SYNTHESIS AND PERFORMANCE OF MAGNETIC CHITOSAN CELLULOSE NANOCOMPOSITE BIOSORBENT FROM OIL PALM EMPTY FRUIT BUNCH FOR HEAVY METALS REMOVAL

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UNIVERSITI SAINS MALAYSIA

2023

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by

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

August 2023

ACKNOWLEDGEMENT

I would like to express my gratitude to ALLAH S.W.T. for giving me the best health and opportunity endlessly in finishing the laboratory work and Master Thesis. This project emphasizes the sustainable waste utilization concept to produce a value-added product from oil palm empty fruit bunches (EFB) to minimize the environmental pollution. A special compliment goes out to both of my supervisors, Prof. Ts. Dr. Norli Binti Ismail and Ts. Dr. Md. Sohrab Hossain and co-supervisor Ts. Nor Afifah Khalil for the valuable guidance. A sincere gratitude goes to the USM fellowship programme for the financial aid during my Master study. My heartiest thanks are extended toward my parents, sisters, husband and friends for the motivation during my studies. Thank you.

TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

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

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
BET	Brunauer-Emmett-Teller analysis
CNF	Cellulose nanofiber
Cu(II)	Copper metal ion
DSC	Differential scanning calorimetry
Cr(VI)	Hexavalent chromium metal ion
HCl	Hydrochloric acid
Pb(II)	Lead metal ion
Mag-Chi-CNF	Magnetic chitosan cellulose nanocomposite
Fe_3O_4	Magnetic oxide
CH_4	Methane gas
OPEFB	Oil palm empty fruit bunches
ppm	Part per million
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
[Bmim]Cl	1-Butyl-3-methylimidazolium chloride

SINTESIS DAN PRESTASI NANOKOMPOSIT SELULOSA KITOSAN MAGNETIK BIOPENJERAP DARIPADA TANDAN BUAH KOSONG KELAPA SAWIT UNTUK PENYINGKIRAN LOGAM BERAT

ABSTRAK

Pencemaran logam berat terutamanya dalam persekitaran akuatik menimbulkan kebimbangan di seluruh dunia. Sumber logam berat terutamanya dalam industri tekstil telah mengeluarkan logam berat toksik melalui pembebasan pewarna ke alam sekitar semasa proses pencelupan gentian dan kemasan. Rawatan air buangan individu melalui kaedah fizikal, biologi atau kimia selalunya sangat mahal dan mengakibatkan sejumlah besar enapcemar. Oleh itu, terdapat keperluan untuk proses rawatan alternatif yang meliputi dari peringkat pra hingga pasca rawatan air sisa melalui penghasilan komposit nanofiber selulosa kitosan magnetik (Mag-Chi-CNF) yang telah disintesis daripada nanofiber selulosa terpencil melalui teknik sol-gel.Beberapa kaedah pencirian telah digunakan untuk mencirikan sifat fizikokimia, morfologi dan terma bagi Mag-Chi-CNF yang diasingkan. Mag-Chi-CNF telah digunakan untuk penjerapan tunggal dan serentak bagi ion logam berat seperti Cu(II), Cr(VI), dan Pb(II) daripada larutan akueus sintetik. Penjerapan ujikaji dijalankan dengan pelbagai parameter penjerapan seperti pH, dos biopenjerap, masa rawatan, dan suhu, secara eksperimen sistem kelompok. Morfologi permukaan mendedahkan Mag-Chi-CNF struktur berliang yang boleh meningkatkan penjerapan logam berat, dengan purata panjang zarah 500 ± 20 nm dan lebar 380 ± 12 nm, masing-masing. Analisis kestabilan terma menunjukkan Mag-Chi-CNF mempunyai sifat kestabilan terma yang tinggi dengan suhu degradasi terma 312 °C. Analisis BET mendedahkan bahawa Mag-Chi-CNF mempunyai luas permukaan yang besar dengan saiz mikro-pori.

Penyingkiran maksimum ion logam berat Cu(II), Cr(VI) dan Pb(II) diperolehi pada pH 5, dos bio-penjerap 0.5 g/L, masa rawatan 45 minit, dan pada suhu 60 °C, didapati sebanyak 96, 93%, dan 94%, masing-masing. Peratusan tertinggi penyingkiran ion logam berat serentak Cu(II) , Cr(VI) dan Pb(II) didapati sebanyak 97%, 90%, dan 90%. Di mana, ia diperolehi pada pH 5, dos bio-penjerap 0.5 g/L, masa rawatan 45 minit, dan pada suhu 60 °C. Penemuan kajian ini menyerlahkan potensi Mag-Chi-CNF terpencil untuk digunakan sebagai penjerab bio untuk pengasingan logam berat daripada efluen industri.

