ISOLATION OF NANO-CRYSTALLINE CELLULOSE FROM WASTE COTTON CLOTHS USING SUPERCRITICAL CARBON DIOXIDE TECHNOLOGY AS BIO-ADSORBENT FOR Cr(VI) REMOVAL

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2022

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by

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Thesis submitted in fulfilment of the requirements for the degree of Master of Science

April 2022

ACKNOWLEDGEMENT

I would like to express my gratitude to ALLAH S.W.T. for giving me good health and opportunity endlessly in finishing experiments and Master Thesis. This masterpiece is a development of new recycling method in order to save the environment and reduce waste throughout the world. A very special compliment goes out to my supervisor, Ts. Dr. Md. Sohrab Hossain and co-supervisor, Assoc. Prof. Dr. Mohamad Haafiz Bin Mohamad Kassim for many lessons and valuable guidance. Moreover, Majlis Amanah Rakyat (MARA) Graduate Excellent Program (GrEP) for the financial aid. My heartiest thanks are extended toward my family, parents (Mohamed Bin Jaafar and Sharifah Mardziah Binti Syed Akil) and Amry Bin Mohd Haris for the motivation during my studies. Thank you.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
AAS	Atomic Absorption Spectroscopy
AFM	Atomic Force Microscopy
ATR-FTIR	Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy
BET	Brunauer-Emmett-Teller analysis
CNCs	Cellulose nanocrystals
DSC	Differential scanning calorimetry
EtOH	Ethanol
Cr(VI)	Hexavalent chromium
HCl	Hydrochloric acid
H_2O_2	Hydrogen peroxide
mag.	Magnification
CH_4	Methane gas
CNF	Nano-fibrillated cellulose
ppm	Part per million
RSM	Response surface methodology
SEM	Scanning electron microscopy
SEM-EDX	Scanning electron microscopy with energy dispersive X-ray
NaOH	Sodium hydroxide
H_2SO_4	Sulfuric acid
TGA	Thermogravimetric analysis
TEM	Transmission electron microscopy
wt.%	Weight percent
XRD	X-ray diffraction analysis

LIST OF SYMBOLS

cm	Centimeter
°C	Degree Celsius
g	Grams
h	Hours
kg	Kilogram
L	Liter
μm	Micrometer
mg	Milligram
mm	Millimeter
min	Minutes
nm	Nanometer
%	Percentage
P	Pressure
sec	Seconds
T	Temperature
t	Time
λ	Wavelength

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PENGASINGAN SELULOSA NANO-HABLUR DARIPADA SISA KAIN KAPAS MENGGUNAKAN TEKNOLOGI KARBON DIOKSIDA LAMPAU GENTING SEBAGAI PENJERAB UNTUK PENYINGKIRAN Cr(VI)

ABSTRAK

Terdapat minat yang semakin meningkat untuk penggunaan sisa kain kapas secara lestari kerana jumlah penjanaan yang sangat besar dan kandungan selulosa yang tinggi. Kaedah pelupusan yang ada adalah pembuangan sampah secara terbuka di tempat pembuangan sampah bersama dengan sampah perbandaran yang lain menimbulkan pencemaran alam sekitar dan pembaziran sumber yang berguna. Sisa kain kapas mengandungi bahan selulosa berkualiti yang dapat dikitar semula dan digunakan kembali dengan penggunaan teknologi yang tepat. Objektif utama kajian ini adalah untuk mensintesis selulosa nano-hablur (CNCs) dari sisa kain kapas untuk menyingkirkan kromium heksavalen, Cr(VI) dari air sisa. Di mana, pemprosesan CNCs dari sisa kain kapas dilakukan dengan menggunakan kaedah konvensional (iaitu, pulpa soda, pelunturan peroksida, dan hidrolisis asid) dan teknologi karbon dioksida lampau genting (scCO_2). Pengaruh pulpa scCO_2 dalam pemprosesan CNCs ditentukan dengan pelbagai tekanan, suhu, masa rawatan, dan penambahan pelarut bersama. Beberapa kaedah analisis digunakan untuk menentukan sifat morfologi, fizikokimia, dan termal. Dalam kajian ini, scCO_2-CNCs berjaya diasingkan dari sisa kain kapas menggunakan pulpa scCO_2 dan hidrolisis asid. Kesan parameter teknologi scCO_2 seperti tekanan, suhu, masa rawatan, dan penambahan pelarut bersama dioptimumkan oleh metodologi tindak balas permukaan (RSM) dan dipasang dengan mencukupi ke dalam model polinomial urutan kedua. Istilah linear-kuadratik dan interaksi antara tekanan dan suhu, serta tekanan dan masa mempunyai kesan yang signifikan terhadap pulpa scCO_2. Keadaan optimum untuk pulpa scCO_2 dalam julat eksperimen pemboleh ubah yang dikaji adalah tekanan 16.69 MPa, suhu 59.09 °C dan 89.08 minit, menghasilkan 97.13% selulosa dan 84% keputihan. scCO_2-CNCs mempunyai struktur seperti batang, dengan panjang 100.03 ± 1.15 nm dan lebar 7.92 ± 0.53 nm. Analisis spektroskopi inframerah Fourier transformasi (ATR-FTIR) menunjukkan sekumpulan berfungsi selulosa di dalam scCO_2-CNCs dengan peratusan indeks penghabluran yang tinggi sebanyak 80.80% yang ditingkatkan oleh hidrolisis asid. scCO_2-CNCs mempunyai sifat kestabilan terma yang tinggi, luas permukaan yang besar dan cas permukaan negatif, yang berpotensi besar untuk digunakan sebagai penjerab untuk penjerapan logam berat. scCO_2-CNCs digunakan sebagai penjerab untuk penjerapan Cr(VI) dalam rawatan air sisa. Prestasi penjerapan scCO_2-CNCs ditentukan, di mana keadaan optimum Cr(VI) pada pH 1, dosis scCO_2-CNCs 1.50 g/L, suhu 60 °C selama 30 minit dan kepekatan awal 100 ppm. Penemuan kajian ini menunjukkan bahawa scCO_2-CNCs yang diasingkan berpotensi digunakan sebagai penjerab untuk pemisahan logam berat dari air sisa. Penggunaan sisa kain kapas yang inovatif ini akan mengurangkan beban sampah perbandaran yang dibuang di tempat pembuangan sampah, meminimumkan pencemaran alam sekitar, dan meningkatkan penggunaan bahan buangan secara lestari untuk produk bernilai-tambah.

