UNIVERSITI TEKNIKAL MALAYSIA MELAKA

PREPARATION AND CHARACTERIZATION OF SEAWEED NANOPOWDER VIA ACID HYDROLYSIS METHOD: A CRITICAL REVIEW

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

by

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APPROVAL

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ABSTRAK

Rumpai laut dilihat sebagai salah satu sumber yang paling penting dalam potensi industri dalam pelbagai aplikasi kerana kandungan selulosa yang tinggi dengan sifat-sifat yang unik. Walau bagaimanapun, tahap perkembangan serbuk rumpai laut perlu ditingkatkan untuk memberi permintaan yang tinggi dan potensi pemasaran besar serbuk rumpai laut. Tujuan kajian ini adalah untuk merancang metodologi penyediaan serbuk nano rumpai laut dari segi pengeluaran nanoselulosa (NC) melalui rawatan kimia. Untuk mensintesis NC daripada rumput laut, parameter penting menggunakan 64 wt% hidrolisis asid selama 250 minit telah dinyatakan. Berdasarkan kajian terdahulu, terdapat sedikit kajian mengenai penggunaan rumpai laut merah sebagai pengeluaran serbuk nano selulosa. Oleh itu, kesan masa hidrolisis dan kepekatan asid dikaji untuk mencari keadaan optimum NC rumpai laut merah kerana kekayaan kandungan selulosa dan peratusan terendah komponen bukan selulosa seperti lignin dan hemiselulosa, yang menjanjikan kualiti yang baik dan hasil serbuk nano yang tinggi. Indeks kristal didalilkan 80% lebih tinggi daripada kajian terdahulu dan ukuran kristal telah dihipotesiskan menjadi 465 nm yang merupakan ukuran terkecil berdasarkan pola graf melalui tinjauan kritikal. Analisis X-ray Pembelauan Spektrometer (XRD) akan digunakan untuk menentukan struktur analisis kristalografi NC dan analisis Fourier Mengubah Spektrometer Inframerah (FTIR) yang mengesahkan bahawa puncak bagi lignin dan hemiselulosa dikeluarkan dari spektrum rumpai laut yang dirawat oleh alkali. Selepas itu, sifat permukaan morfologi diperhatikan dengan menjalankan analisis Imbasan Elektron Mikroskopi (SEM) sebelum dan selepas rawatan alkali dan juga selepas hidrolisis asid, yang mana morfologi permukaan serbuk nano dirawat lebih halus daripada yang tidak dirawat. Oleh itu, rumpai laut membekalkan bahan mentah alternatif dan aspek ini memberi sumber selulosa yang melestarikan kepada pengeluaran NC.

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ABSTRACT

Seaweeds are viewed as one of the most significant sustainable resources with industrial potential in various applications due to its high content of cellulose with unique properties. Nevertheless, the levels of development of seaweed powder have to be increased to provide high demand and a huge potential market of seaweed powder. The purpose of this study is to plan a methodology for the preparation of the seaweed nanopowder in terms of nanocellulose (NC) production via chemical treatment. In order to synthesize NC from seaweed, the significant parameters using 64 wt% acid hydrolysis for 250 min had been postulated. Based on the past study, there has been little study on using red seaweed as a cellulose nanopowder production. Hence, the effect of hydrolysis time and hydrolysis acid concentration are studied in order to find the optimum conditions of NC of red seaweed due to the richness of cellulose content and lowest percentage of noncellulosic components such as lignin and hemicellulose, which is promising a good quality and high yield of nanopowder. The crystallinity index was postulated as 80% higher than the late research and crystallite size had been hypothesized to 465 nm which was the smallest size based on graph pattern due to the critical review. The X-Ray Diffraction (XRD) analysis used to determine the crystallography structures of seaweed NC and Fourier Transform Infrared (FTIR) analysis which confirmed that peaks for lignin and hemicellulose are removed from the spectra of the alkali-treated seaweed. After that, the surface morphology property was observed by carrying out Scanning Electron Microscopy (SEM) analysis before and after alkali treatment and also after acid hydrolysis, which was the surface morphology of treated nanopowder was smoother than untreated. Thus, seaweed provides an alternative raw material and this aspect gives a sustainable cellulose source to the NC production.