SYNTHESIS AND PERFORMANCE OF MAGNETIC CHITOSAN CELLULOSE NANOCOMPOSITE BIOSORBENT FROM OIL PALM EMPTY FRUIT BUNCH FOR HEAVY METALS REMOVAL

ABSTRACT

Heavy metals contamination especially in the aquatic environment posessevere environmental pollution concerns worldwide. Sources of heavy metals especially in textile industries has been discharging toxic heavy metals through the release of dyes into the environment during fibre dyeing and finishing processes. Individual wastewater treatment through physical, biological, or chemical method is often very costly and results in large amount of sludge. Thus, there is a need for alternative treatment processes that covers from pre to post wastewater treatment stage.Magnetic chitosan cellulose nanofiber (Mag-Chi-CNF) nanocomposite was synthesized from the isolated cellulose nanofiber by sol-gel technique. Several characterization methods were utilized to characterize the physicochemical, morphological, and thermal properties of the isolated Mag-Chi-CNF. Subsequently, the isolated Mag-Chi-CNF was utilized for single and simultaneous adsorption of heavy metals ions such as Cu(II), Cr(VI), and Pb(II) from synthetic aqueous solution. The adsorption was conducted by varying adsorption parameters such as pH, bio- sorbent doses, treatment time, and temperature. The surface morphologies of Mag- Chi-CNF revealed the porous structure that may enhance heavy metal adsorption, withaverage particle length of 500 ± 20 nm and width of 380 ± 12 nm, respectively. Thermal stability analysis shows the Mag-Chi-CNF have high thermal stability properties with thermal degradation temperature of 312 °C. BET analysis revealed thatMag-Chi-CNF had a had a high surface area of 1.01 m^2/g, with an average pore volume of 0.001 cm^3/g, and pore width of 2.2 nm, respectively with meso-pores structure. The maximum removal of single heavy metals ion of Cu (II), Cr(VI) and Pb(II) obtained at pH 5, bio-sorbent doses of 0.5 g/L, treatment time of 45 min, and at temperature 60 °C were found to be 96, 93%, and 94%, respectively. The highest percentage removal of simultaneous heavy metals ions of Cu(II), Cr(VI) and Pb(II) were found to be 97%, 90%, and 90%, respectively. The findings of the present study highlighted the potential of the isolated Mag-Chi-CNF to be utilized as a promising bio-sorbent for the heavy metals' separation from industrial effluent.

CHAPTER 1

INTRODUCTION

1.1 Background of study

Heavy metal contamination in the aquatic ecosystem poses severe environmental pollution concerns worldwide. The main sources of heavy metals in the aquatic ecosystem are industrial activities such as tannery, textiles industries, pigment and paint production, and glass manufacturing processes (Carolin et al., 2017). Although some heavy metals in micronutrient are essential for many biological activities, but higher concentrations may cause toxicity effects due to their non-biodegradable nature and accumulation tendency in living organisms (Peng et al., 2014). For instance, hexavalent chromium [Cr(VI)] is a highly toxic heavy metal ion. It is mutagenic and carcinogenic to living organisms and a notorious environmental pollutant. The presence of Cr(VI) in the aquatic ecosystem may pose a severe threat to the aquatic plants and animals (Sun et al., 2014).

Meanwhile, copper metal ion [Cu(II)] and lead metal ion [Pb(II)] have widespread application in manufacturing various products, such as building construction materials, household products, electronic products, electroplating, battery manufacturing process, pharmaceuticals machinery, and automotive parts (Peng et al., 2014). However, these Cu(II) and Pb(II) are toxic elements for the aquatic organisms. An excessive amount of Cu(II) and Pb(II) in the aquatic environment poses a life threat to the fish, algae, and invertebrates (Carolin et al., 2017). Therefore, removing these heavy metals from the aquatic ecosystem is crucial to preserve human health, aquatic life, and the environment.

Heavy metals particularly, lead (Pb), chromium (Cr) and copper (Cu) are widely used to produce colour pigments of textile dyes. Wastewater treatment is crucial to allow human and industrial effluents to not bring danger to human health before being disposed. (Li et al., 2004; Normala et al., 2010). In Malaysia, under the Environmental Quality Act (1979), there are regulations on discharge of wastes into Malaysian waters that focuses on regulations that prohibit discharging of environmentally hazardous substances, pollutants or wastes into Malaysian waters according to acceptable conditions as specified by the Act. The industrial effluent regulation limits (Standard A) for Copper (Cu), lead (Pb) and chromium (Cr) are 0.20, 0.10 and 0.005 mg/L while the regulation limits (Standard B) for Copper (Cu), lead (Pb) and chromium (Cr) are 1.0, 0.5 and 0.05 mg/L respectively.