ISOLATION OF NANO-CRYSTALLINE CELLULOSE FROM WASTE COTTON CLOTHS USING SUPERCRITICAL CARBON DIOXIDE TECHNOLOGY AS BIO-ADSORBENT FOR Cr(VI) REMOVAL

ABSTRACT

There is an increasing interest in sustainable utilization of waste cotton cloths due to the enormous volume of generation and its high cellulose content. The existing disposal method is open dumping in landfills along with other municipal waste poses environmental pollution and waste of useful resources. Waste cotton cloths contain quality cellulosic materials that can be recycled and reused with the utilization of proper technology. The main objective of this study is to synthesis cellulose nanocrystals (CNCs) from waste cotton cloths for removing Cr(VI) from wastewater. Wherein, the processing of CNCs from waste cotton cloths were conducted using the conventional method (i.e., soda pulping, bleaching and acid hydrolysis) and supercritical carbon dioxide (scCO_2) technology. The influence of the scCO_2 pulping in CNCs processing was determined with varying pressure, temperature, time, and addition of co-solvent. Several analytical methods were used to determine morphological, physicochemical, and thermal properties. In the present study, scCO_2-CNCs were successfully isolated from waste cotton cloths using scCO_2 pulping and acid hydrolysis. The effects of scCO_2 technology parameters such as pressure, temperature, treatment time, and addition of co-solvent were optimized by RSM and were adequately fitted into the second-order polynomial model. The linear-quadratic terms and interaction between pressure and temperature, and pressure and time had significant effects on scCO_2 pulping. The optimum condition for scCO_2 pulping within the experimental range of studied variables was pressure of 16.69 MPa, the temperature of 59.09 °C and 89.08 min, resulted in $yield_{cellulose}$ and whiteness of 97.13% and 84%, respectively. $scCO_2$-CNCs had a rod-like structure with a length of 100.03 ± 1.15 nm and a width of 7.92 ± 0.53 nm. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) analysis shows a functional group of cellulose in $scCO_2$-CNCs with a high percentage crystallinity index of 80.80% enhanced by acid hydrolysis. $scCO_2$-CNCs had a high thermal stability property, large surface area and a negative surface charge, which a great potential to be utilized as an adsorbent for heavy metals adsorption. $scCO_2$-CNCs were used as an adsorbent for Cr(VI) adsorption in wastewater treatment. The adsorption performance of $scCO_2$-CNCs were determined, where the optimum condition of Cr(VI) at pH 1, doses of 1.50 g/L, treatment time of 30 min, the temperature of 60 °C and initial concentration of 100 ppm. The findings of the present study show that the isolated $scCO_2$-CNCs has the potential to be uses as adsorbent for the separation of heavy metals from waste water. This innovative utilization of waste cotton cloths would reduce the municipal waste load disposed of in a landfill, minimize environmental pollution, and enhance the sustainable utilization of waste materials for a value-added product.

CHAPTER 1

INTRODUCTION

1.1 Background of study

In the 21st century, sustainable waste management concept has become the main interest of environmentalists to reduce environmental pollution and greenhouse gas emissions (Ferronato and Torretta, 2019). There is a growing concern related to generation of waste cotton cloths with an increasing of cotton cloths production and a rising of fast-fashion demand in textile and fashion industries (Husein et al., 2019; Niinimaki et al., 2020). It is estimated more than 28 million tons of cotton cloths are used throughout the world (Johnson et al., 2020). About 20% of world waste cotton cloths are either reused as wiping cloths, pass to friends and relative, or sold as pre-loved items, while another 80% are end up in open dumps in landfill site (Huang et al., 2020; Racho and Waiwong, 2020). It has been estimated more than 10 million tons of waste cotton cloths are disposed every year throughout the world (Huang et al., 2020; Johnson et al., 2020).

Current disposing method for waste cotton cloths on dumping site led to environmental pollution and waste of useful resources (natural cellulose fibre) (Wang et al., 2017). Although, waste cotton cloths are biodegradable, chemical dye and colour present in waste cotton cloths may pose a severe threat to the environment, soil and aquatic ecosystem (Utebay et al., 2019; Ma et al., 2018). Nevertheless, cellulose is found to be rich in waste cotton cloths, while recycling cotton from waste cotton cloths have many advantages, such as wide availability, cheap, renewable, abundant, strong, durable and biodegradable (Theivasanthi et al., 2018).

Waste cotton cloths comprises of three components which are cellulose, hemicellulose and lignin. Hemicellulose and lignin are present in the primary walls and are difficult to completely remove (Shaikh et al., 2021). Lignin, made of phenyl-propane units connected by carbons C-C covalent bonds, is acting as a binding agent to hold the cells together and considered to be the reticular polymer (Blanco et al., 2018). Therefore, pulping process is needed to isolate cellulose from waste cotton cloths. Pulping is a process where cellulose fibre (also known as pulp fibre/ nano-fibrillate cellulose, CNF) is isolated from lignocellulose, such as woods and other plant materials (non-woods) by removing hemicellulose and lignin barrier that binds cellulose fibre together (Smole et al., 2018). However, current pulping methods, such as soda pulping, Kraft and sulfite pulping use toxic chemicals, such as sodium hydroxide (NaOH), which poses threat to the environment and human health (Riley, 2012). Thus, a waterless and greener pulping process approach is urgently needed to minimize the environmental pollution.

Supercritical carbon dioxide (scCO_2) technology is a current interest in pulping process which consists of isolating cellulose while removing lignin (delignification) and hemicellulose using carbon dioxide (CO_2) as solvent (Zeng et al., 2017). scCO_2 technology is an environmental-friendly pulping process as it uses CO_2 as solvent, mild operating temperature and easy-recovery solvent (Sarip et al., 2016). CO_2 has several advantages, such as abundant, inexpensive, non-toxic, inert and easy-recovery (Che Hamzah et al., 2016). In addition, scCO_2 technology is widely used method for chemical separation and pulping in these recent years, such as pulping lignocellulose, extraction of essential oil and extractives in foods, medicine and health-care, oleochemical, and petrochemical industries (Sarip et al., 2016).

Cellulose nanocrystals (CNCs) is the crystalline region of cellulose, isolated from cellulose pulp fibre (nano-fibrillated cellulose, CNF) using acid hydrolysis by removing amorphous region of cellulose while leaving only crystalline region of cellulose, which poses a higher resistance to acids (Blanco et al., 2018; Shankaran, 2018). CNCs exhibited elongated crystalline of cylindrical rod-like and needle-like shape with a width of 2-70 nm, length of 100-600 nm and crystallinity index of 75-88% (Trache et al., 2020). CNCs has a very limited flexibility than nano-fibrillated cellulose due to CNCs do not contain amorphous region (Islam and Rahman, 2019).

