PREPARATION AND CHARACTERIZATION OF NANOCELLULOSE FROM ORANGE PEEL WASTE

Submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for Bachelor Degree of Manufacturing Engineering (Hons.)

by

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment of the requirement for the Degree of Bachelor of Manufacturing Engineering (Hons). The member of the supervisory committee is as follow:

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ABSTRAK

Kulit oren ialah serat semula jadi yang boleh didapati secara komersil dengan minat yang semakin meningkat untuk menggunakannya sebagai bahan mentah dalam pelbagai aplikasi kerana kepekatan selulosa yang tinggi dalam tumbuhan. Penyelidikan ini bertujuan untuk menentukan penyediaan nanoselulosa daripada sisa kulit oren dengan menggunakan kaedah rawatan kimia iaitu kaedah hidrolisis asid. Bagi menyediakan keadaan optimum nanoselulosa sisa kulit oren yang mempunyai kehabluran tinggi dalam struktur kristalnya dengan menggunakan kaedah hidrolisis asid dan kesan terhadap pelbagai kepekatan asid terhadap indeks kehabluran, saiz kristal dan morfologi nanohablur selulosa telah dikaji. Walau bagaimanapun, berdasarkan kajian terdahulu, penggunaan sisa kulit oren sebagai kajian merupakan suatu kajian yang terhad terhadap jenis asid dan kepekatan asid optimum yang merupakan parameter penggunaan kaedah hidrolisis. Oleh itu, dalam kajian ini, proses penyediaan nanoselulosa sisa kulit oren dengan menggunakan kaedah hidrolisis asid dengan jenis asid terbaik menggunakan asid sulfurik (H_2SO_4) dan asid hidroklorik (HCl), kepekatan asid optimum 30wt% pada masa hidrolisis malar (120min) dan suhu malar (45°C) dikaji secara menyeluruh. Daripada keputusan yang diperolehi, H_2SO_4 adalah kaedah terbaik untuk hidrolisis asid yang diperlukan untuk menghasilkan selulosa kristal yang tersebar dengan baik dengan kesan pengagregatan yang minimum dan kepekatan asid optimum ialah 30wt% dengan masa hidrolisis 120min dan suhu 45°C dengan indeks kehabluran tertinggi dan saiz kristal iaitu masing-masing 87.69% dan 3.19nm. Nanoselulosa sisa kulit oren boleh menjadi bahan hijau yang menjanjikan dimana ianya sesuai dengan trend reka bentuk dan pembangunan kemampanan global.

ABSTRACT

Orange peel is a commercially available natural fiber with an increasing interest in using it as a raw material in a variety of applications due to its high cellulose concentration in the plant. This research aims to determine the preparation of nanocellulose from orange peel waste by using chemical treatment of acid hydrolysis method. In order to provide the optimum conditions of nanocellulose of orange peel waste which are possessed high crystallinity in their crystal structure by using acid hydrolysis method and the effects of various acid concentrations on the crystallinity index, crystallite size and morphology of cellulose nanocrystals were studied. However, based on the previous study, using orange peel waste there is limited study has been reported on type of acid and optimum acid concentration as a parameter of using hydrolysis method. Therefore, in this study, the process of preparation orange peel waste nanocellulose by using acid hydrolysis method with the best type of acid used sulphuric acid (H_2SO_4) and hydrochloric acid (HCl), optimum acid concentration 30wt% at constant hydrolysis time (120min) and constant temperature (45°C) is comprehensively studied. From the result obtained, H_2SO_4 is the best method for acid hydrolysis needed to generate well-dispersed crystalline cellulose with minimal aggregation affect and the optimum acid concentration is 30wt% with 120min hydrolysis time and 45°C temperature with the highest crystallinity index and crystallite size which is 87.69% and 3.19nm respectively. Orange peel waste nanocellulose can be promising green material that fits well with global sustainability design and development trends.