Several technologies have been utilized for the elimination of heavy metals from industrial effluent, including adsorption, precipitation, flotation, ion-exchange, and membrane filtration (Zhao et al., 2020; Selvaraj et al., 2018). Among these techniques, adsorption is considered the most promising method to remove heavy metal from effluent owing to its distinct advantages over other technologies, including easy to operate, cost-effective, and element trace metals ion (Mnasri et al., 2019; Tighadouini et al., 2018). Several materials are utilized as the adsorbent for the separation of heavy metals from industrial effluents, including clay, bentonite, activated carbon, chelating materials, and natural polymer (Shahrokhi et al., 2021; Yao et al., 2019). However, the low sorption efficiency of these adsorbents has limited their application for the adsorption of heavy metals (Peng et al., 2014; Sun et al., 2014). On the other hand, an ideal adsorbent to remove heavy metals from industrial effluent contains a large surface area, high thermal and mechanical stability, high selectivity, easy accessibility, cost-effectiveness, biodegradable, and environmentally friendly (Peng et al., 2017).

There is increasing interest of utilizing bio-based materials from the natural resources in various industrial and environmental applications due to the rapid depletion of global petrochemical-based resources and environmental pollution concern (Yao et al., 2019). Among the various bio-based materials, the plant cellulosic materials have attracted wide interest because of environmentally friendly nature, abundance availability, biodegradability and renewability (Karim et al., 2016). Le Phuong et al. (2019) utilized bamboo fibre as a renewable material in the synthesization of the sustainable and biodegradable nonwoven composite membrane. Karim et al. (2016) utilized banana fibre obtained from the banana leaves as bio-sorbent for the dye removal from wastewater. Wang et al. (2020) synthesized superhydrophobic coating and sorbent using hydrophobic cellulose nanofiber suspension for oil-water separation.

Cellulose nanofiber (CNF) isolated from lignocellulosic biomass has been extensively utilized as an adsorbent, owing to its high surface area, high porosity, abundance availability, non-toxicity, reusability and biodegradability (Yasin et al., 2020; Oyewo et al., 2020). Abundance of hydroxyl functional groups on the surfaces cellulose nanofibrils (CNFs) allows wide range of surface modifications and good approach for the binding of different contaminants, such as heavy metal. The presence of hydroxyl groups in the cellulose carbon chain makes the cellulose nanofiber a promising adsorbent for the elimination of heavy metals from industrial effluent through electrostatic interaction that happens between the positively charged heavy metals and negatively charged carbon adsorbents, particularly with the presence of functional groups. (Yang et al., 2019;Peng et al., 2017). Studies reported that poor chemical resistance and weak mechanical strength are the significant barriers to use CNF as the adsorbent for heavy metals separation from industrial effluent (Sun et al., 2014). This is due to the hydrophobic polymer matrix that significantly lowered the potential for cellulosic materials to be used as a reinforcing agent in polymer matrices, specifically for microscale materials (Gan, P et al., 2020). Moreover, it requires expensive technology like the membrane filtration process to separate the bio-sorbent after the adsorption process (Peng et al., 2014).

In the recent year, magnetic bio-sorbents have received a considerable interest among environmental scientists to separate heavy metals from various industrial effluents (Li et al., 2020). The unique advantages of the magnetic bio-sorbent include cost-effectiveness, high mechanical strength, high thermal stability, non-toxic nature, and environmental-friendly (Gu et al., 2020). In addition, the magnetic bio-sorbent can be easily separated from the aqueous solution using a magnet after the adsorption process. Therefore, an engineering conversion of cellulose nanofiber into a magnetic bio-sorbent is urgently needed to eliminate the existing limitation of CNF, and to be used as a promising bio-sorbent. Peng et al. (2014) utilized the magnetic cellulose chitosan nanocomposite as a bio-sorbent to remove Cu(II) metal ion from an aqueous solution. Previous studies reported that the synthesized magnetic cellulose-chitosan nanocomposite (Mag-Chi-CNF) could be utilized as a potential bio-sorbent owing to its distinct characteristics, such as large surface area, porous structure, and affinity adsorb Cu(II), Cr(VI), and Pb(II) metals ion from aqueous solution (Peng et al., 2017).

Sun et al. (2014) reported that the magnetic cellulose composite is the most promising adsorbent for removal of Cr(VI) from aqueous solution owing to its high adsorption ability, rapid adsorption rate, and easy regeneration of the bio-sorbent under a magnetic field. It is essential to have consistent raw materials supply at large industrial-scale operations in the practical engineering application. As heavy metal contamination in the aquatic ecosystem poses serious environmental pollution concerns, the development of bio-based materials (bio-sorbent) has gained attention for the greener separation of heavy metals from industrial effluents (Bari et al., 2009). The utilization of the lignocellulosic biomass as a bio-sorbent is attractive because of the abundance availability, low cost, biodegradable, and reusable (Peng et al., 2017). Generally, the lignocellulosic biomass mainly consists of lignin, cellulose, and hemicellulose, with high hydroxyl groups and other reactive functional groups on the surface (Oyewo et al., 2020).