CNCs serve as a promising renewable source and have been utilized in many advance applications, such as for pharmaceutical, foods, packaging, bio-catalysts and bio-sorbent (Wang et al., 2017). It is due to its distinct key features, which are lightweight, abundant availability, unique optical properties, large surface area, high mechanical and thermal strength, environmental-friendly nature, and biodegradability (Huang et al., 2020; Sukhavattanakul & Manuspiya, 2020). Over these recent years, studies have been conducted on the isolation of CNCs from various lignocellulose sources materials, such as plant cell walls, bamboo, wastepaper, paper cup waste, cotton, cotton fabrics, algae, and bacteria (Lamaming et al., 2015; Rasheed et al., 2020; Jiang et al., 2020; Nagarajan et al., 2020, Huang et al., 2020; Huang et al., 2020; Zhao et al., 2019; Ambrosio-Martin et al., 2015). Furthermore, Jiang et al. (2020) isolated CNCs from wastepaper using H_2SO_4 acid, while Nagarajan et al. (2020) obtained CNCs from paper cup waste using citric acid ($C_6H_8O_7$) for reinforcement composite films and packaging, respectively.

Nevertheless, waste cotton cloths have an abundant availability and high cellulose content (up to 90%), which made it a sustainable source for a various value-added products, such as CNCs (Wang et al., 2017; Huang et al., 2020). In addition, isolation of CNCs from waste cotton cloths would comply with the 3R's (reduce, reuse, recycle) concept of sustainability as the present study reused of waste materials, reduce municipal waste disposed of in the landfill and recycled waste materials. In addition, isolation of CNCs from waste cotton cloths contribute to sustain utilizing waste resources and reduce waste disposed of in dumping site. Hence, reduce environmental pollutions.

Acid hydrolysis serves as the most promising method for preparation of CNCs from cellulose pulp, isolated from various lignocellulose sources (Huang et al., 2020). Sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) are commonly used inorganic acids in acid hydrolysis to remove amorphous regions in cellulose to isolate CNCs (Wang et al., 2017). However, CNCs produced using these acids (HCl and nitric acids) have a poor dispersability in water, while CNCs isolated using H_2SO_4 has a good dispersability (Blanco et al., 2018). Previous studies have reported that CNCs isolated using HCl hydrolysis had a weak oxidizing ability, low thermal degradation and poor dispersion ability (Blanco et al., 2018). In contrast, CNCs isolated using H_2SO_4 hydrolysis has better thermal stability and provide the most stable cellulose suspension due to presence of sulfate group on the surface of CNCs. Furthermore, Maciel et al (2021) studied effect of H_2SO_4 hydrolysis reported that H_2SO_4 concentration influenced CNCs length while the optimal experimental condition of H_2SO_4 hydrolysis were 64 wt.% acid concentration, 1 h reaction time and 50 ºC.

1.2 Problem statement

There is an increasing concern on minimization of municipal waste generation and sustainable utilization of waste materials. The rise of fast-fashion demand has led to an increase in cotton cloths production, which later contributed to a serious problem as a huge amount of waste cotton cloths is generated every year throughout the world. Waste cotton cloths comprise about 4% of total municipal waste disposed to landfill in Malaysia. Thus, recycling and reuse of waste cotton cloths potentially minimize municipal waste generation.

The existing cellulose isolation method requires multiple processing steps including pulping, bleaching and hydrolysis processes. These processes require the addition of hazardous chemicals and the huge amount of fresh water. It generates toxic wastewater that must be treated before disposal. Thus, it urgent need to determine a waterless technology for the isolation of cellulose from waste cotton cloths.

scCO_2 technology has been utilized to isolate cellulose from lignocellulose biomass (Sri Aprilia et al., 2017). These reported that scCO_2 pressure, temperature and time influenced delignification of lignocellulose fibre and its properties during pure fibre isolation. However, in order to enhance the fibre processing and delignification, this process may require the addition of co-solvent.

Acid hydrolysis is the most promising method to isolate CNCs from various cellulose sources. The most common inorganic acids are sulfuric acid, H_2SO_4 and hydrochloric acid, HCl used in acid hydrolysis to remove amorphous region to isolate CNCs. However, previous studies reported that CNCs isolated using HCl hydrolysis had a weak oxidizing ability, low thermal degradation and poor dispersion ability. Conversely, acid hydrolysis using H_2SO_4 provided the most stable cellulose suspension due to the presence of sulfate group on the surface of crystallites. Therefore, isolated CNCs using H_2SO_4 hydrolysis gained better mechanical and thermal stability.

Heavy metals pollution raises serious environmental concerns. Adsorption is viewed as one of the most effective methods for removing heavy metals from wastewater using various lignocellulose fibre as bio-sorbent. Thus, it bears considerable interest to utilize CNCs from waste cotton cloths as a bio-sorbent for heavy metals separation.

1.3 Objectives of study

The objectives of the study are as follows:

1. To determine the influence of $scCO_2$ technology process parameters: pressure, temperature, time, and addition co-solvent on the isolation of cellulose from waste cotton cloths.

2. To identify physicochemical, thermal and morphological properties of isolated cellulose nanocrystals (CNCs) from cellulose in waste cotton cloths using H_2SO_4 acid hydrolysis.

3. To determine the adsorption performance of isolated $scCO_2$-CNCs on the removal of Cr(VI) from synthetic wastewater.

1.4 Scope of study

The scope of study has been identified in order to achieve the objectives. In the present study, cellulose nanocrystals (CNCs) were isolated from waste cotton cloths collected from a landfill using supercritical carbon dioxide ($scCO_2$) technology ($scCO_2$ pulping) and H_2SO_4 hydrolysis. The influences of $scCO_2$ technology parameters; pressure, temperature, treatment time and addition of co-solvent were analysed to determine the optimum condition for high $yield_{cellulose}$ and whiteness. Then, CNCs were used as bio-sorbent for adsorption of Cr(VI) from aqueous solution in wastewater treatment.

Several analytical methods were used to determine morphological, physicochemical, thermal properties of CNCs. Analyses of CNCs were done using field emission scanning electron microscopy (SEM), energy-filtered transmission electron microscopy (TEM), atomic force microscopy (AFM), scanning electron microscopy with energy dispersive X-ray (SEM-EDX) and Brunauer-Emmett-Teller (BET). Attenuated total reflectance Fourier-transform infrared spectroscopy (FTIR) was done to determine functional groups and chemical compounds in CNCs.

Meanwhile, crystallinity index analysis was done using X-ray diffraction (XRD), while thermal stability analyses using thermogravimetric analysis (TGA) and differential scanning electron (DSC). Besides, surface charge and particle size distribution of CNCs were done using Zeta potential analysis. The adsorption of Cr(VI) using CNCs were done using atomic adsorption spectrometry (AAS). The findings of the present study of utilization waste material (waste cotton cloths) provided a sensible information for isolation of CNCs.

1.5 Significance of study

Supercritical carbon dioxide ($scCO_2$) technology is a current interest in pulping process which consists of isolating cellulose while removing lignin (delignification) and hemicellulose using CO_2 as solvent (Zeng et al., 2017). $scCO_2$ pulping is an environmental-friendly pulping process as it uses CO_2 as solvent, mild operating temperature and easy-recovery solvent (Sarip et al., 2016). Besides, CO_2 has several advantages, such as abundant, inexpensive, non-toxic, inert and easy-recovery (Che Hamzah et al., 2016).

