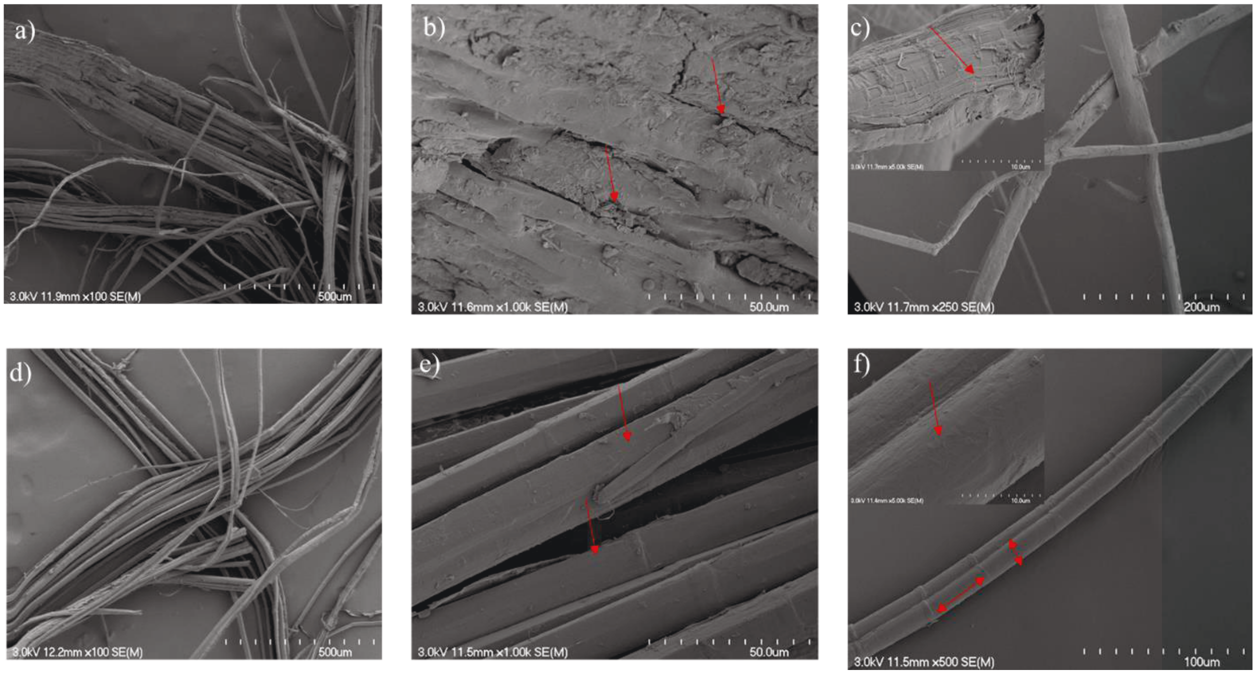

Figure 5. 5 SEM images of milkweed fibers a) piece of untreated stem b) surface of untreated stem piece c) Individual untreated fibers d) piece of stem after treatment e) surface of treated stem f) individual fibers after treatment.

5.5.2 FT-IR CHARACTERIZATION

FT-IR was used to determine the functional properties of cellulose fibers before and after treatment of three different sources. The results are shown in figure 5.6a-c, flax, hemp and milkweed respectively. The peaks present at 3400 cm^{-1} and 1635 cm^{-1} regardless of the source are the stretching and bending vibrations of the hydroxyl groups present in the cellulose in both raw and purified cellulose fibers.(140) The peak at 1735 cm^{-1} shown for BT-flax, hemp and milkweed spectrum ascribed to the presence of the ferulic and P-coumeric acid in lignin and the existence of the hemicellulosic acetyl and uronic ester groups. However, this peak intensity was comparatively low for AT-flax, hemp and milkweed spectra due to the absence of lignin.

