Isolation, Characterization and Optimization of Cellulose Nanocrystals using Deep Eutectic Solvent Treatment from Rice Straw

by

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LIST OF ABBREVIATIONS

3D	Three dimensional
AFEX	Ammonia fiber explosion
AGU	Anhydroglucose unit
ANOVA	Analysis of variance
ASC	Sodium chlorite acidified by acetic acid
BNC	Bacterial nanocellulose
BP	Bleached DES treated pulp
ChCl	Choline chloride
CMC	Carboxymethyl cellulose
CNC	Cellulose nanocrystal
CNF	Cellulose nanofibril
CNW	Cellulose nanowhisker
CrI	Crystallinity index
CTMP	Chemi-thermo-mechanical pulping
CV	Coefficient of variation
DES	Deep eutectic solvent
DLS	Dynamic light scattering
DTG	Differential thermogravimetric
EDX	Energy dispersive x-ray spectroscopy
FAO	Food and Agriculture Organization
FCCCD	Face-centered central composite design
FDA	Food and Drug Administration
FE-SEM	Field-emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
FWHM	Full width at half maximum
HBA	Hydrogen bond acceptor
HBD	Hydrogen bond donor
K_2CO_3-Gly DES	Potassium carbonate-glycerol deep eutectic solvent
L_{200}	Crystallite size
LCC	Lignin-carbohydrate complex
NCC	Nanocrystalline cellulose
NH_4OH-KOH	Ammonia-potassium hydroxide
OA-ChCl DES	Oxalic acid-choline chloride DES

OA-CNC	Oxalic acid-choline chloride cellulose nanocrystal
OFAT	One-factor-at-a-time
PdI	Polydispersity index
PGW	Pressure groundwood
PSD	Particle size distribution
R^2	Coefficient of determination
RS	Rice straw
RSM	Response surface methodology
SA-CNC	Sulphuric acid cellulose nanocrystal
SC-CO2	Supercritical carbon dioxide
SD	Standard deviation
SEM	Scanning electron microscopy
SGW	Stone groundwood
TCI	Total crystallinity index
TEM	Transmission electron microscopy
TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl
TGA	Thermogravimetric analysis
TMP	Thermo-mechanical pulping
TRS	Total reduced sulphur
UP	Unbleached DES treated pulp
UV-Vis	Ultraviolet-visible
XRD	X-ray diffraction

LIST OF SYMBOLS

A	Temperature
A_{1373}	Absorbance value at 1373
A_{2917}	Absorbance value at 2917
B	Reaction time
C	BP to OA-ChCl DES mass ratio
I_{200}	Highest peak intensity of the crystalline region
I_{AM}	Minimum intensity of the amorphous region
T_{max}	Maximum degradation temperature
T_{onset}	Onset temperature
Y	OA-CNC yield
θ	Theta

Pengasingan, Pencirian dan Pengoptimuman Selulosa Nanokristal daripada Jerami Padi dengan Menggunakan Kaedah Rawatan Pelarut Eutektik