Waste cotton cloths have an abundant availability and high cellulose content (up to 90%), which made it a sustainable source for a various value-added products, such as CNCs (Huang et al., 2020). In addition, isolation of CNCs from waste cotton cloths would comply with the 3R's (reduce, reuse, recycle) concept of sustainability as the present study reused of waste materials, reduce municipal waste disposed in landfill and recycled waste materials. In addition, isolation of CNCs from waste cotton cloths contribute to sustain utilizing waste resources and reduce waste disposed in dumping site. Hence, reduce environmental pollutions. CNCs isolated using H_2SO_4 hydrolysis had better thermal stability and provide the most stable cellulose suspension due to presence of sulfate group on the surface of CNCs.

CNCs could be utilized as a promising bio-adsorbent for removing heavy metals such as Cr(VI) from the industrial effluent. The major findings of the present study show the potential of recycling waste cotton cloths collected from landfill to produce a value-added product such as cellulose nanocrystals, hence to be utilized as renewable bio-adsorbent for Cr(VI) removal from aqueous solution in wastewater treatment using adsorption process. Thus, the sustainable utilization of waste cotton cloths into a value-added product can be a promising approach in reducing carbon footprint and environmental pollutions. Sustainable development goals (SDG) are the blueprint to achieve a better sustainable future. The present study has several targets of the Sustainable Development Goals (SDG), which can contribute to clean water and sanitation (SDG 6), sustainable cities and communities (SDG 11), and responsible consumption and production (SDG 12).

SDG 6 (clean water and sanitation) is to ensure availability and sustainable management of water and sanitation for all. In the present study, the cellulose nanocrystals ($scCO_2$-CNCs) were used as a bio-adsorbent for adsorption of Cr(VI) heavy metals from synthetic wastewater. The removal of Cr(VI) from synthetic wastewater would contributed to people have access to a safe and clean drinking water, and adequate sanitation services (SDG 6.1), improve water quality by reducing pollution and minimize release of hazardous chemicals and materials (SDG 6.3), to ensure sustainable supply of freshwater (SDG 6.4), and to protect and restore water-related ecosystems (i.e. rivers and lakes) using wastewater treatment (SDG 6.6 and 6.6a).Wherein, SDG 11 (sustainable cities and communities) is to make cities and human settlements inclusive, safe, resilient and sustainable. In the present study, the waste cotton cloths were collected from a landfill. The recycling of waste cotton cloths into a value-added product (cellulose nanocrystals) would contribute to a better municipal solid waste management to improve public health, reduce environmental pollution and landfill demand due to existing disposal method. (SDG 11.6).

SDG 12 (responsible consumption and production) is to ensure sustainable consumption and production patterns. In the present study, the waste cotton cloths were collected from a landfill. The waste cotton cloths contain an abundant of cellulose as it is sustainable natural resources (SDG 12.2). The recycling of waste cotton cloths into a value-added product (cellulose nanocrystals) would contribute to a better municipal solid waste management to improve public health, reduce environmental pollution and landfill demand due to existing disposal method. (SDG 12.5). Besides, the present study utilized a green approach using supercritical CO_2 technology ($scCO_2$) for pulping process. It is a waterless technology and uses environmental-friendly pulping solvent (CO_2 gas) which can contribute to minimize environmental pollutions (SDG 12.8a).

CHAPTER 2

LITERATURE REVIEW

2.1 Waste cotton cloths

2.1.1 Source and generation

Waste cotton cloths have an abundant availability and high cellulose content (up to 90%), which made it a sustainable source for a various value-added products (i.e. nanocellulose) (Huang et al., 2020). Cellulose is found to be rich in waste cotton cloths, as recycling cotton from waste cotton cloths have many advantages, such as wide availability, cheap, renewable, abundant, strong, durable and biodegradable (Theivasanthi et al., 2018).

Waste cotton cloths, made from 100% natural cotton fibre, is a worn out, torn, rejected, scrap and unwanted cotton cloths discarded by generators or person can be classified as one of textile type of Municipal Solid Waste (MSW). It is continuously generated in bulky amount and has abundant sources from various waste generators (i.e. single and multi-family dwellings) from different sources (i.e. residential and commercial) (Wang et al., 2017; Bjorquist et al., 2018). Figure 2.1 shows variation of sources of waste cotton cloths which are from commercial, institutional, hospitals, healthcare, residential, industrial and process manufacturing. Meanwhile, waste cotton cloths generators are stores, hotels, hospitals, single and multi-family dwellings.

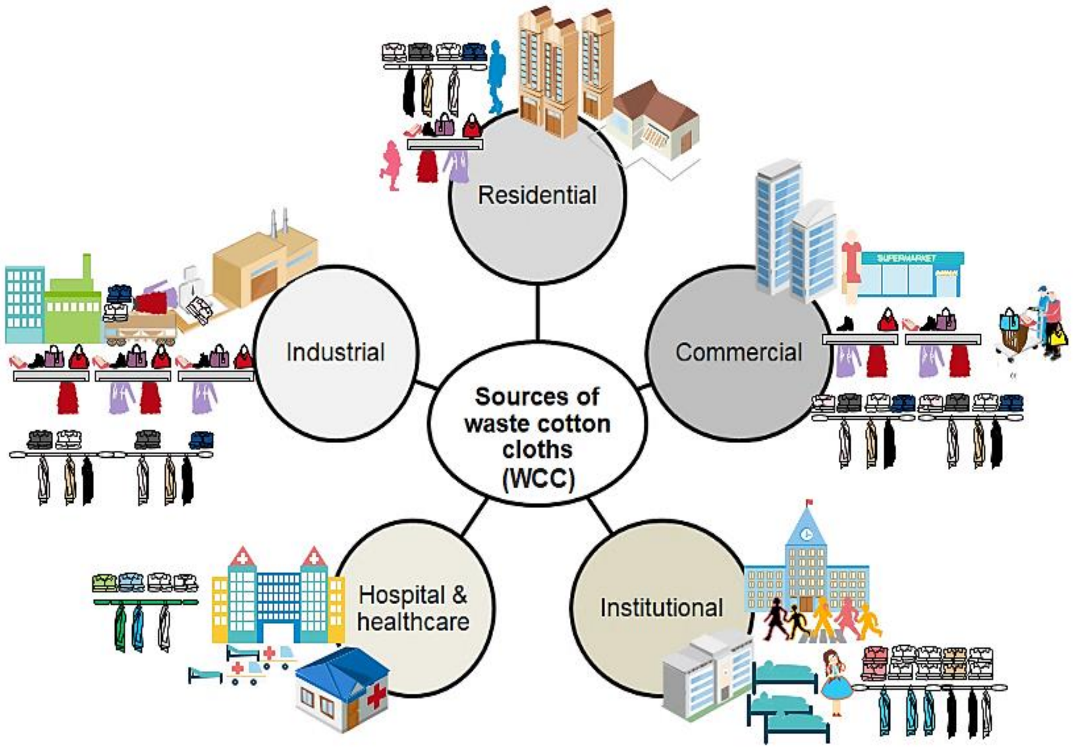

Figure 2.1 Sources of waste cotton cloths.