Recently, there is a considerable interest in utilizing cellulose nanofiber (CNF) as the bio-sorbent in wastewater treatment due to its unique key-features, such as large surface area, smaller particles size, high porosity, excellent mechanical strength, and high thermal properties (Zhang et al., 2014; Bisla et al., 2020). The cellulose nanofiber has been isolated from the various sources of lignocellulose biomass, including bamboo, rice straw, sugarcane bagasse, cotton, and oil palm biomass (Zhang et al., 2014; Septevani et al., 2020). In addition, Malaysia is the second largest palm oil producer and exporter country. Wherein, it is being reported that the palm oil industries in Malaysia are generating over 43 million tonnes of oil palm biomass (Septevani et al., 2020). The high cellulose content of OPEFB (up to 50%) and its high generation make the OPEFB ideal for producing cellulose nanofiber to use as an adsorbent (Padzil et al., 2020).

Over the years, various techniques have been implemented to isolate the cellulose from various lignocellulose biomasses, including chemical process, mechanical process, and chemo-mechanical process (Fatah et al., 2014). Among these various processes, the acid hydrolyses process has been extensively utilized to isolate

CNF from the various lignocellulosic fibres (Fatah et al., 2014). H_2SO_4 or HCl are the most frequent inorganic acids used in acid hydrolysis process to remove amorphous regions for producing CNF. On the other hand, Fahma et al. (2010) stated that the acid hydrolysis using H_2SO_4 provided the most stable suspension due to the presence of the sulphate group on the surface of the cellulose crystallites.

In the present study, a magnetic cellulose nanofiber nanocomposite was synthesized using nanocellulose isolated from the oil palm empty fruits bunches (OPEFB). Wherein the Fe_3O_4 was utilized as magnetite to coat the surface of the CNF. Several characterization methods were utilized to characterize the synthesized magnetic oil palm cellulose nanocomposite (Mag-Chi-CNF), and to determine its reusability in heavy metals adsorption. Subsequently, Mag-Chi-CNF nanocomposite was then utilized for the adsorption of Cu(II), Cr(VI), and Pb(II) from aqueous solution. Moreover, the adsorption isotherm and kinetics behaviour were assessed by fitting the experimental data with several theoretical models.

1.2 Problem statement

Chitosan and lignocellulosic fibre (OPEFB) have been reported as an excellent bio-sorbent, because of their abundance availability, biocompatibility, biodegradability, presence of hydroxyl groups, and amine groups in the carbon chain. However, weak mechanical strength and poor chemical resistance of chitosan and cellulosic fibre are limiting their use as effective bio-sorbents. The application of nanomaterials in heavy metal adsorption requires distinct equipment for filtration to separate bio-sorbents from the effluents. Therefore, an innovative approach is urgently needed to produce novel bio-sorbent with distinct key-features including easy to separate, reusable, eco-friendly, and rapidly eliminate the heavy metals ion from the aqueous solution.

No study has yet to conduct on the synthesis nanocellulose-chitosan nanocomposite under a magnetic field for being used as bio-sorbent. Hence, the present research has undertaken to synthesize magnetic chitosan cellulose nanofibers (Mag-Chi-CNF) nanocomposites, where Fe_3O_4 would be utilized as a magnetic for coating on the surface of the nanocomposite. Mechanical, physicochemical, morphological and thermal properties Mag-Chi-CNF will be characterized to determine its reusability in heavy metals adsorption and separation from environmental contaminates. Subsequently, Mag-Chi-CNF would be applied for simultaneous adsorption of Cu(II), Cr(VI), and Pb(II) from the aqueous solution.

1.3 Objectives of Study

The objectives of the study are as follows:

i. To determine the influence of Mag-Chi-CNF nanocomposite as bio-sorbent for the removal of Cu (II), Cr(VI) and Pb (II) from the aqueous solution by synthesizing Mag-Chi-CNF nanocomposite by sol-gel method using an ionic liquid as a solvent and characterize physicochemical, morphological, and thermal properties of Mag-Chi-CNF composite.

ii. To determine the influence of Mag-Chi-CNF nanocomposite as bio-sorbent for the removal of Cu (II), Cr(VI) and Pb (II) from the aqueous solution.

iii. To assess isothermal behavior for the removal of Cu(II), Cr(VI) and Pb(II) using Mag-Chi-CNF nanocomposite as bio-sorbent.

1.4 Scope of Study

The scope of study has been identified to achieve the objectives. In this study, a magnetic cellulose nanofiber nanocomposite (Mag-Chi-CNF) was synthesized using cellulose nanofiber (CNF) isolated from the oil palm empty fruits bunches (OPEFB). Wherein the Fe_3O_4 was utilized as magnetite to coat the surface of the CNF through sol-gel method. Several characterization methods were utilized to characterize the synthesized magnetic oil palm cellulose nanofiber, and to determine its reusability in the heavy metals' adsorption in aqueous solution. Subsequently, Mag-Chi-CNF nanocomposite was utilized for the separation of heavy metals Cu(II), Cr(VI), and Pb(II) from aqueous solution. Moreover, the adsorption isotherm and kinetics behaviour were assessed by fitting the experimental data with several theoretical models.