DEDICATION

Only

my beloved father, Saad bin Na'aman

my appreciated mother, Azizah binti Zairan

my adored sister, Siti Sazira, Noor Ayuni, Nur Syazwani, Ainur Fazliana

my adored brother, Muhammad Faizal

my partner, Abdul Aziz bin Samin

for giving me moral support, money, cooperation, encouragement and also understandings

Thank You So Much & Love You All Forever

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LIST OF ABBREVIATIONS

XRD	-	X-Ray Diffraction
FTIR	-	Fourier Transform Infrared
SEM	-	Scanning Electron Microscope
TEM	-	Transmission Electron Microscopy
CNC	-	Cellulose Nanocrystals
CNF	-	Cellulose Nanofibers
BNC	-	Bacterial Nanocellulose
BC	-	Bacterial Cellulose
H_2SO_4	-	Sulphuric Acid
HCl	-	Hydrochloride Acid
NaOH	-	Sodium Hydroxide
NaCl	-	Sodium Chloride
PVA	-	Polyvinyl Alcohol
Crl	-	Crystallinity Index
H_3PO_4	-	Phosphoric Acid
HNO_3	-	Nitric Acid
OH	-	Hydroxide
Na^+	-	Natrium
H_2O	-	Water
OPW	-	Orange Peel Waste

LIST OF SYMBOLS

α	-	Alpha
°C	-	Degree Celsius
°	-	Degree
%	-	Percent
g	-	Gram
GPa	-	Gigapascal
kv	-	Kilovolt
kN	-	Kilonewton
mA	-	Milliampere
µm	-	Micrometer
nm	-	Nanometer
cm^{-1}	-	$100m^{-1}$
mg	-	Milligram
MPa	-	Megapascal
nm	-	Nanometre
wt%	-	Weight Percentage
µm	-	Micrometre
min	-	Minutes
ml	-	millimetre
pH	-	Potential of Hydrogen

CHAPTER 1

INTRODUCTION

Chapter 1 covers the background of the study, problem statement, objectives, scope, the importance of study and organization of the report. Background of the study explains how this project is significant to make a nanocellulose from orange peel waste (OPW). The problem statement demonstrates the problem that inspired the idea for this project. Following that, objectives depict the overall goal of this project, whereas scopes depict the constraints and method used to create this project.

1.1 Background of Study

Citrus fruits, which include oranges, limes, grapefruits, and lemon, are among the most popular and well-known types of fruits worldwide. Due to its waste material, orange peel is one of the underutilised waste materials. Citrus fruits are high in vitamin C, a nutrient that boosts the immune system and keeps skin looking youthful. They also contain vitamin A and B, dietary fibres, folic acid, amino acids, and minerals like calcium, potassium, and phosphorus, all of which are beneficial to health. This study is supported by (Kerri *et al*. 2017).

Alkaline treatment can be used to extract nanocellulose, a natural fibre, from cellulose that contains cementing materials such as lignin and hemicellulose. The alkaline treatment is critical for the production of highly pure cellulose nanocrystals (Ng *et al.* 2017).

Alkaline treatment increases the density of fiber by removing the nanocellulosic component that is hemicellulose and lignin by using sodium hydroxide (NaOH). This treatment remove lignin and hemicellulose and it also increase the amount of cellulose exposed on the fiber surface. Consequently, alkaline treatment increases the degree of crystallinity.

All plant materials, including citrus fruits and natural lignocellulosic materials, are made up of three organic components that are cellulose, hemicelluloses, and lignin. Cellulose is a linear D-glucose that form microfibrils which is responsible for the polymer's strength and resistance. While hemicellulose is a form of polysaccharide whose structure varies depending on the source, such as the type of plant and plant tissue. Lignin is a high molecular weight complex and amorphous polymer with three-dimensional network which is linked by phenylpropane monomers. It provides support to the plant cell wall; microbial resistance and it has hydrophobicity of the cell wall (Monika *et al.* 2017).

The hydrolysis process conditions, such as type of acid, optimum acid concentration, constant hydrolysis temperature, and constant hydrolysis time are critical in the production of cellulose nanocrystals. As a result, the motivation of this project is to investigates the type of acid used, as well as the optimum acid concentration used during the hydrolysis treatment, constant temperature and constant hydrolysis time, as a parameter in order to develop nanocellulose from orange peel waste. The temperature and time will be considered a constant parameter and two different acidic is used during acid hydrolysis as a parameter.