There is a growing concern related to generation of waste cotton cloths with increasing of cotton cloths production and a rising of fast-fashion demand in textile and fashion industries (Husein et al., 2019; Niinimaki et al., 2020). It is estimated more than 28 million tons of cotton cloths are used, and more than 10 million tons of waste cotton cloths are disposed every year throughout the world (Huang et al., 2020; Johnson et al., 2020). Table 2.1 shows the estimated solid, textile and waste cotton cloths generation from 2007-2012.

Based on Table 2.1, textile wastes, comprises nearly 70-80% of waste cotton cloth, is one of solid wastes types composes of 8.28% of total global solid wastes where it is mainly generated from residential, commercial, institutional, hospital, healthcare and industrial as total of 92-95.60 and 7.88-9.00 million tons with generation rate of 0.25 and 0.12 kg/capita.day of textile wastes were generated and discarded throughout the world and Malaysia in 2010-2012, respectively (Rosli, 2018).

Besides, global waste cotton cloths have an extensive sources of 70-80% of total amount global textile wastes of 65.66-75.04 while Malaysia, 5.2-7.2 million tons contributed approximately 8.84% of global waste cotton cloths production with generation rate of 0.19 and 0.10 kg/capita.day in 2007 to 2012, respectively (Wang et al., 2017). The waste generation is estimated to be double by 2020 to 2025 due to the increase in cotton cloths production from 2000 to 2014 as 100 billion are produced per annum, which is 13 times than global population, increased in global production rises due to high demand in fashion industry (Rosli, 2018). However, there is limited study on waste cotton cloths generation in Malaysia and worldwide.

Table 2.1 Estimated solid, textile and cotton cloth wastes generation in 2007-2012 (Hoornweg and Bhada-Tata, 2012).

	Types of wastes					
	Solid wastes		Textile wastes		Waste cotton cloths	
	Global	Malaysia	Global	Malaysia	Global	Malaysia
Total amount (Million tons)	1,128-1,138	130-180	92.00-95.60	7.88-9.00	65.66-75.04	5.20-7.20 (4% of M'sia solid waste)
Average total amount (Million tons)	1,133	155	93.80	8.44	60.13	6.20
Average percentage (%)	100	13.68	100	12.03	100	8.84
Average generation rate (kg/capita.day)	0.81	0.74	0.25	0.12	0.19	0.10 (1-piece cloth)

Note: Mass of 1 cloth= approx. 100-150 g.

2.1.2 Physicochemical compositions

Waste cotton cloth, composed of 80-90% of total organic material is made from 100% cotton fibre (up to 90% cellulose) (Bernal et al., 2017). Cellulose is joined by β-1,4-glycosidic bonds as main component in waste cotton fibre with 85-88% followed with hemicellulose, lignin, proteins and extractives of 5-20%, <10% and 1.1-1.9%, respectively (Kumar and Singh, 2018; Bernal et al., 2017). Besides, waste cotton cloths also have chemical dye and colour presented in the waste cotton cloths fibre (Wang et al., 2017; Bjorquist et al., 2018). The physicochemical properties of cotton fibre and waste cotton cloths fibre are tabulated in Table 2.2.

Cellulose, a natural polysaccharides and biodegradable polymer, is the major component in lignocellulose and can be found in structural components of rigid cell wall of plants (Theivasanthi et al., 2018). Cellulose has an abundant source mainly from lignocellulose biomass and municipal solid waste (i.e. waste cotton cloths) (Shankaran, 2018). Plants are the main biomass sources of cellulose and have the most extensive distribution in nature, such as tree, bamboo and cotton (Xie et al., 2016). Cellulose fibre structure consisted of crystalline and amorphous region, where it is formed by large numbers of glucose units (monosaccharide) combined by β-1,4 glycosidic bonds (Chawla et al., 2015). Cellulose chemical structure difficult to break as it has a strong tendency to form intra- and intermolecular hydrogen bonds due to the presence of multiple hydroxyl groups (Theivasanthi et al., 2018). Figure 2.2 (a) shows the chemical structure of cellulose.

Hemicellulose is a linear and branched heteropolymers of d-xylose, l-arabinose, d-galactose, d-glucose and d-mannose where it is easier to hydrolyse as it contains no crystalline polymer (Chaturvedi and Verma, 2013). Hemicelluloses are generally categorized according to the main sugar residue in the backbone (i.e. xylans, mannans, and glucans, with xylans and mannans) (Chawla et al., 2015). Hemicellulose typically accounts for approximately 15–35% of lignocellulose biomass (Lee et al., 2014). The structure of hemicellulose polysaccharides is more complex than cellulose, has many branches and acetyl groups (-$COCH_3$) (Alam et al., 2014). Thermal degradation of lignocellulose starts with hemicellulose (low thermal degradation temperature due to presence of acetyl groups). Besides, due to its branched structure, hemicellulose is amorphous and much more susceptible to hydrolysis by acids than cellulose (Huang et al., 2014). Hence, hemicellulose can be completely removed without degrading cellulose (Chawla et al., 2015). Figure 2.2 (b) shows the chemical structure of hemicellulose.

Lignin, typically accounts for 17–33% of lignocellulose is a large complex and heterogeneous polymer. It composed largely of three different phenyl-propane units and methoxy groups as the monomer units, and linked by ether bonds (Lee et al., 2014). The presence of lignin component in plant cell wall made acid hydrolysis difficult, as it prevents cellulose from being hydrolysed and preventing swelling of fibres, which will affect chemicals accessibility to the cellulose by acting as a shield or physical barrier (Behera et al., 2014). However, lignin can be hydrolyse using pulping process such as soda pulping (Lee et al., 2014). Figure 2.2 (c) shows the chemical structure of lignin.

Figure 2.2 shows the waste cotton cloths fibre is an elongated 30 mm, comprises of cuticle (pectin, waxes and fats) (Ioelovich, 2015). Pectin, in middle lamella layer is a cross-linked polysaccharides that forms gels to glue cell walls components together; primary wall, winding layer, secondary wall and lumen (Smole et al., 2018). In nature, bundles of cellulose molecules usually packed together to form micro-fibrils (micro-fibrillated cellulose), which consisted of crystalline regions alternate with amorphous regions (Huntley et al., 2015). Wherein, the crystalline cellulose consists of strong hydrogen bonds and has a high tensile strength. Thus, it needs a very low pH (concentrate acid), high temperature and longer treatment times are required to hydrolyse cellulose into nanocellulose (Alexander, 2012).