ABSTRAK

Selulosa nanokristal (CNC) merupakan bahan nano yang boleh diperbaharui telah digunakan secara meluas dalam pelbagai aplikasi disebabkan oleh sifat-sifat fizikokimia yang cemerlang. Tujuan kajian ini adalah untuk menilai prestasi pelarut eutektik alkali dalam proses pemulpaan, pelarut eutektik asid dalam proses hidrolisis asid dan mengoptimumkan hasil selulosa nanokristal asid oksalik-kolin klorida (OA-CNC). Dalam kajian ini, pulpa selulosa dan CNC berjaya diekstrakkan daripada jerami padi (RS) dengan menggunakan kaedah baharu. Pulpa selulosa diperolehi melalui proses pemulpaan dengan menggunakan pelarut eutektik alkali. CNC dihasilkan daripada pulpa selulosa melalui proses hidrolisis asid dengan menggunakan pelarut eutektik asid. Pelarut eutektik kalium karbonat-gliserol (K_2CO_3-Gly DES) yang bernisbah molar 1:7 telah dipilih sebagai pelarut eutektik alkali yang berpotensi untuk proses pemulpaan. Parameter saringan untuk proses pemulpaan ditentukan melalui kaedah satu-faktor-pada-satu-masa (OFAT). Hasil kajian ini mendedahkan bahawa suhu pemulpaan 140 °C, masa tindak balas 100 minit dan nisbah jisim RS kepada K_2CO_3-Gly DES 1:10 menghasilkan kandungan selulosa yang tertinggi sebanyak 73.8% bagi pulpa selulosa rawatan DES tanpa peluntur (UP). Analisis spektroskopi inframerah transformasi Fourier (FTIR), mikroskopi elektron pengimbas (SEM), spektroskopi serakan tenaga sinar-x (EDX) mengesahkan bahawa komponen selain selulosa telah disingkirkan daripada RS selepas proses pemulpaan menggunakan pelarut eutektik alkali dan proses pelunturan. Analisis termogravimetrik (TGA) menunjukkan bahawa kestabilan termal UP standing dengan pulpa selulosa rawatan DES berpeluntur (BP). Pelarut eutektik asid oksalik-kolin klorida (OA-ChCl DES) yang bernisbah molar 1:1 telah disediakan dan dipilih sebagai pelarut asid yang berpotensi untuk proses hidrolisis asid menggunakan pelarut eutektik asid. Menurut eksperimen OFAT, suhu 80 °C, masa tindak balas 4 jam dan nisbah jisim BP kepada OA-ChCl DES 1:10 telah dipilih untuk mengoptimumkan proses hidrolisis asid menggunakan pelarut eutektik asid melalui kaedah reka bentuk komposit pusat berpusat muka (FCCCD). Kondisi operasi optimum seperti suhu 79.5 °C, masa tindak balas 4 jam dan nisbah jisim BP kepada OA-ChCl DES 1:12.64 menjana hasil OA-CNC sebanyak 55.08%. Sifat-sifat fizikokimia OA-CNC dibandingkan dengan selulosa nanokristal asid sulfurik (SA-CNC) yang disediakan melalui proses hidrolisis asid sulfurik. Analisis FTIR, EDX dan analisis potensi zeta mengesahkan bahawa kewujudan kumpulan karboksil yang bercas negatif di permukaan OA-CNC dan kumpulan sulfat yang bercas negatif di permukaan SA-CNC selepas proses hidrolisis asid menggunakan pelarut eutektik asid dan proses hidrolisis asid sulfurik masing-masing. Analisis TGA mendedahkan bahawa kestabilan termal OA-CNC lebih tinggi daripada SA-CNC. Analisis mikroskopi elektron pengimbas pelepasan medan (FE-SEM), mikroskopi elektron penghantaran (TEM) dan analisis saiz zarah membuktikan bahawa OA-CNC berada dalam julat saiz nano. Penemuan ini telah menunjukkan kaedah baharu dalam penyediaan OA-CNC melalui proses pemulpaan menggunakan pelarut eutektik alkali dan proses hidrolisis asid menggunakan pelarut eutektik asid.