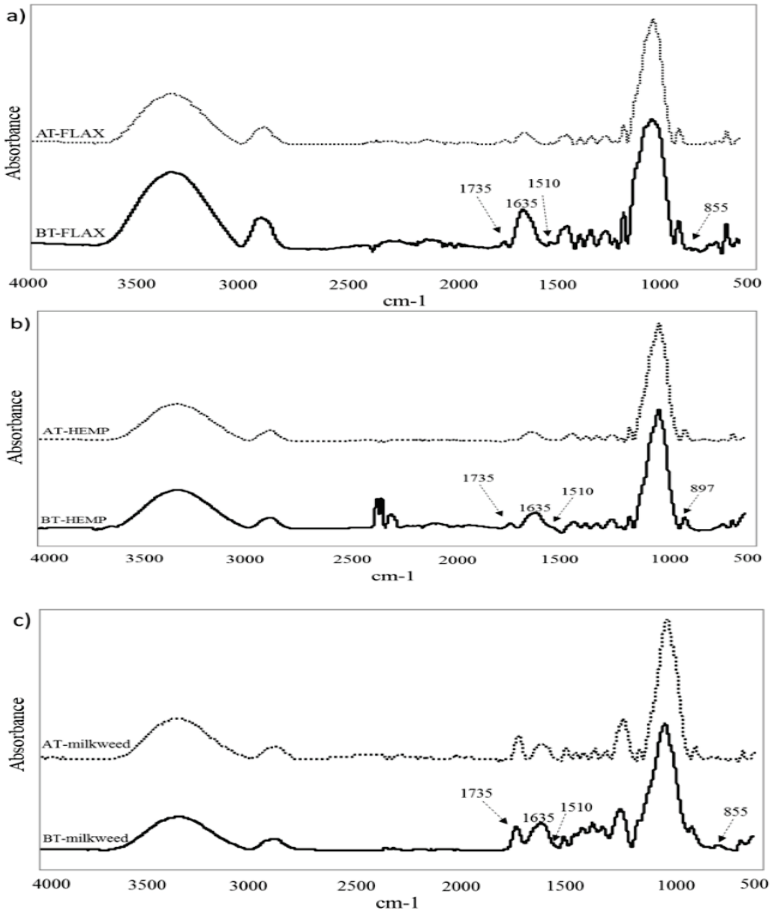

Figure 5. 6 FT-IR spectra of a) Flax b) Hemp c) Milkweed fibers before (solid line) and after treatment (dotted lines).

The presence of the 1510 cm^{-1} is corresponding to the aromatic stretch of -C=C- present in lignin.(189,227) The twin peak present at 815 and 855cm^{-1} represents the presence of methoxy groups attached to the aromatic ring prevailing in the lignin.(228) Whereas in the case of the AT-flax, hemp and milkweed the peak disappeared which revealed the removal of the lignin with hydrogen peroxide treatment. Regardless of the treatment the peak at 1061 and 897 cm^{-1} are related to C-O, C-H stretching and rock vibration of the cellulose respectively.(139,140) Prominently, in the case of the AT-milkweed the peak intensity at 1735 cm^{-1} increased and inversely the peak at 1635cm^{-1} decreased compared to the BT-milkweed fibers. This signified the presence of high amount of hemicelluloses compared to that of flax and hemp.(229)

5.5.3 THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis was used to understand the thermal stability of the fibers before and after treatment of the flax, hemp and milkweed fibers. The results are shown in figure 5.7(a-c) representing the loss of weight against temperature and the inserted image shows the relevant Dtg curves with respective to the source. Regardless of treatment the initial weight loss was observed from 50-150ºC for flax, hemp and milkweed corresponding to the moisture present in the fibers due to the hydrophilic behavior of the ligno-cellulosic materials.(140) The decomposition of the raw fibers was observed in several steps which shows the presence of the different components in the fibers. In general, the initial decomposition of the hemicelluloses and lignin arise between 200-270°C. The main weight loss will occur between 320-450°C due to the cellulose Glycosidic chains rupture present in the cellulosic materials.(230,231) While in the case of the flax, hemp and milkweed raw fibers the decomposition started at 238, 240 and 234ºC respectively due to the presence of pectins, lignin and hemicelluloses. The main degradation was observed at 318, 324 and 297ºC for flax, hemp and milkweed respectively, which can be attributed to the pyrolysis of cellulose.