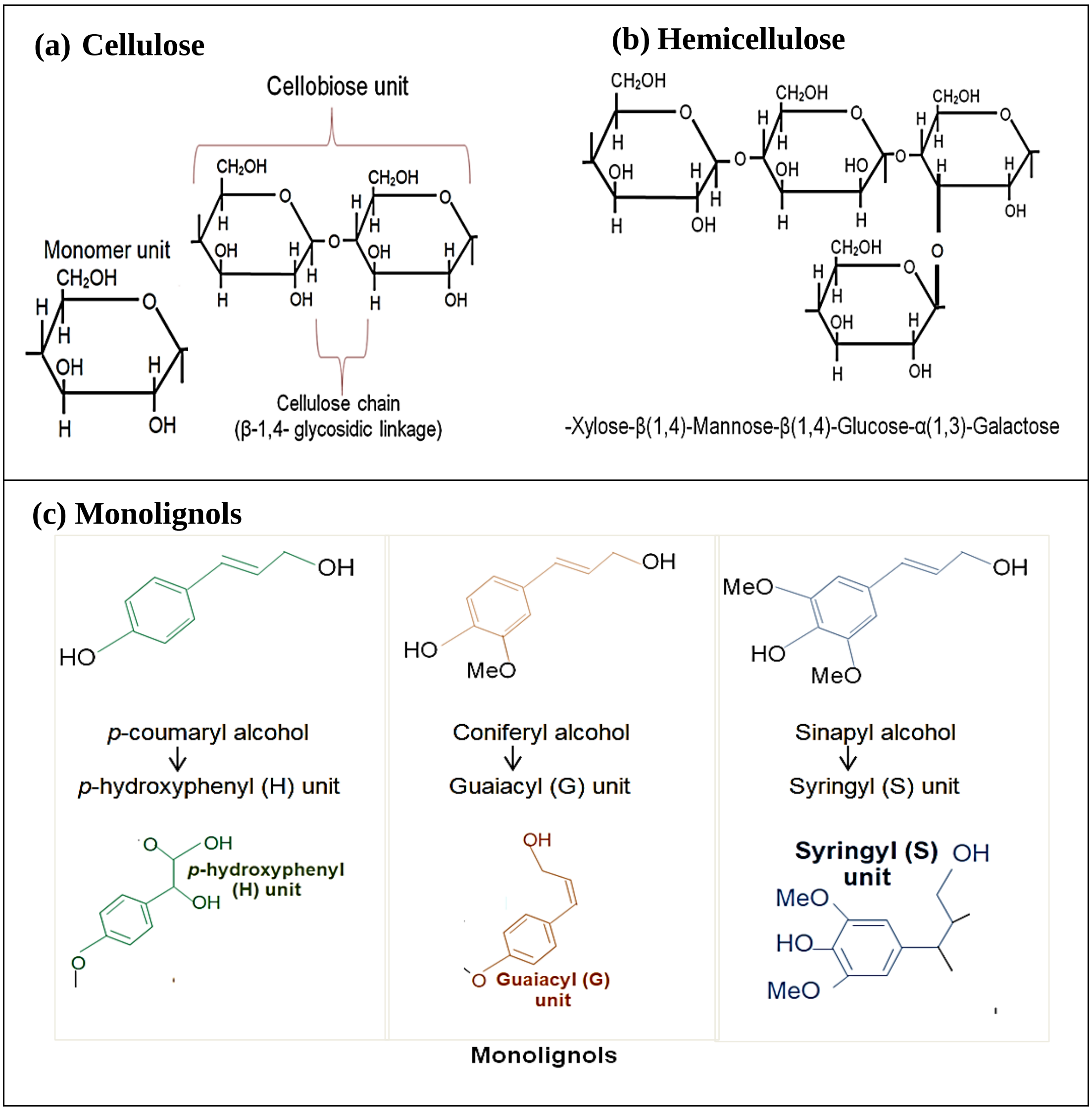

Figure 2.2 Chemical structure of (a) cellulose, (b) hemicellulose, and (c) monolignols.