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ABSTRACT

Cellulose nanocrystal (CNC) is a renewable nanomaterial that has been used in various applications due to its excellent physicochemical properties. The aim of this research study is to evaluate the performance of the alkaline DES in lignocellulose pulping, acidic DES in acid hydrolysis process as well as optimizing the yield of oxalic acid-choline chloride cellulose nanocrystal (OA-CNC). In this study, cellulose pulp and CNC were successfully extracted from the rice straw (RS) using a novel green approach. The cellulose pulp was obtained through alkaline deep eutectic solvent (DES) pulping of RS using an alkaline DES. CNC was further produced from the extracted cellulose pulp through acidic DES hydrolysis using an acidic DES. The 1:7 molar ratio of potassium carbonate-glycerol DES (K_2CO_3-Gly DES) was chosen as the potential alkaline pulping solvent. The screened pulping parameters were determined using the one-factor-at-a-time (OFAT) method. The results revealed that the pulping temperature of 140 °C, 100 min reaction time and 1:10 RS to K_2CO_3-Gly DES mass ratio produced the highest cellulose content of 73.8% for the unbleached DES treated pulp (UP). The Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) spectroscopy analyses confirmed that the non-cellulosic materials were removed from the RS after subjected to the alkaline DES pulping and bleaching process. The thermogravimetric analysis (TGA) indicated that the thermal stability of UP was comparable to that of bleached DES treated pulp (BP). The 1:1 molar ratio of oxalic acid-choline chloride DES (OA-ChCl DES) was prepared and chosen as the potential acidic solvent for the acidic DES hydrolysis process. According to the OFAT experiment, the temperature of 80 °C, 4 h reaction time and 1:10 BP to OA-ChCl DES mass ratio were obtained and further used for optimizing the acidic DES hydrolysis process through the face-centered central composite design (FCCCD). The optimal operating conditions were found as temperature (79.5 °C), reaction time (4 h) and BP to OA-ChCl DES mass ratio (1:12.64) at which 55.08% of the OA-CNC yield was achieved. The physicochemical properties of OA-CNC were compared with the sulphuric acid cellulose nanocrystal (SA-CNC) that prepared through sulphuric acid hydrolysis. The FTIR, EDX and zeta potential analyses confirmed the presence of negatively charged carboxyl groups on the OA-CNC surface and negatively charged sulphate groups on the SA-CNC surface after acidic DES hydrolysis and sulphuric acid hydrolysis, respectively. The TGA results revealed that the OA-CNC has a higher thermal stability than the SA-CNC. The field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and particle size analyses proved that the OA-CNC was in nano-sized range. These findings have demonstrated a novel green approach for the preparation of OA-CNC using alkaline DES pulping and acidic DES hydrolysis.

CHAPTER 1 : INTRODUCTION

1.1 Research background

Over the past few decades, there has been a growing interest for the development and preparation of cellulose nanocrystal (CNC) in diverse research areas as well as various application fields. Owing to the progressive development of the modern society, ever-growing energy demand, environmental issues, climate change and diminishing fossil fuel reserves across the world, the search for alternative renewable resources is necessary in order to achieve a long-term global sustainability as well as securing the energy supply (Luque et al., 2008). In conjunction with this matter, lignocellulosic biomass serves as one of the most abundant renewable feedstock for the production of biofuels and bio-based products, which contributes immensely to the sustainable development goals.

CNC is generally classified as a sustainable bio-based nanomaterial, which derived from the disintegration of lignocellulosic biomass. CNC is often referred to as cellulosic material at nanoscale dimension that exhibits numerous intrinsic properties and functionalities (Shak, Pang, & Mah, 2018). CNC has a few unique physicochemical properties such as low density, renewability, biocompatibility, biodegradability, tunable surface chemistry, optical transparency, non-toxic, improved thermal properties and mechanical strength (Habibi, Lucia, & Rojas, 2010; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011). These remarkable characteristics allow the CNC to be utilized in the construction, packaging, automobile, composite and biomedical applications (Lee, Hamid, & Zain, 2014).