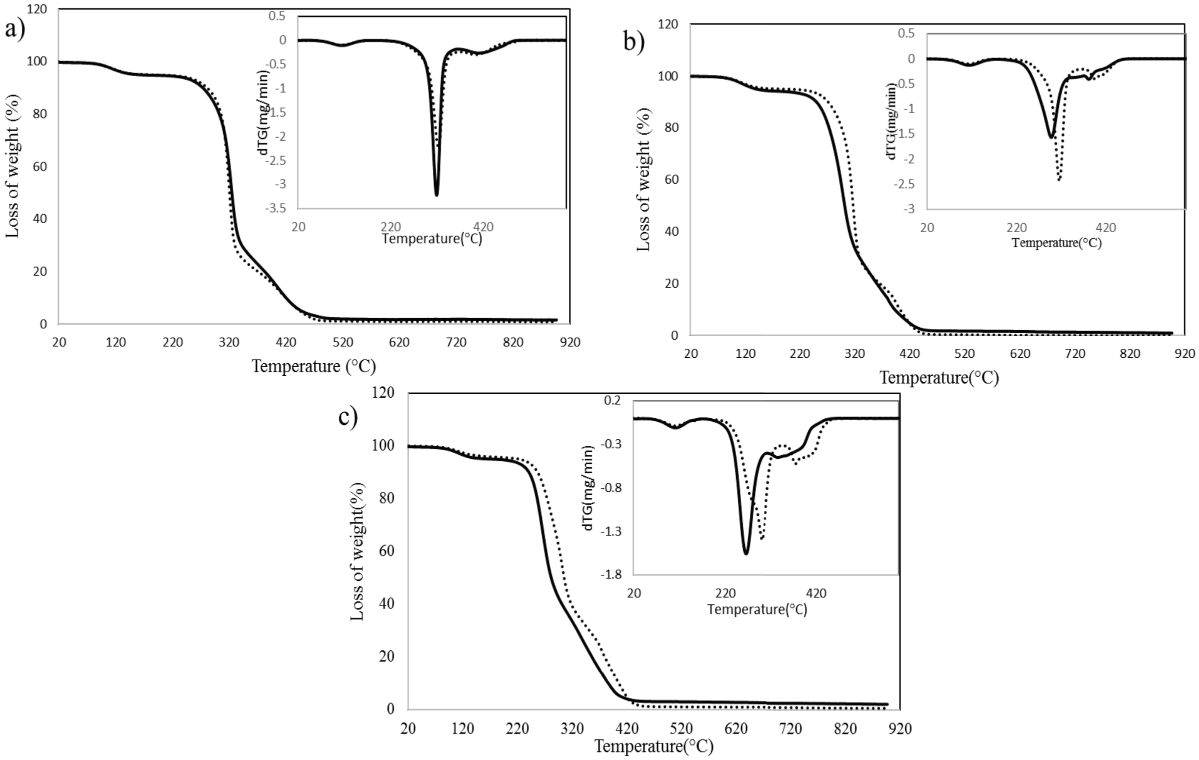

Figure 5. 7 TGA and Dtg curves of a) Flax b) Hemp c) Milkweed fibers before treatment (solid line) and after treatment (dotted lines).

However, after treatment the initial degradation temperature was improved to 248, 272 and 241ºC compared to the raw fibers which confirmed the elimination of lignin, pectins and limited number of hemicelluloses and the results can be seen clearly in the inserted image from figure5.7(a-c). The second degradation of the treated fibers was significantly improved like 324, 316 and 302ºC for flax, hemp and milkweed respectively. The degradation temperature values related to the weight loss for BT and AT flax, hemp and milkweed is reported in Table 5.2. Evidently, the results show that the thermal stability of the AT fibers was improved compared to that of the raw fibers due to the removal of amorphous materials like lignin, hemicellulose etc.