Several characterization methods were utilized to determine physicochemical, morphological, and thermal properties of Mag-Chi-CNF, including scanning electron microscopy with energy dispersive X-ray (SEM and SEM-EDX), transmission electron microscopy (TEM), and Brunauer-Emmett-Teller (BET). Meanwhile, Fourier-transform infrared spectroscopy (FTIR) was conducted to determinefunctional groups and chemical compounds in Mag-Chi-CNF. Besides, crystallinity index analysis was carried out using X-ray diffraction (XRD). The thermal properties analyses were analysed using thermogravimetric analysis (TGA) and differential scanning electron (DSC). The absorption of Cu(II), Cr(VI), and Pb(II) using Mag-Chi-CNF were conducted using atomic adsorption spectrometry (AAS). The findings of the present study on utilization biomass (OPEFB) provided a sensible information for isolation of magnetic cellulose nanofiber nanocomposite (Mag-Chi-CNF).

CHAPTER 2

LITERATURE REVIEW

2.1 Oil palm empty fruit bunch

2.1.1 OPEFB waste generation

Oil palm empty fruit bunches (OPEFB) is a biomass which commonly discarded in a high volume from oil palm plantation industries. OPEFB has an extensive source and a high cellulose content (up to 50%), which made it a sustainable source for various value-added products (Fatah et al., 2014). Cellulose content has found to be rich in OPEFB, as it has many advantages, including abundant sources, cheap, renewable sources, and biodegradable. Malaysia as the second largest producer after Indonesia, provides more than 80% of the world production with nearly 5.4 million hectares of plantation area and about 423 palm oil mills are running in the country. The massive plantation areas with huge amount of palm oil mills have led Malaysia to be recorded as the top palm oil exporter with varies palm oil products in the world [Chiew et al.,2013;Kong et al.,2014].In Malaysia, oil palm empty fruit bunch (OPEFB) with maximum of 22–23 million tons is highly generated as a residue per annum. OPEFB is deemed as the cheapest natural fiber with good properties and has good potential as an alternative main raw material to substitute woody plants, which are expensive for various industries. OPEFB potentially developed as an alternative to main raw material to be substituted with woody plants which are expensive for many industries and that makes it deemed as the cheapest natural fibre [Padzil, F et al.,2020].Besides that, Malaysia produces an estimated 21.59 million tonnes of OPEFB waste per year, which could lead to disposal environmental problem as the OPEFB has a low biodegradability attribute (MPOB, 2021).

Figure 2.1 Oil palm empty fruit bunches (OPEFB)

2.1.2 Physicochemical properties

Cellulose has an extensive source which mainly can be obtained from lignocellulose biomass. Cellulose is the major component in lignocellulose consisted of both amorphous and crystalline cellulose region, which the regions alternate with each other in a straight carbon chain (Wang et al., 2017). The amorphous is the flexible and entangle structure, while crystalline cellulose consisted of rod-like structure. Figure 2.2 illustrated the cellulose chemical structure is formed by many monosaccharides, and linked by β-1,4-glycosidic bonds to produce polysaccharides. Cellulose has a strong and durable structure due to a high intermolecular force and the presence of hydroxyl groups (-OH) on the carbon chain (Ma et al., 2018; Mohamed et al., 2022). The physicochemical properties of oil palm empty fruit bunches are tabulated in Table 2.2. Oil palm empty fruit bunches (OPEFB) contains a high amount of cellulose content as the main component, which up to 40 to 50 wt.%. It is followed by hemicellulose and lignin content with 15 to 30 wt.% and 20 to 35 wt.%, respectively.

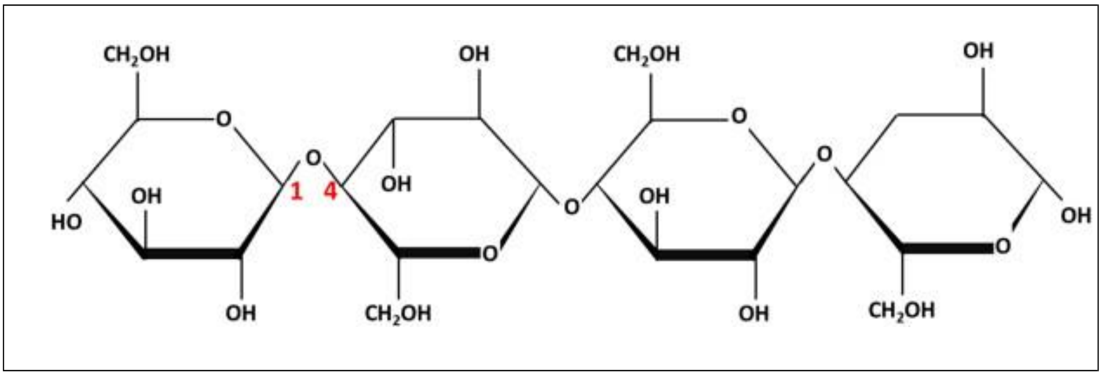

Figure 2.2 Cellulose polymer containing glucose monomers linked by β-1,4 glycosidic bonds (Jude A. et al., 2020)