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DEDICATION

Only

my beloved father, Baharudin bin Baharom

my appreciated mother, Siti Hamaton binti Awang Kechil

my siblings,

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

BC	-	Bacterial cellulose
Ca^{2+}	-	Calcium ions
CNC	-	Celulose nanocrystal
CNF	-	Cellulose nanofibril
CNB	-	Cellulose nanobaterial
CrI	-	Crystallinity index
D	-	Crystallite size
DOE	-	Design of experiment
FWHM	-	Full width half maximum
FTIR	-	Fourier Transform Infrared
H_2O	-	Hydrogen dioxide
H_2SO_4	-	Sulphuric acid
KOH	-	Potassium hydroxide
Na^+	-	Sodium ion
NaOH	-	Sodium hydroxide
NC	-	Nanocellulose
PLA	-	Polylactic acid
PVA	-	Polyvinyl alcohol
SCB	-	Sugarcane bagasse
SEM	-	Scanning electron microscopy
SRC	-	Semi refined carrageenan
XRD	-	X-ray diffraction

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LIST OF SYMBOLS

cm	-	Centimetre
m	-	Metre
%	-	Percent
g/cm^3	-	Grams per centimetre cube
wt%	-	Weight percent
mm	-	Millimetre
GPa	-	Giga Pascal
°C	-	Degree Celsius
cP	-	Centipoise
$N.s.m^{-2}$	-	Newton second per meter square
nm	-	Nanometer
ml/g	-	Mililitter per gram
Min	-	Minute
g	-	Gram
h	-	Hour
mm/min.	-	Millimetre per minute
rpm	-	Revolution per minute
W	-	Watt
I_{max}	-	Maximum intensity
I_{min}	-	Minimum intensity
θ	-	Angle
β	-	Betha
λ	-	Wavelength
cm^{-1}	-	Per centimeter
μm	-	Micrometer
kV	-	kilovolt
T_f	-	Thickness after immersion
/min	-	Per minute

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CHAPTER 1

INTRODUCTION

This chapter explains the details of the background of the study, problem statement, objectives, research scopes, and the significance of this research. As requested by the respective industry (Saanen Sdn Bhd), the term of seaweed nanopowder will be applied throughout the study, which is representing the nanocellulose (NC), specifically falls into cellulose nanocrystal (CNC) type.

1.1 Research Background

Seaweed or the other name is macroalgae which is plant-like creatures that for the most part live on a rock or other hard substrate in the coastal zone. Many demonstrate a settled zonation along the edges of the oceans, where the profundity of the water is 50 meters (around 165 feet) or less. The kinds of seaweed becoming close to the high-water mark, where plants are frequently presented to air, a contrast from those developing at lower levels, where there is little or no exposure. Seaweed also can be categorized by three major groups which are brown algae (*Phaeophyceae*), green algae (*Chlorophyta*), and red algae (*Rhodophyta*) (Nurshahida *et al.,* 2018).

In the course of the most recent couple of decades, seaweeds have drawn critical worldwide attention because of its possible use in pharmaceuticals, fertilizer, biofuels, synthetic substances, biomedical, hydrocolloids, food enhancements, beauty care products and numerous different fields (Bhutiya *et al.,* 2018). Furthermore, aquaculture cultivation with the balance produced through natural harvesting provides 96% of world seaweed production for human use and various applications which on a fresh weight annually basis is ca.24.9 million tons (Radulovich *et al.,* 2015). With being 88% of the value and 76% of

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the tonnage, seaweeds as sea vegetable usage for direct human consumption is very significant (Chopin, 2012).

Cellulose and its derivatives are the most well-known natural polymer on earth as it is a structural component in the main cell wall of green plants. As one of the applications, seaweed cellulose will be incorporated into paper and plastic composites to improve its thermal properties. According to Liu *et al.* (2017), it is stated that cellulose is known to be used as a raw material in papermaking, food, and additives traditionally and nowadays, the extraction of nanocellulose (NC) from cellulose and observation on its applications are becoming more interesting research areas with the introduction of booming nanotechnology. In view of its abundance and its fibrillar nanostructure in the cellulose structure, it is the reason what makes the cellulose compound as high potential to be used as a nanomaterial. This polysaccharide has a very special feature that makes it an extraordinary material, such as high rigidity, mechanical properties, low cost, and biodegradable.