In general, the preparation of CNC involves several pretreatment steps. These include the pulping and bleaching of the woody or non-woody lignocellulosic biomass to extract the cellulosic fibers from the lignocellulosic matrix before proceeding with the acid hydrolysis process using strong and concentrated inorganic acids for hydrolyzing the amorphous region of cellulose, thereby releasing individual crystallite that is commonly referred to as CNC. Pulping is a process that usually involves either chemical, mechanical or semi-chemical pretreatments to remove lignin and hemicellulose from lignocellulosic matrix, producing a fibrous material known as cellulose pulp (Liew & Chong, 2016). To date, pulping processes are still the most common methods used to fractionate the lignocellulosic biomass for the production of paper pulp, fiberboard and cellulose derivatives, as well as the conversion of cellulose-enriched pulp into nanocellulose (García, Gandini, Labidi, Belgacem, & Bras, 2016). Among all available chemical pulping processes, kraft pulping appears to be the most dominant, with 90% of total production capacity at the global scale (Azadi, Inderwildi, Farnood, & King, 2013). In kraft pulping, white liquor containing sodium hydroxide (NaOH) and sodium sulfide (Na_2S) is used to dissolve the lignin and hemicellulose at high temperature and pressure, while leaving the cellulose intact (Brandt, Gräsvik, Hallett, & Welton, 2013). Despite of its worldwide popularity and efficiency, the application of white liquor in kraft pulping somehow releases volatile sulphur compounds into the atmosphere, apart from polluting the water sources (Bajpai, 2014).

Numerous alternative chemical pulping processes have also been studied such as organosolv pulping (Jiménez, Pérez, López, Ariza, & Rodríguez, 2002), acidic magnesium-based sulphite pulping (Marques, Evtuguin, Magina, Amado, & Prates, 2009) and sulphur-free soda pulping (Francis, Shin, Omori, Amidon, & Blain, 2006), which involved a variety of aqueous organic and inorganic solvents to remove lignin and hemicellulose from the lignocellulosic matrix while retaining the cellulose. However, there are a few disadvantages associated with the conventional pulping methods which include hazardous, volatile, flammable and odorous gases emissions (Bajpai, 2014). At the beginning of the twenty-first century, Swatloski et al. (2002) had discovered the potential of the hydrophilic ionic liquid for dissolving the cellulose, thereby gaining a substantial interest among the scientists in this research field. Nevertheless, there are a few drawbacks in the ionic liquid pretreatment of lignocellulosic biomass such as high synthesis cost, high toxicity, low biodegradability, long-term recyclability aspect of ionic liquid and partial separation of cellulose from the lignocellulosic matrix (Clough et al., 2015; Vigier, Chatel, & Jérôme, 2015). All these aqueous organic and inorganic solvents are mainly applied in the pulping processes to produce unbleached cellulose pulp that prior to the bleaching treatment. Then, the bleached cellulosic fibers are isolated before proceeding with the acid hydrolysis process in order to produce CNCs.

CNCs are rod-like and whisker-shape nanoparticles, most commonly obtained from the cellulosic materials such as algae, cotton, tunicates, woody and non-woody pulp through the acid hydrolysis process (Beck-Candanedo, Roman, & Gray, 2005; Shak et al., 2018). In general, cellulose microfibril contains both crystalline (ordered) and amorphous (disordered) regions (Moon et al., 2011). When the cellulosic fiber is subjected to the acid hydrolysis, the amorphous domain is preferentially hydrolyzed while liberating individual crystallite that is commonly referred to as CNC (García et al., 2016). Each CNC rod generally has a diameter about 2-30 nm and length of up to a few hundred nanometers, depending on the source of cellulose and the types of acids that are used in the acid hydrolysis process (Börjesson & Westman, 2015; Dufresne, 2019). To date, acid hydrolysis is the most widely used technique for the preparation of CNCs from bleached cellulose pulp by employing strong and concentrated inorganic acids such as sulphuric acid (H_2SO_4), hydrochloric acid (HCl) and phosphoric acid (H_3PO_4) (Camarero Espinosa, Kuhnt, Foster, & Weder, 2013; Trache, Hussin, Haafiz, & Thakur, 2017). Acid hydrolysis is indeed an effective and time-saving method to produce the CNC. However, there are several drawbacks associated with the usage of these inorganic acids in the acid hydrolysis such as severe corrosion of processing equipment, environmental pollution and involves a large-scale water consumption (Du et al., 2019; Xie, Du, Yang, & Si, 2018). Owing to this, there are many sustainable and eco-friendly alternatives based on the replacement of chemicals have been extensively studied for the past few years to overcome the above mentioned drawbacks such as solid acid hydrolysis (Liu et al., 2014), recyclable organic acid hydrolysis (Chen, Zhu, Baez, Kitin, & Elder, 2016), IL pretreatment (Abushammala, Krossing, & Laborie, 2015) and acidic deep eutectic solvent (DES) hydrolysis (Sirviö, Visanko, & Liimatainen, 2016).