Table 5. 2 The relative weight loss at Different Temperatures for BT and AT flax, hemp and milkweed

Relative weight loss (%)	Flax Temperature (ºC)		Hemp Temperature (ºC)		Milkweed Temperature (ºC)	
	BT	AT	BT	AT	BT	AT
20	293	298	269	288	253	267

40	318	319	292	312	270	291
60	330	328	310	316	290	309
80	362	354	351	359	355	376

5.5.4 X-RAY DIFFRACTION

X-ray diffraction was performed on the BT and AT flax, hemp and milkweed fibers to understand the influence of the hydrogen peroxide treatment on crystalline structure of the cellulose. The results are shown in figure 5.8(a-c) for flax, hemp and milkweed respectively. Irrespective of the source and treatment, the diffractograms showed the presence of the crystalline cellulose. The diffractograms for untreated fibers at 2θ=16.4°, 22.6°correspond to the (110) and (002) (140,232)crystallographic reflections respectively. The intensity of the crystalline peaks increased after treatment. Interestingly, AT fibers diffractograms shows the new peak at 34.4° along with 16.4° and 22.6°these peaks are conforming the cellulose-I.

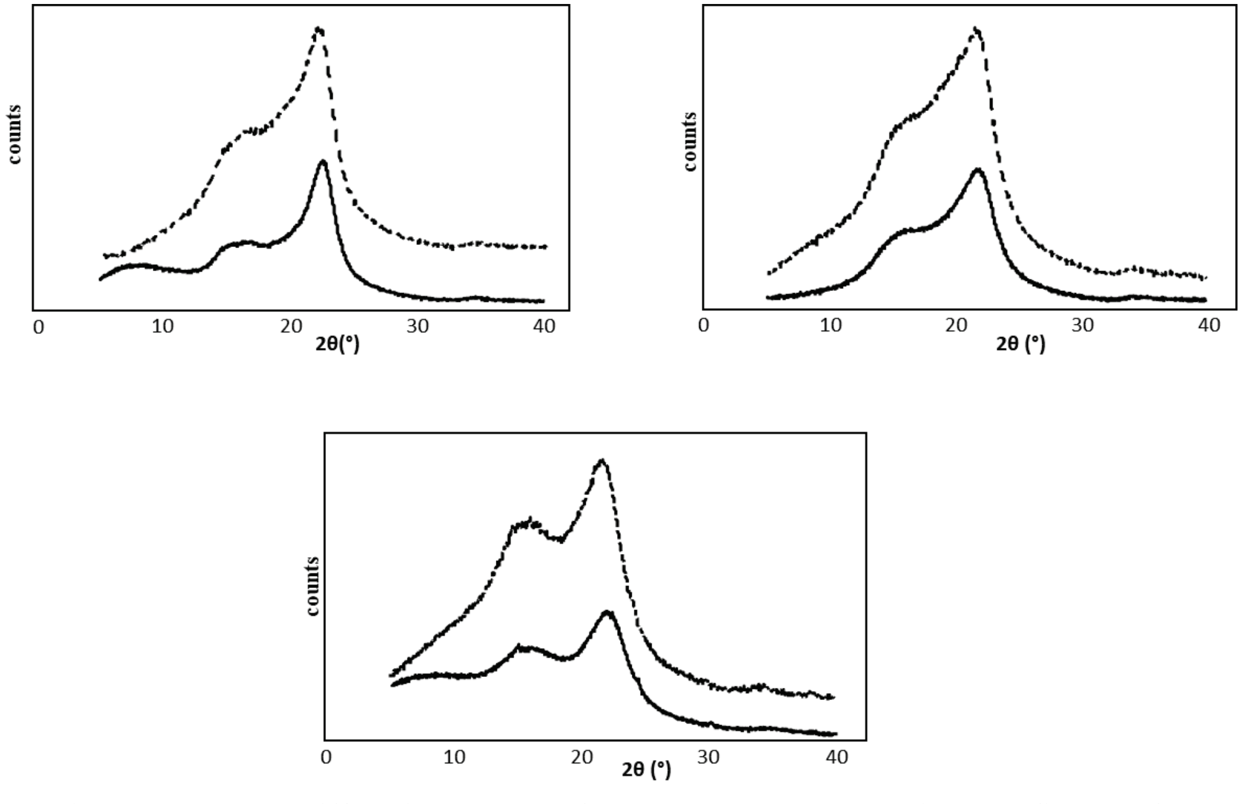

Figure 5. 8 X-ray diffraction patterns for a) Flax b) Hemp c) Milkweed fibers before treatment (solid line) and after treatment (dotted lines).