As a result, the purpose of this research is to develop a strategy for the preparation and characterization of nanocellulose from orange peel waste via chemical treatment methods such as acid hydrolysis. Due to the limitations of the previous study, only a few studies have been published on the effect of different type of acid and acid concentration as a parameter of hydrolysis of nanocellulose from orange peel waste. Additionally, the orange peel waste nanocellulose will be analysed using X-ray Diffraction (XRD) analysis, Fourier Transform Infrared (FTIR) analysis and Scanning Electron Microscope (SEM) .

1.2 Problem Statement

This study emphasizes the preparation and the characterization of nanocellulose from orange peel waste (OPW) via chemical treatment. In order to prepare nanocellulose OPW several procedures need to be done which start from the orange peel soaking in the distilled water to separate the albedo and flavedo, while in this study albedo was chosen as a raw material, then will be subjected to alkaline treatment, bleaching process and acid hydrolysis treatment. The outcome of this studies is dependent on the chosen parameters such as type of acid, optimum acid concentration, constant temperature, and constant hydrolysis time. OPW is one of the underutilized waste materials, however, there are possibility to produce high-yield and high crystallinity due to its high fibre content. In order to achieve high-yield and high-quality nanocellulose, an efficient method for producing of nanocellulose with excellent properties at low cost is still a challenges.

Therefore, acid hydrolysis with concentrated mineral acids is the most frequently used method for the preparation of nanocellulose. However, the method has several critical flaws, including being hazardous to the environment and human body, corroding process equipment and causing excessive degradation of raw cellulose material, and being expensive. sulphuric acid (H_2SO_4) and hydrochloric acid (HCl) was able to overcome the difficulties associated with hydrolyzing cellulose due to its medium acidity, and OPW nanocellulose with good nanoscales and high yield were successfully produced (Ji *et al*. 2019). Therefore, this current problem must be improved by developing the optimal design parameter for the acid hydrolysis treatment on this experiment by varying type of acid used and optimum acid concentration and the constant hydrolysis time and temperature. Throughout the process of nanocellulose from OPW, a diverse set of experiments with varying parameters is used.

In contrast, recent acid hydrolysis studies only focused on the optimal hydrolysis time to get the best crystal structure of nanocellulose OPW. Nevertheless, only a few studies have been done on the various type of acid used and optimum concentrations used in hydrolysis. Hence, this study will investigate the effect of type of acid as well as optimum acid concentration on nanocellulose preparation from OPW in term of crystallinity and crystallite size.