Table 2.1 Chemical compositions of oil palm empty fruit bunches (Chang et al., 2014)

Chemical compositions	**Weight percentage (wt. %)**
Cellulose	40-50
Lignin	20-35
Hemicellulose	15-30
Protein	1.1-1.5
Ash	0.5-2.0
Pectin substance	0.7-1.9
Oil, fat and wax	0.4-1.0

Lignin is heterogeneous polymers with a complex structure and linked by ether bonds (R-O-R'). The component is composed for up to 35 wt.% of lignocellulose (Chang et al., 2014). Lignin is made of three different phenyl-propane as its monomer units, which includes *p*-hydroxylphenyl, guaiacyl, and syringyl units, as shown in Figure 2.3. Lignin acts the physical barrier that binds the cellulose fibre together in the plant's cells (Fatah et al., 2014). Wherein, the existence of lignin component in the plant cell wall has also made the cellulose fibre difficult to be hydrolysed by acids into a smaller nano-size. Besides, lignin structure prevents the swelling of cellulose fibre during acid hydrolysis, which may affect the chemical accessibility to the cellulose. Therefore, pulping process using alkali treatment is required to isolate the cellulose fibre, by hydrolysing the complex lignin structure into a smaller monomer unit (Ang et al., 2010).

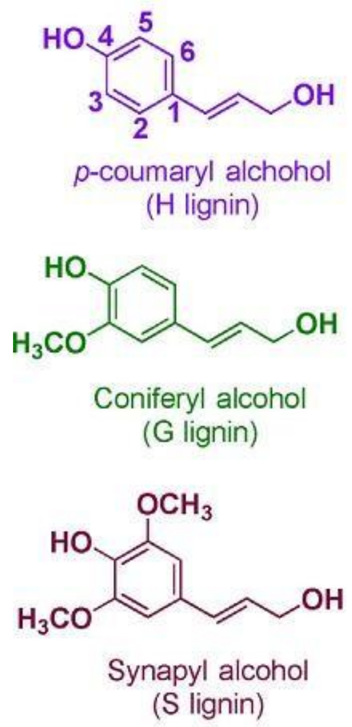

Figure 2.3 Lignin monomers (monolignols) (Garedew et al., 2020)

Hemicellulose is one of the main components in lignocellulose biomass, which typically accounts for up to 30 wt.% of lignocellulose (Chang et al., 2014). It has a linear and branched heteropolymers, which made up of several monomer units such as d-glucose, d-galactose, d-xylose, d-rhamnose, d-mannose, and l-arabinose, as shown in Figure 2.4. Hemicellulose acts as the glue in the lignocellulose to binds the cellulose and lignin structure together. The component acting as the binding agents to hold the cell walls together to create a rigid structure for the plants (Zhao et al., 2019). Due to its branched structure, hemicellulose is amorphous and susceptible to alkali treatment and acid hydrolysis, compared to lignin (Fatah et al., 2014). The thermal degradation of hemicellulose is lower than lignin and cellulose, due to its branched nature and presence of acetyl groups (-$COCH_3$) (Ang et al., 2010). To isolate the cellulose fibre, both lignin and hemicellulose component in the biomass is hydrolysed during the pulping process, thus leaving pure cellulose fibre.

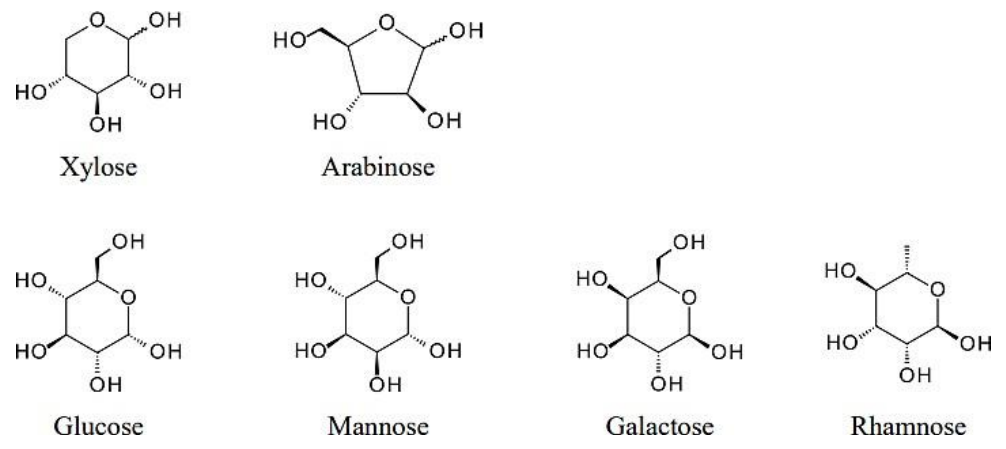

Figure 2.4 Hemicellulose monomers (Vallejo-Montesinos et al., 2016)