Before hydrogen peroxide treatment, cellulose fibers were embedded with amorphous materials like hemicelluloses, lignin, pectins and waxes. However, after treatment substantial amount of amorphous materials was removed due to this the diffractograms showed the more intense peaks at (110) and (002) reflections. Nevertheless, after treating the fibers with hydrogen peroxide the crystalline patterns remained the same owing to the fact that H_2O_2 treatment had no influence on the crystalline structure of cellulose. The crystallinity of the cellulose is very important parameter for many applications like packaging, composites etc. The degree of crystallinity of the fibers before and after treatment was determined by using the following equation. (140,232)

$$I_C = I_{002}-I_{110}/I_{002}$$

Ic= degree of crystallinity, I_{110} is the minimum intensity at 2θ= 16.4° and I_2 is the intensity associated with the crystalline region of cellulose (2θ = 22°). The degree of crystallinity for BT flax, hemp and milkweed fibers was 56 %, 46 % and 42% respectively. For AT flax, hemp and milkweed fibers the degree of crystallinity increased to 62, 54 and 45% respectively. This can be attributed to the significant removal of lignin, hemicelluloses and pectins.

5.6 CONCLUSION

Lignocellulosic materials from agriculture biomass have great tendency to replace the classical sources adopted by the industries. In this study, we reported a simple and single step process to purify the raw flax, hemp and milkweed fibers by using hydrogen peroxide. The SEM results showed the morphology of fibers were individualized and the surface was smoothened. The FT-IR measurements exhibited the removal of the lignin. The thermal stability of the purified fibers was significantly improved in comparison with raw fibers. The XRD results ensured that the hydrogen peroxide treatment does not affect the crystallinity. This simple process can contribute to the wide range of research carried in the extraction of cellulose from agriculture and industrial wastes.

CHAPTER 6

CONCLUSION AND FUTURE PERSPECTIVES

6.1 CONCLUSION GÉNÉRALE

L'objectif principal de cette thèse de doctorat était de répondre à la transition vers le développement durable et de se concentrer sur une source innovante de nanomatériaux. En effet, ce projet propose une réponse à la demande de la société actuelle qui recherche des matériaux recyclables et biodégradables. Dans ce cadre, la nanocellulose est considérée comme un des matériaux les plus prometteurs. Il n'y a pas si longtemps, l'extraction de la nanocellulose ne visait que le bois. Dernièrement, les sources alternatives telles que l'agriculture et la biomasse industrielle ont commencé à apparaître.

À partir de la perspective susmentionnée, les travaux présentés ont été consacrés à l'extraction de la nanocellulose (NC) à partir de sources peu conventionnelles: biomasse agricole et industrielle et à leurs applications dans divers domaines. D'où la toute première publication abordée au chapitre 2 au cours de la première année (2017) de cette thèse, qui présentait une étude détaillée sur la préparation et les propriétés de la nanocellulose obtenue à partir de déchets agricoles et industriels, l'application de NC de diverses sources et les tendances industrielles les plus récentes de NC à base de bois.

1) L'article de synthèse insiste sur l'utilisation des déchets agricoles et industriels dans le domaine de la nanotechnologie qui devrait être explorée de manière plus approfondie par les chercheurs et les industries.

Les sources susmentionnées sont non seulement facilement disponibles, rentables et présentent des propriétés diverses, mais elles peuvent également produire des nanomatériaux à valeur ajoutée qui créeront une valeur économique et constitueront une matière première appropriée pour la production de CN. Alors que les applications de la CN ont été explorées dans différents domaines tels que les composites, les films, les hydrogels et les aérogels, il convient d'explorer de nombreuses nouvelles applications, telles que des matériaux intelligents, des fibres de carbone plus rigides, des encres d'imprimerie et des dispositifs électroniques. Compte tenu des préoccupations environnementales croissantes et de la tendance à privilégier les matériaux écologiques, les chercheurs devraient réfléchir à des applications originales pour faire progresser les nanomatériaux à base de cellulose en tenant compte de matières premières durables telles que les déchets agricoles et industriels.