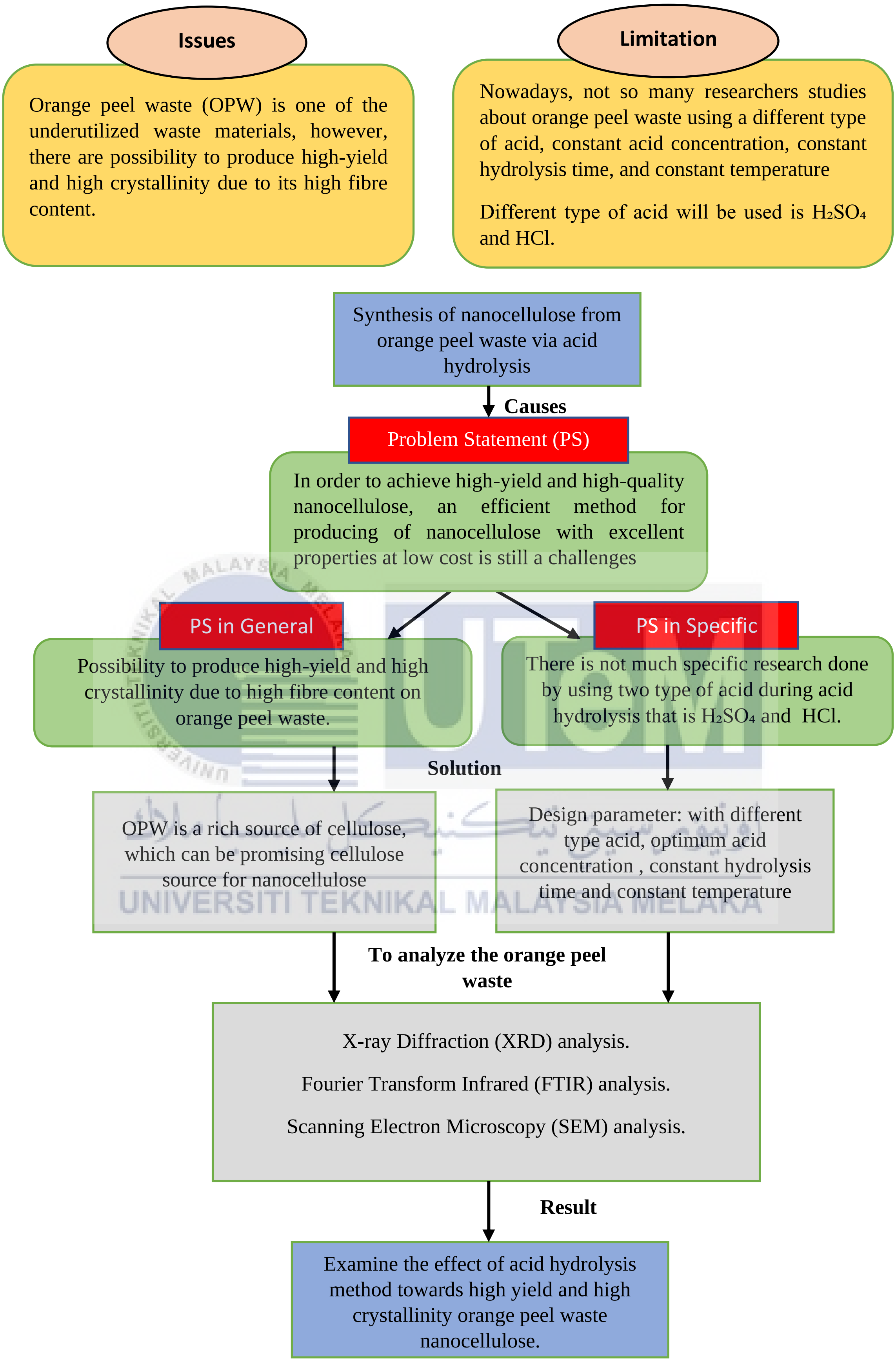

Figure 1.1: The summarization of problem statement and research gap

1.3 Objective

The objectives are as follows:

1. To prepare nanocellulose from orange peel waste (OPW) using acid hydrolysis method using different type of acid.
2. To determine the crystallinity of nanocellulose OPW by using X-ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) analysis.
3. To characterize the surface morphology and structure of OPW waste by using Scanning Electron Microscopy (SEM) analysis.

1.4 Research Scope

This study focuses on the chemical fractionation of orange peel. For the preparation of nanocellulose from OPW, from the raw material preparation followed by alkaline treatment and acid hydrolysis treatment is used to extract the cellulose fiber. To obtain highly purified cellulose, lignin is removed using an alkaline treatment. The samples were subjected to concentration, time, and temperature variations. The primary objective is to characterize and apply OPW via acid hydrolysis with the acid concentration, as well as to investigate the crystallinity and crystallite size and characterization of cellulose nanocrystals. To achieve the objective, research was carried out using a variety of scopes.

The first objective of this research is to investigate the method of preparing nanocellulose from OPW via acid hydrolysis. To extract the cellulose nanocrystals, the acid hydrolysis method was used. This is due to the fact that acid hydrolysis is the most efficient method for dissolving glycosidic bonds in cellulose and consumes the least amount of energy. The type of acid, optimum acid concentration, constant temperature, and constant hydrolysis time is the parameters that will be optimized in this method. In this study, various type of sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) will be used

Then, as mentioned in the second objective, to analyze the crystallinity and crystallite size of cellulose extracted from orange peel waste by using X-ray Diffraction (XRD) analysis. By calculating the crystallinity index (Crl) by using Segal equation and crystallite size by using Scherer equation, the XRD analysis is used to investigate the crystallinity of the nanocellulose OPW. Following that, the experiment result is supported by Fourier Transform Infrared (FTIR) analysis. After acid hydrolysis has accomplished, FTIR is used to determine the presence of lignin and hemicellulose structures. Finally, the surface morphology changes and structure of nanocellulose OPW will be characterized. Scanning Electron Microscopy (SEM) analysis was used to investigate the surface morphology changes and structure of nanocellulose OPW in order to accomplish this final objective.