2.1.3 Existing disposal methods for oil palm empty fruit bunches

There is a growing attentiveness to the sustainable utilization of oil palm empty fruit bunches (OPEFB) to reduce carbon footprints and minimize the environmental pollutions. The existing disposing methods for oil palm empty fruit bunches (OPEFB) in plantation landfill has led to notorious environmental pollution and demolition of valuable useful resources (Fatah et al., 2014). In addition, the continuous disposal of OPEFB in landfill site per annum throughout the world has led to serious landfill issue. Although, OPEFB are biodegradable, the decomposition process of OPEFB in the landfill site by aerobically or anaerobically may emit the potent greenhouse gases into the atmosphere, including carbon dioxide (CO_2) and methane gas (CH_4) (Fatah et al., 2014). Besides, cellulose is found to be rich in OPEFB, where recycling OPEFB into value-added products such as cellulose nanofiber (CNF) poses many advantages, including cheap, wide availability, renewable, abundant sources, and biodegradable (Mohamed et al., 2021). In addition, the isolation of cellulose nanofiber by recycling the OPEFB may reduce the waste materials being disposed in landfill site.

2.2 Chitosan

Chitosan is produced through deacetylation process from one of the most abundant polymers in the world, chitin. Chitin is a common part of fungi's cell walls, insects' exoskeletons, crustaceans and molluscs' radulae. It is a linear polysaccharide comprised of -1,4-N-acetylglucosamine (Abdul Khalil et al.,2016). Chitosan has been the suitable version of chitin polymer due to its solubility in diluted organic acids thus, having a higher availability to be applied in chemical reactions (Rodriguez-Vazquez et al., 2015). Chitosan, other than its biopolymers characteristics (biodegradability, non-toxicity and biocompatibility) has been also considered as an effective adsorbent to eliminates organic and inorganic pollutants from water and wastewater due to its low cost, hydrophilicity, cationicity, high content of adsorption sites (OH and NH_2 groups), and great adsorption capability (Vakili et al., 2019). Among various forms of treated chitosan such as fiber, gel, granules, powder and membrane, granules are often used as a biosorbent in water purification from heavy metals (Kulka et al., 2023).

In recent years, chitosan (common name of poly-β-(1 → 4)-D-glucosamine, containing randomly distributed N-acetyl-D-glucosamine units) shown in Figure 2.5 has been investigated as cheap adsorbent for wastewater (Qiu et al., 2020). Gkika et al. (2023) states that high concentration of nitrogen content makes chitosan more commercially appealing than the alternative of synthetic substituted cellulose.

However, their poor mechanical and thermal properties restricted its widespread application. According to Zhang et al. (2016), chitosan has weaknesses such as inadequate mechanical strength, low thermal stability and low acid stability which limit its application. Thus, some researchers have applied physical and/or chemical modification to further improve its adsorption properties for metal ions. Besides that, modified chitosan is observed as an appropriate choice that shows sufficient adsorption capacity as it can generates multiple cationic positions on the chitosan's surface which improve its solubility, therefore supporting the production of substances with higher polarity and improved electrostatic repulsion to be an adsorbent (Gkika et al., 2023).

According to Francis et al. (2023), chitosan modification results in the formation of chitosan by-products which enhanced the properties, increase in the number of adsorption sites and capacity. Many review articles described on the use of chitosan as adsorbents in removing dyes and/or toxic heavy metals from wastewater. For instance, study done by Wang et al. (2014) that synthesized magnetic nanoparticle infused chitosan beads with magnetic iron oxide (Fe_3O_4) which improves the separation of the adsorbent. Other than that, some studies also highlight on the use of surfactants, metal oxides and ionic liquid that has been also infused into chitosan to improve the adsorption performance.