Nanocellulose (NC) can be categorized into three main types; cellulose nanocrystal (CNC), cellulose nanofibril (CNF), and cellulose nanobacterial (CNB). With respect to the different sources and extraction processes, they are different in terms of morphology, particle size, crystallinity, and several features although each of types is similar in chemical composition (Lavoine *et al.,* 2012; Moon *et al.,* 2011). The CNC is high-strength NC, typically isolated by acid hydrolysis from cellulose fibrils. It is also known as cellulose nanocrystals (CNC), nanocrystal of cellulose, or cellulose nanowhiskers by Dufresne (2013). At the end of the result, NC will be generated in powdery mildew. The researchers stated that the material can be utilized as an option in contrast to conventional cellulose suspensions in the production of bio-based polymer nanocomposites that can be utilized. For instance, in lightweight structures for the car manufactures and as a membrane or filter material for biomedical use (Corp, 2012).

Natural fiber CNC has high crystallographic advantages that can be produced through chemical treatments such as acid hydrolysis which cause it to be widely used. Figure 1.1 shows the schematic of nanocrystalline cellulose which can be extracted from cellulose fibrils by acid hydrolysis. Jonoobi *et al.* (2015) reported that CNC is a sustainable resource representing over 50% of the world's abundant plant resources. In addition, it has many great features that make it suitable for reinforcing purposes.

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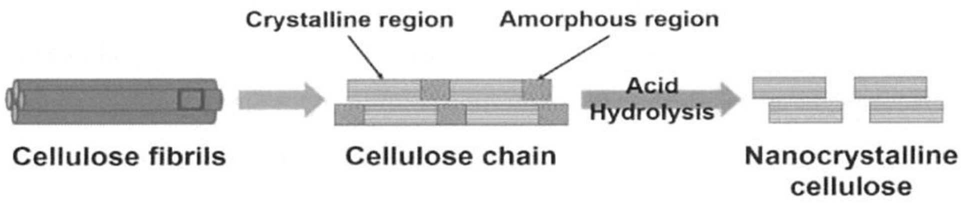

Figure 1.1: Schematic of nanocrystalline cellulose which can be extracted from cellulose chains using acid hydrolyzed amorphous region and left only crystalline region (Phanthong *et al.*, 2018).

Ng *et al.* (2015) stated that cementing material like lignin and hemicellulose of NC or CNC can be removed by alkaline treatment. Alkaline treatment is required before the extraction of CNC to obtain highly purified cellulose fiber. Selected fibers were immersed in 6% concentration of NaOH for 24 hours at room temperature.

Hence, the aim of this current work is to plan the preparation and characterization of cellulose nanopowder that derived from red seaweed using acid hydrolysis (H_2SO_4) method by different hydrolysis time and acid concentration. This is due to a shortage of prior studies using red seaweed as the beginning material for NC extraction with a complete characterization has been done. The crystallinity index (CrI) and crystallite size of NC obtained will be further analyzed and characterized by postulating review data using the selected tools such as Fourier Transform Infrared spectroscopy (FTIR), X-ray diffraction microscopy (XRD), and Scanning Electron Microscopy (SEM). Therefore, a well-characterized cellulose structure and crystallinity can be evaluated due to the optimum condition of hydrolysis focusing on the effect of hydrolysis time and acid concentration.

1.2 Problem Statement

This research is accentuating the preparation and characterization of seaweed nanopowder utilizing acid hydrolysis method which is high in crystallinity and stable colloidal suspension. In order to synthesize this seaweed nanopowder, several chemical processes need to be conducted. Several procedures need to be conducted and start it with the extraction of the nanopowder from the seaweed by using alkali treatment pursued by the

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acid hydrolysis treatment. The use of alternative types of seaweed in this study is due to some good advantages of macroalgae that being attention among the research. In addition, this study can help to expand in the food field as well as cosmetics because some countries make seaweed as their basic food. Furthermore, the seaweed market in world production is getting high demand from 2011 to 2015 (Ferdouse *et al.,* 2018).