Dans la partie suivante de la thèse, la carotte a été au premier plan. Les carottes gaspillées et rejetées demeuraient un problème pour les agriculteurs locaux. Par conséquent, la nanocellulose était extraite avec succès des fibres de carotte. Comme détaillé au chapitre 3, les NFC et les CNC ont été obtenus à partir des fibres de carotte. Des études complémentaires ont porté sur l'effet du temps de broyage sur la fibrillation des fibres de carotte afin de produire du NFC. Pour la première fois, des films de nanocellulose de carotte ont été préparés. Les propriétés et la transparence des films ont également été étudiées en gardant à l'esprit les applications dans lesquelles ces films peuvent être utilisés.

Par conséquent, ce travail de thèse :

2) Contribue à montrer que les déchets de carottes peuvent être valorisés.

3) Souligne également l'importance de considérer les déchets de l'agriculture et de l'industrie comme une source alternative de cellulose et de nanocellulose, susceptible de créer une économie intelligente.

4) Démontre que les films nanocellulosiques préparés à partir de cette biomasse peuvent ouvrir la voie à de futures applications à valeur ajoutée telles que la filtration, le conditionnement des aliments et les soins personnels.

Cette dernière partie des travaux nous a amenés à étudier les films nanocellulosiques pour diverses applications telles que l'emballage, le mulching et la construction. Ainsi, des films ont été préparés, oxydés par approche TEMPO et revêtus de TiO_2 et leurs propriétés ont été étudiées. Les propriétés barrières sont en effet importantes pour étudier la stabilité des films en présence d'oxygène et d'eau, sans oublier les applications dans lesquelles ces films doivent être utilisés.

Ainsi, le chapitre 4 couvre la recherche approfondie sur les propriétés de barrière des films nanocellulosiques revêtus de TiO_2. Les résultats obtenus contribuent donc à:

5) L'augmentation de la nature hydrophobe du film revêtu de TiO_2 qui est l'un des défauts des films nanocellulosiques classiques.

6) La diminution du taux de transmission de l'oxygène pour les films revêtus, ce qui signifie qu'ils peuvent éventuellement convenir pour une application d'emballage alimentaire.

7) Montrer que cela peut être un domaine intéressant à explorer en termes de films nanocellulosiques pour que les chercheurs les utilisent dans diverses applications étant donné que leur transparence et leur flexibilité ont également été améliorées après le revêtement de TiO_2.

Le chapitre 5 traite de la nouvelle stratégie d'épuration de la biomasse agricole. Une approche à étape unique a été mise au point pour purifier la biomasse agricole à l'aide de peroxyde d'hydrogène, qui implique habituellement divers produits chimiques et étapes complexes. L'accent principal a été mis sur la biomasse agricole canadienne: le lin, le chanvre et l'asclépiade.

8) Cette méthode de purification simple en une étape peut donc contribuer au domaine de la recherche sur l'extraction de nanocellulose à partir de différentes sources.

Pour terminer, ces travaux de recherche jettent les bases de nouveaux progrès dans la valorisation de la biomasse agricole et industrielle. C'est l'une des rares recherches à avoir enraciné l'importance de ces biomasses dans l'extraction et la conversion de nanocellulose.

6.2 GENERAL CONCLUSION

The main objective of this PhD thesis was set to meet the transmission towards sustainable development and to focus on the innovative source of nano material. This project, indeed, chose to fulfill the quest of the current society which is looking for recyclable, biodegradable material. In this framework, nanocellulose is thought as the most promising material. Until not long ago, the target for the extraction of nanocellulose was only wood. Lately, the alternate sources like agriculture and industrial biomass rather wastes have started evolving.

Exactly with respect to the aforementioned perspective, this work had been dedicated to the extraction of nanocellulose from the not very conventional sources: Agriculture and industrial biomass and their applications in various fields. Hence the very first publication discussed in **chapter 2** during the first year (2017) of this thesis presented a detailed study on the preparation and properties of nanocellulose obtained from crop and industrial wastes, application of NC from various sources, and the most recent industrial trends of wood-based NC.