OBJECTIVE		**SCOPES**
1. To prepare nanocellulose from orange peel waste (OPW) using acid hydrolysis method based on selected parameters	→	**Parameter -** Type of acid H_2SO_4 and HCl, optimum acid concentration (30-40wt%), constant hydrolysis time (120 min), constant temperature (45°) **Alkaline treatment -** Sodium Hydroxide (NaOH) **Acid hydrolysis treatment -** Different concentration of H_2SO_4 and HCl with 30-40 wt%
2. To determine the crystallinity of nanocellulose orange peel waste by using X-ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) analysis	→	**XRD analysis** – To calculated crystallinity in a cellulose sample based on Crl formula and crystallite size. **FTIR analysis –** Reveal the presence of lignin and hemicellulose.
3. To characterize the surface morphology and structure of nanocellulose orange peel waste by using Scanning Electron Microscopy (SEM) analysis.	→	**SEM Analysis -** To study the surface morphology and structure of OPW on raw material, after alkaline treatment of NaOH, and after acid hydrolysis by using acid H_2SO_4 and HCl**.**

Figure 1.2: The mapping matrix of the scopes and objectives

1.5 Significant of Research

Citrus fruit processing industries produce massive amounts of waste materials like peel and pulp that are not properly managed. In the current study, citrus waste was chosen to extract cellulose and nanocellulose. The goal of this study is to find out how crystallinity of OPW nanocellulose can be successfully produced and its crystallite size. The hydrolysis parameters, such as optimum acid concentration, constant hydrolysis time, and constant temperature, have recently been investigated. However, limited research has been done on the use of an appropriate type of acid used with optimum acid concentration during hydrolysis process. Thus, the nanocellulose OPW extraction studies will be carried out by using parameter of type of acid used, optimum acid concentration, constant hydrolysis time and constant temperature during the hydrolysis process.

Finally, the use of this eco-friendly material aligns with technology trends toward sustainable design and development, energy efficiency, and water conservation. The production of natural fibers does not emit greenhouse gases into the atmosphere, which contribute to global warming. However, the manufacturing processes for synthetic fibers like glass fiber or carbon fiber emit carbon dioxide, which can contribute to ozone depletion.

CHAPTER 2

LITERATURE REVIEW

This chapter presents a literature review of previous research that is aligned to this topic, which has been defined and carried out over an interval of time. Based on the research into the preparation of nanocellulose from orange peel waste (OPW), the characterisation and analysis of the cellulose from OPW, related information from earlier studies is extracted for use as references and discussion.

2.1 Nanocellulose Fiber

Cellulosic fibres are found in all natural fibers and are made up of cellulose, hemicellulose, lignin, and pectin. Lignin is a complex and amorphous polymer with a three-dimensional network of phenylpropane monomers of high molecular weight. It helps to strengthen the plant's cell wall. Cotton, hemp, flax, jute, ramie, and wood are all examples of plant cells that contain cellulose. Agricultural by-products containing cellulose include sugarcane bagasse, jute, ramie, banana, orange, and corncob. Furthermore, cellulose, which is made up of proteins and carbohydrates, can be found in a wide variety of bacterial species, tunicates, algae, and sea creatures.

Next, George *et al.* (2015) found that cellulose is made up of monomers linked together by glycosidic oxygen bridges and formed by condensation. The chemical structure of cellulose are shows on Figure 2.1. due to the abundance of cellulose sources, there has been a surge in interest in studying cellulose fibers in recent years. Nanocellulose research began because natural fibers can be used to create new ecologically and biodegradable products.