In recent decades, DES has been emerged and acknowledged as the most promising green solvent in the biological and chemical applications. DES was first introduced by Abbott et al. (2003). DES is defined as a homogenous mixture composed of hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) that are able to self-associate by forming a new eutectic phase, with a melting point lower than its individual components (Tomé, Baião, da Silva, & Brett, 2018). Mbous et al. (2017) have stated that the DESs exhibit some common characteristics which are similar to those of the ionic liquids such as high solubility, low volatility, low melting point, low vapour pressure, dipolar nature, chemically and thermally stable. DES is easy to prepare by simply mixing the HBD and HBA at moderate temperature without post-synthesis purification

(Francisco, van den Bruinhorst, & Kroon, 2013; Zhang, De Oliveira Vigier, Royer, & Jérôme, 2012). All these properties allow the DES to be designed and fine-tuned in specific applications such as lignocellulose pretreatment for fermentable sugar production (Procentese et al., 2018), bioethanol production (Xu et al., 2018) and biodiesel production (Troter, Todorović, Dokić-Stojanović, Stamenković, & Veljković, 2016).

The design and preparation of environmentally benign solvents in lignocellulose pretreatment still pose a great challenge for the researchers in order to achieve the fundamental principles of green chemistry (Anastas & Zimmerman, 2003). In this case, the emergence of DES plays an important role in replacing the conventional solvents which are applied in the pulping, bleaching and acid hydrolysis processes owing to its excellent physicochemical properties. This enables DES to be modified and tailored based on the desired application. Therefore, it is worth mentioning that the DES might be the key factor for a greener and sustainable biochemical processing of lignocellulosic biomass in the biorefinery concept. The aim of the present study is to prepare the CNC from rice straw (RS) through a multi-step pretreatment, which involves the use of alkaline DES in the lignocellulose pulping as well as acidic DES in the acid hydrolysis. The application of these DESs is to substitute the conventional chemical solvents that are commonly used in pretreatment methods for producing the CNC.

1.2 Problem statement

The agricultural sector in Malaysia produces enormous amount of rice straw (RS) annually after the paddy harvesting activity. The agricultural practices that are commonly exercised by the paddy farmers such as burning the RS residues, tilled back into the soil or left to decompose in the paddy field would contribute to the release of greenhouse gases and particulate matter into the atmosphere, which further lead to global warming (Gadde, Bonnet, Menke, & Garivait, 2009). In fact, RS can be utilized as the renewable biomass for the production of CNC through a green biorefinery approach.

The preparation of CNC generally involves several pretreatment steps, which include pulping and bleaching of the lignocellulosic biomass to produce bleached cellulosic fibers before proceeding with the acid hydrolysis process. However, hazardous solvents are mostly applied in these pretreatment processes. In recent decades, DES has emerged as a promising green solvent in various biological and chemical applications due to its superior physicochemical properties. Although DES has shown the ability to dissolve lignocellulosic components, its application in lignocellulose pulping and acid hydrolysis are still scarce (Škulcová, Majová, Šima, & Jablonský, 2017; Smink, Juan, Schuur, & Kersten, 2019). In this research study, alkaline DES is proposed as an alternative green solvent for the lignocellulose pulping to evaluate the performance of delignification process by comparing the physicochemical properties among the RS, unbleached DES treated pulp (UP) and bleached DES treated pulp (BP).

The common drawback of inorganic acid hydrolysis is that the CNCs usually have a lower thermal stability, thereby limiting its application in the processing of CNC based