1) The review article emphasized the use of agricultural and industrial wastes in the field of nanotechnology which should be more thoroughly explored by researchers and industries.

The aforementioned sources are not only easily available, cost-effective, and diverse in properties, but they also can produce value-added nano-materials which will create economic value and act as a suitable raw material for NC production. While the applications of NC have been explored in different fields such as composites, films, hydrogels, and aerogels, many new age applications in the form of smart materials, stiffer carbon fibers, printing inks, and electronic devices should be explored. With the ever-increasing environmental concerns and movement toward green materials, researchers should think about outside-the-box applications to move cellulose nanomaterials forward considering alternative sustainable raw materials like agricultural and industrial wastes.

In the next part after the detailed literature review, the first focus was on carrot. The wasted and rejected carrots remained a problem for the local farmers and hence nanocellulose was successfully extracted from the carrot fibers. As detailed in **chapter 3**, both NFC and CNC were obtained from the carrot fibers. Further investigations, for example, the effect of grinding time on the fibrillation of carrot fibers to produce NFC was studied. For the first time, films from the carrot nanocellulose were prepared. The properties and transparency of the films were also studied keeping in mind the applications in which these films can be used.

Hence,

2) this PhD work contributes to show that carrot wastes can be valorized.
3) It also emphasizes the importance of considering the agriculture and industrial wastes as an alternate source of cellulose and nanocellulose which eventually can create a smart economy.
4) Nanocellulosic films prepared from this biomass can pave the way for future value-added applications as in filtration, food packaging and personal care.

This last part of the previous work led us to study the nanocellulosic films for various applications like packaging, mulching and building applications. Thus, number of films were prepared, TEMPO oxidised and coated with TiO_2 and their properties were investigated. Barrier properties are indeed important with respect to study the stability of the films in the presence of oxygen and water. Not to forget the applications in which these films are to be used, this study is crucial. So, the **chapter 4** overlays the extensive research on the barrier properties of TiO_2 coated nanocellulosic films. The results can therefore contribute to:

5) increase in hydrophobic nature of the TiO_2 coated film which is one of the set back for the regular nanocellulosic films.
6) less oxygen transmission rate for the coated films which means that they can possibly suitable for food packaging application.
7) Show that this can be interesting area to explore in terms of nanocellulosic films for the researchers to use them in various applications given that there transparency and flexibility were also improved after TiO_2 coating.

Chapter 5 deals with the novel strategy in the purification of agricultural biomass. Only single step was developed to purify the agriculture biomass using hydrogen peroxide which otherwise involves various chemicals and complex stages. The main focus was on the Canadian agriculture biomass: flax, hemp and milkweed.

8) This simple one step purification method can consequently contribute to the realm of nanocellulose extraction research from different sources.

To end, this research work hopes to set the ground for the further progress in the valorization of agriculture and industrial biomass. It is one of the very few researches which rooted the importance of these biomasses in the nanocellulose extraction and converting wastes into value-added products. We hope this work will further create inquisitiveness in the researchers and industries from this field towards these sources.

6.3 PERSPECTIVES

1. Study of rheology of paints with carrot NCF reinforcement.

The NFC extracted from carrot fibers will be mixed with paints which is expected to improve the rheological properties. The high entangled network of NFC during fibrillation will play a major role in modifying the rheology of paints and thus decreasing the drying and cracking.

2. Finetuning the oxidation times and the coating of TiO_2 and study further properties of the nanocellulosic films to use them in food packaging application.

The mechanical properties of the oxidized TiO_2 coated films dropped in the preliminary tests. This could be due to the TEMPO oxidation time. The oxidation time can affect or modify the network of NFC fibers in the films and so studying the oxidation at different times can be interesting to know the effect on mechanical properties. Improved mechanical properties and barrier properties can result in the food packaging applications.

3. The purified flax, hemp and milkweed biomasses will be used to extract NCF. Initial study of hydrogel preparation from this NFC was made. The results will be discussed during the PhD defence. Some other applications like personal care products will also be studied using this NFC.

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