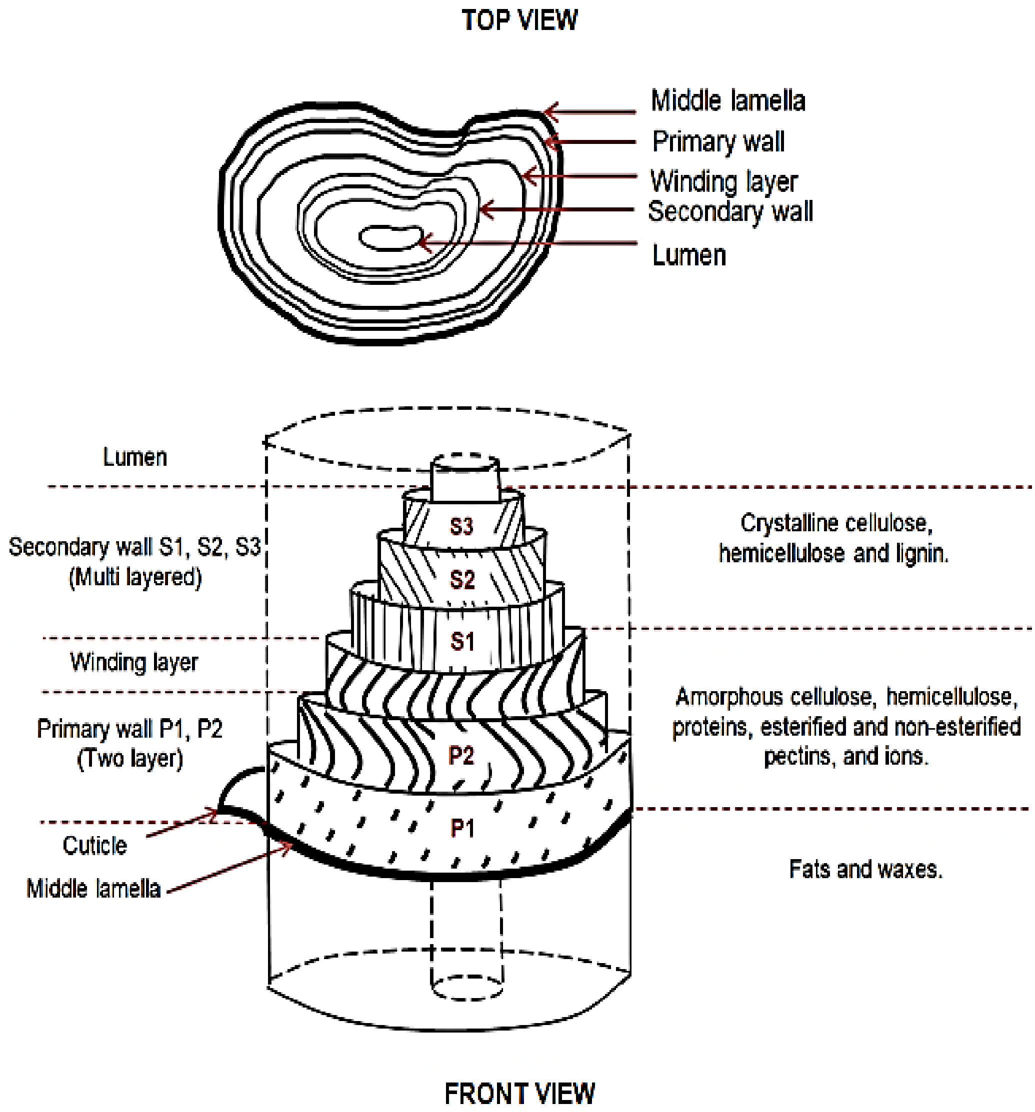

Figure 2.3 Cross-sectional of waste cotton cloths fibre.

Table 2.2 Chemical compositions (dry basis wt.%) of cotton fibre and waste cotton cloths (Ioelovich, 2015; Huntley et al., 2015)

Chemical compositions	Cotton fibre	Waste cotton cloths
Cellulose, $(C_6H_{10}O_5)_n$	71.3-95	85-88
Hemicellulose, $(C_5H_8O_4)_n$	5-40	5-20
Lignin, $(C_9H_{10}O_2, C_{10}H_{12}O_3, C_{11}H_{14}O_4)_n$	0.4-30	<10
Protein	1.1-1.9	1.1-1.9
Ash	0.7-2.0	0.7-2.0
Pectin substance	0.7-1.9	0.7-1.2
Malic, citric and other organic acids	0.8	0.8
Oil, fat and wax	0.4-1.0	0.4-1.0
Total sugar	0.3	0.3
Pigment	Trace	Dye and colour

2.2 Waste cotton cloths management

2.2.1 Reuse, recycle and disposal

The current disposing methods for waste cotton cloths on dumping site led to environmental pollution and waste of useful resources (natural cellulose fibre) (Wang et al., 2017). Besides, the continuous generation and dumping of waste cotton cloths in landfill throughout the world every year has led to increase landfill demand issue (Wang et al., 2017; Rosli, 2018). Nevertheless, cellulose is found to be rich in waste cotton cloths, while recycling cotton from waste cotton cloths have many advantages, such as wide availability, cheap, renewable, abundant, strong, durable and biodegradable (Theivasanthi et al., 2018).

About 20% of world waste cotton cloths are either reused as wiping cloths, pass to friends and relative, or sold as pre-loved items, while other 80% were end up in open dumps in landfill site. In addition, isolation of CNCs from waste cotton cloths would comply with the 3R's (reduce, reuse, recycle) concept of sustainability as the present study reused of waste materials, reduce municipal waste disposed in landfill and recycled waste materials to value-added products.

2.2.2 Socio-environmental impact

Figure 2.4 shows the socio-environmental impact of current disposing methods for waste cotton cloths. The continuous generation and dumping of waste cotton cloths in landfill throughout the world every year has led to increase landfill demand issue, as landfill created prolonged survival of pathogenic microorganisms (Wang et al., 2017; Rosli, 2018). Decomposing either aerobically or anaerobically emitted greenhouse gases, such as CO_2 and methane gas (25 times harmful than CO_2) (Sanchez et al., 2015). Although, waste cotton cloths are biodegradable, chemical dye and colour present in waste cotton cloths may pose a severe threat to the environment, soil and aquatic ecosystem (Utebay et al., 2019; Ma et al., 2018). Nevertheless, cellulose is found to be rich in waste cotton cloths, while recycling cotton from waste cotton cloths have many advantages, such as wide availability, cheap, renewable, abundant, strong, durable and biodegradable (Theivasanthi et al., 2018).

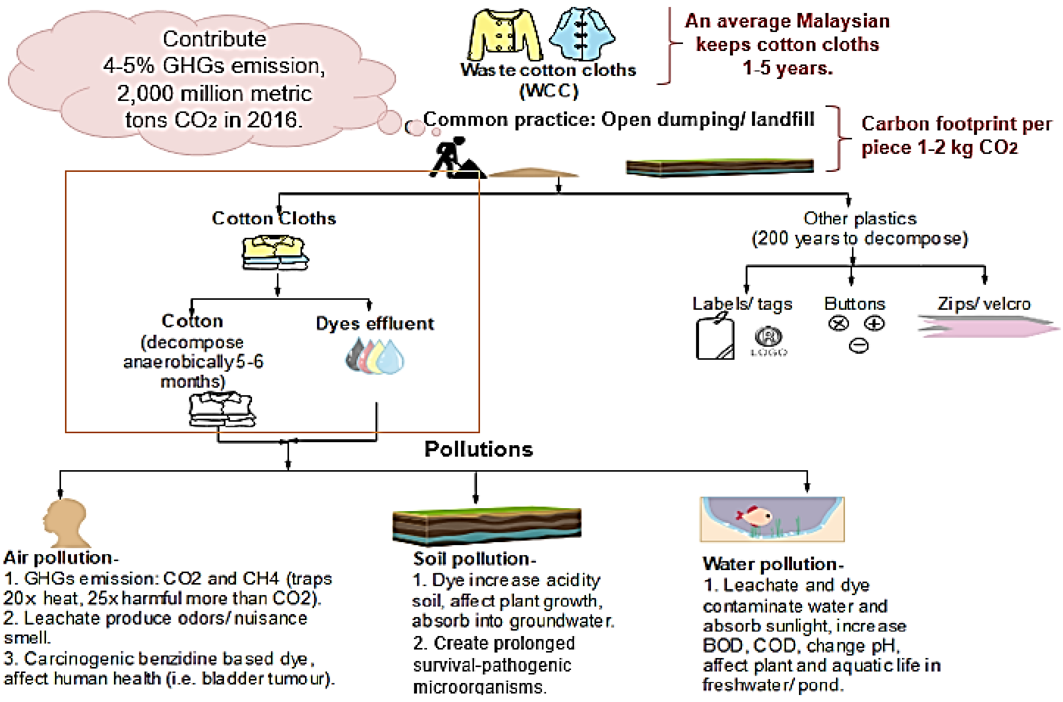

Figure 2.4 Socio-environmental impact of waste cotton cloths current disposal methods.