There are a few shortcomings by utilizing conventional method through seaweed powder processing, such as lower yield of seaweed powder production and also unavailability of schematic and optimized methodology for the preparation of high-quality and high-yield of seaweed powder at the laboratory scale and mass production, has impeded the possibility of huge market potential. Moreover, to date constrained studies have been considered on the preparation of derived nanopowder from seaweed by using acid hydrolysis method, and its characterization with the effect of time and concentration on the crystallinity need to be exploited.

To provide high demand and a huge potential market of seaweed powder, it needs to upgrade the yield rate of seaweed powder production. Therefore, to overcome limitations of conventional seaweed processing methods, optimization the seaweed powder processing for high-quality and high-yield using statistical design of experiment (DOE) approach will also be applied through this study. However, due to the restriction of the COVID pandemic, the study will be conducting via postulating the critical review analysis. The procedures should start with the extraction of the nanopowder from the seaweed by using the alkaline treatment. It is depending on the parameters that have been chosen such as the concentration of the acid used and acid hydrolysis time to provide the highest quality and highest yield of seaweed nanopowder. The selection of red seaweed as the starting material of nanocellulose (NC) source is due to the richness of cellulose content and the lowest percentage of non-cellulosic components such as lignin and hemicellulose, which is promising a good quality and high yield of nanopowder. Figure 1.2 shows a summary of the problem statement and research gap of seaweed nanopowder.

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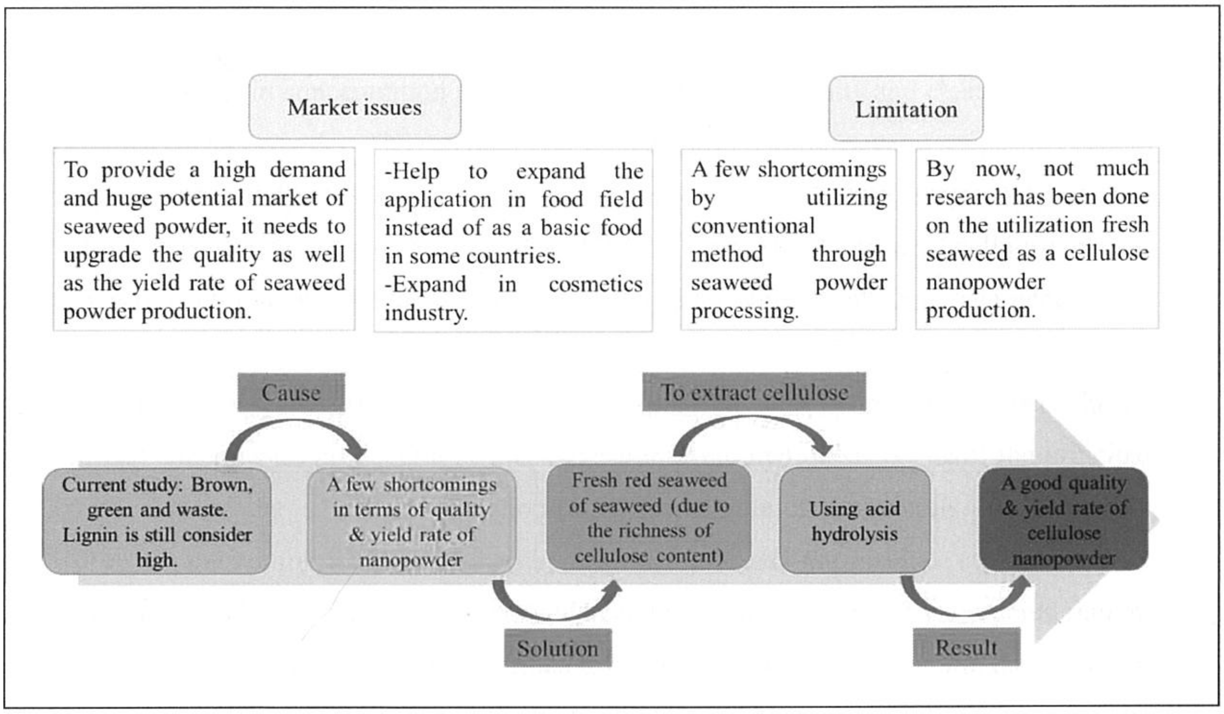

Figure 1.2: The summarization of problem statement and research gap

1.3 Objectives

The objectives are as follows:

(a) To plan methodology for the preparation of seaweed nanopowder via acid hydrolysis method at different acid concentrations and acid hydrolysis time.