2.3 Isolation cellulose nanocrystal from waste cotton cloths

Cellulose nanocrystals (CNCs) is a cellulose-derivative, represented the crystalline region of cellulose, which in nano-size (Ravi Shankaran, 2018). CNCs is generally isolated from lignocellulose source materials, such as empty fruit bunch (EFB), rice husk, bagasse and cotton (Huang et al., 2020; Sukhavattanakul & Manuspiya, 2020). CNCs is produced by removing amorphous region using acid hydrolysis leaving only crystalline region of cellulose (known as nanocrystalline cellulose, NCC or cellulose nanocrystals, CNCs), which poses a higher resistance to acid (Blanco et al., 2018). CNCs, also known as nano-whiskers, exhibited elongated crystalline with cylindrical rod-like or needle-like shape with 2-70 nm in width, 100-600 nm in length and 75-88% of crystallinity index (Trache et al., 2020). It with a very limited flexibility than nano-fibrillated cellulose due to CNCs do not contain amorphous region (Md Nazrul and Rahman, 2019). Figure 2.5 shows the mechanism of the isolation of CNCs from nano-fibrillated cellulose in waste cotton cloths fibre.

In a recent year there are studies have been conducted on the isolation of cellulose fibre or cellulose nanocrystal for various value-added application, as shown in Table 2.3. Although several studies have been isolated CNCs from leftover cotton fabrics in textile industry, no study yet consider disposed waste cotton cloths in landfill. In addition, isolation of CNCs from waste cotton cloths would comply with the 3R's (reduce, reuse, recycle) concept of sustainability as the present study reused of waste materials, reduce municipal waste disposed in landfill and recycled waste materials.

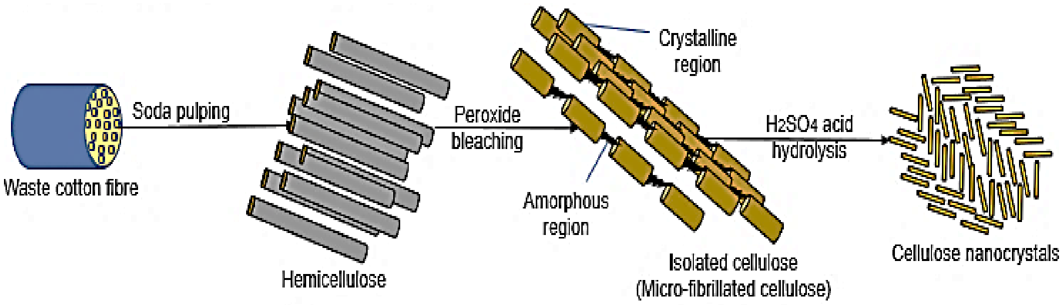

Figure 2.5 Mechanism of isolation of cellulose nanocrystals (CNCs).

Table 2.3 Isolation of CNCs from waste cotton cloths.

Raw materials	Methods	Applications	References
Degreasing cotton	Mixed H_2SO_4 and HCl hydrolysis	Film packaging	Wang et al. (2017)
Textile waste from industry	H_2SO_4 hydrolysis	Reinforcing agent soy-protein film	Huang et al. (2020)
Textile waste from industry	Three-step oxidation	Reinforcing agent soy-protein film	Huang et al. (2020)
Cotton fabric	H_2SO_4 hydrolysis and ultrasonication	PVA film	Xiong et al. (2012)
Cotton fabric	H_2SO_4 hydrolysis	Composites	Yue et al. (2012)
Waste cloths from landfill	H_2SO_4 hydrolysis and ultrasonication	-	Mohamed et al. (2021)

CNCs serve as a promising renewable source and have been utilized in many advance applications, such as for pharmaceutical, foods, packaging, bio-catalysts and bio-sorbent. It is due to its distinct key features, which are lightweight, abradant availability, unique optical properties, large surface area, high mechanical and thermal strength, environmental-friendly nature, and biodegradability. Isolation of CNCs from waste cotton cloths contribute to sustain utilizing waste resources and reduce waste disposed in dumping site. Hence, reduce environmental pollutions.

Several studies done reported that utilization of textile waste materials is a promising approach for sustainable utilization of waste materials to isolate CNCs. For example, Huang et al. (2020) isolated CNCs from textile waste into reinforcing agent of soy protein film using H_2SO_4 hydrolysis and three-step oxidation process. Meanwhile, Shi et al. (2021) isolated micro-crystalline cellulose (MCC) from waste cotton cloths using hydrothermal method, resulted to a comparable physicochemical and thermal properties as commercial MCC. On the other hand, Maciel et al. (2021) used unwoven industrial textile cotton waste and H_2SO_4 while Wang et al. (2017) waste cotton cloths and mixed acid (sulfuric acid and hydrochloric acid) hydrolysis process. Besides, Xiong et al. (2021) isolated CNCs from MCC derived from waste cotton fabrics using acid hydrolysis assisted ultrasonic treatment. Zhong et al. (2021) isolated CNCs from recycled denim fabrics into reinforcing agent in polyvinyl alcohol (PVA) film using H_2SO_4 hydrolysis, which uses of CNCs enhanced mechanical properties.

Table 2.4 shows size and percentage yield of CNCs isolated from the various cellulosic sources, including cotton fibre, cotton fabrics, and bed sheet. The CNCs produced using sulfuric acid (H_2SO_4) had a higher cellulose yield and smaller size, compared to hydrochloric acid (HCl) hydrolysis. Dias Maciel et al. (2021) isolated CNCs from unwoven industrial textile cotton waste using sulfuric acid hydrolysis with a varying acid concentration ranging from 50 wt.% to 64 wt.% and reaction times of 60 min and 75 min. The study reported that the optimal experimental condition of the acid hydrolysis process was the sulfuric acid concentration of 64 wt.% and a 60 min reaction time. The characterization of isolated CNCs showed that the sulfuric acid concentration influences the CNCs' lengths, where the increase the acid concentration, the smaller the CNC length. It can be attributed to effective hydrolysing of amorphous cellulose during acid hydrolysis, which increases the crystallinity of cellulose (Huang et al., 2020; Wang et al., 2017).

Acid hydrolysis serves as the most promising method for preparation of CNCs from cellulose pulp, isolated from various lignocellulose sources. Sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) are commonly used inorganic acids in acid hydrolysis to remove amorphous regions in cellulose to isolate CNCs. However, the dispersibility of CNCs produced from these acids is different where CNCs obtained from dispersed readily in water (Blanco et al., 2018). Previous studies have reported that CNCs isolated using HCl hydrolysis had a weak oxidizing ability, low thermal degradation and poor dispersion ability (Blanco et al., 2018). In contrast, CNCs isolated using H_2SO_4 hydrolysis has better thermal stability and provide the most stable cellulose suspension due to presence of sulfate group on the surface of CNCs. Furthermore, Maciel et al. (2021) studied effect of H_2SO_4 hydrolysis reported that H_2SO_4 concentration influenced CNCs length while the optimal experimental