(b) To postulate the crystallinity index and crystallite size via critical review analysis.

(c) To correlate the postulated crystallinity index and crystallite size with its morphological, structural, and compositional review data.

1.4 Research Scopes

The research concentrates on the preparation of nanopowder in terms of nanocellulose from seaweed by utilizing sulphuric acid (H_2SO_4) via acid hydrolysis method

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with optimum acid concentration and to investigate the crystallinity and characterization of the seaweed nanopowder. The research will be executed based on several scopes in order to carry out this study. For the preparation of nanopowder, alkaline treatment, and acid hydrolysis treatment is used to extract the cellulose fiber. Highly purified cellulose can be achieved by eliminating the lignin and hemicellulose by using the alkaline treatment.

In this research, the first objective is to plan the acid hydrolysis approach in the seaweed nanopowder production as the suggestion. Acid hydrolysis is one of the principal procedures for the synthesis of nanopowder from cellulosic materials. Acid quickly hydrolyzes the combined parts of the chain of cellulose and the disorder region. In other words, acid can hydrolyze the disorders and keep the remaining parts of the ordered region. Prior to that, alkali treatment was performed to break hydrogen linkages within the cellulose-chain structure to make the NC extraction effective in the acid hydrolysis process. The seaweed was treated with sodium hydroxide (NaOH) to obtain distilled cellulose before the acid hydrolysis process was performed which was carried out under a different condition such as hydrolysis time, acid concentration, and temperature correlation. Sulphuric acid (H_2SO_4) in this process is employed as the agent of acid hydrolysis since it can lead to a stable NC-colloidal suspension compared with other acid types. Furthermore, since they have interacted with each other, acid content and time of hydrolysis have differed.

As to reach objective number two and three, the crystallinity index and crystallite size have been postulated and supported via the critical review analysis based on previous research. Then, the tools are chosen to describe the surface morphology and the crystals structure of seaweed nanopowder. In this research, there were three characterization instruments were used which are X-ray diffraction microscopy (XRD), Fourier Transform Infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). The XRD analysis utilized to assess the crystallinity index (CrI) and crystallite size. Next, FTIR analysis had been examined the effect of elemental chemical composition for various chemical stages and thermal stability. The presence of hemicellulose structure and lignin is detected by FTIR analysis after hydrolysis of acid treatment is done. Finally, the result of this research was used SEM analysis to evaluate the surface morphology and structure of seaweed nanopowder.

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1.5 Significant of Research

The potential of seaweeds to develop over an incredibly shorter period of time has the benefit of competing with edible plants and food stocks (first generation biomass) and agricultural waste (second generation biomass), that were the initial main sources of various applications such as bioethanol processing polysaccharides and nanocellulose (NC) (Mahdi *et al.,* 2016; Singh *et al.,* 2017). Commonly, seaweed is a very multipurpose product widely used for food indirect human use. Apart from that, the demand for seaweed production keeps on developing for various applications. It is significant to investigate the appropriate method in order to produce nanopowder in terms of nanocellulose (NC) which is obtained from seaweed. In addition, the research analysis on the preparation of NC from seaweed is done in order to determine the crystalline NC of seaweed.

Up to now, a few detailed studies were carried out on the use of seaweed as a raw material in the extraction of NC from seaweed. NC has numerous benefits that have been an attraction for the researcher. Apart from the food industry, NC from seaweed is generally used as reinforcing material for polymer composite due to good increasing abilities. Besides can help to protect coastal communities from environmental disasters and degradation, seaweed is also can remove toxin from seawater as it grows.

On the other hand, the use of green material as the raw material has been concentrated. Instead of other existing cellulosic sources, it provides an alternative raw material and this aspect gives a sustainable cellulose source to the NC production. Thus, the use of natural fibers as the raw material can be seen clearly in the production of seaweed which has a low impact on human prosperity and the environment. It is also more important to increase the analysis on the use of natural materials for present and future applications.

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