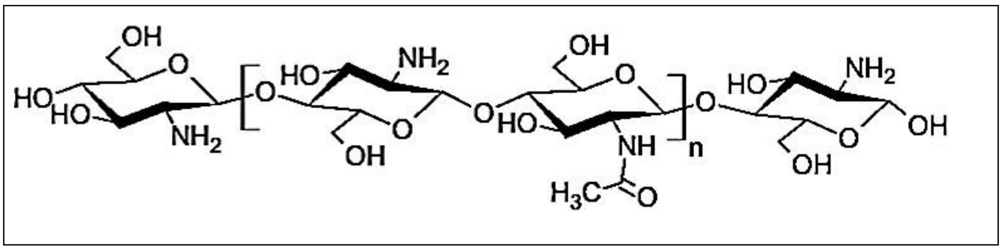

Figure 2.5 Chemical structure of chitosan

2.3 Synthetization of magnetite chitosan cellulose nanocomposite

Recently, there is a considerable interest in utilizing cellulose nanofiber (CNF) as the bio-sorbent in wastewater treatment due to its unique key-features, such as large surface area, smaller particles size, high porosity, excellent mechanical strength, and high thermal properties (Zhang et al., 2014; Bisla et al., 2020). Cellulose nanofiber (CNF), also known as nano-cellulose, is referred to the crystalline structure of the cellulose (Septevani et al., 2020). CNF is a natural polysaccharide that is generally isolated from biomass resources, such as bamboo, rice straw, sugarcane bagasse, cotton, and oil palm biomass (Huang et al., 2020). Besides, Malaysia is the second-largest palm oil producer and exporter country. It is being reported that the palm oil industries in Malaysia are generating over 43 million tonnes of oil palm biomass (Septevani et al., 2020).

The high cellulose content of OPEFB (≥44%) and its huge generation make the OPEFB ideal for producing CNF to use as a bio-sorbent (Padzil et al., 2020). Therefore, the high cellulose content and abundant availability of waste cotton cloths have highlighted the potential to utilize waste cotton cloths as a promising raw material for synthesizing into a value-added product. CNF have been viewed as a promising material in many advance applications because of their distinct key features, including wide availability, large surface area, excellent thermal and mechanical strength, environmental friendliness, and biodegradability, make CNF an encouraging raw material for many advanced implementations (Peng et al., 2017). Due to exhibiting many desirable properties, CNF have been utilized in many advance applications, including packaging materials, reinforcement in composite materials, antimicrobial agents, biocatalysts, and adsorbent. Over the years, CNF have been isolated from various lignocellulosic biomass, including bamboo, wastepaper, cotton, fabrics, and bacteria. However, OPEFB contains over 50 wt.% cellulose and a sustainable source.

Over the years, various methods have been implemented to isolate the cellulose from various lignocellulose biomasses, including chemical process, mechanical process, and chemo-mechanical process (Ding et al., 2017). Among these various processes, the acid hydrolysis process has been extensively utilized to isolate CNF from the various lignocellulosic fibres (Wang et al., 2017). Sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) are the most frequent inorganic acids used in acid hydrolysis process to remove amorphous regions for producing CNF (Huang et al., 2020). The mechanisms of isolation of cellulose nanofiber from lignocellulose using acid hydrolysis involves hydrolysing the amorphous region, thus leaving only the cellulose crystalline region (cellulose nanofiber) (Fatah et al., 2014; Mohamed et al., 2021). Wherein, the isolated CNF exhibited an elongated crystalline and rod-like structure with size dimension approximately 10-30 nm in width, 100-200 nm in length, and 80-90% of crystallinity index.

Studies have reported that CNF isolated using HCl hydrolysis had a weak oxidizing ability, low thermal degradation, and poor dispersion ability. On the other hand, Fahma et al. (2010) stated that the acid hydrolysis using H_2SO_4 provided the most stable suspension due to the presence of the sulphate group on the surface of the crystallites. Therefore, the CNF isolated using the H_2SO_4 hydrolysis process gained a better mechanical and thermal stability (Ma et al., 2018). The study reported that the utilization of OPEFB in CNF is a promising approach for the sustainable utilization of waste materials to produce a value-added product. For instance, Huang et al. (2020) isolated CNF from textile waste materials using sulfuric acid hydrolyses process to be utilized as a reinforcing agent of soy protein film. Fatah et al. (2014) isolated CNF from OPEFB as a reinforcing agent in composites materials. Tambiraj and Shankaran (2017) isolated CNF from waste fabrics using the acid hydrolysis process. The study reported that waste materials are promising raw materials for the isolation of CNF, due to its high cellulose content. The utilization of waste cotton cloths for CNC isolation will provide sensible information on the utilization of waste materials for value-added product production.

Previous study reported on the isolation of cellulose nanofiber (CNF) from lignocellulose biomass using acid hydrolysis process. The surface morphologies of CNF revealed the nano-size and rod-like structure, with particle diameter ranging from 100 nm to 200 nm. XRD analyses shows the crystallinity index of CNF was found to be around 80%. Thermal stability analyses revealed that CNF has a high thermal stability with thermal degradation temperature 300 °C to 350 °C. Meanwhile, BET analysis revealed that CNF had a large surface area with micro-pore size, which is suitable to be utilized as bio-sorbent for heavy metals. The findings of the previous study revealed the potential of recycling OPEFB into a value-added product. The isolated CNF could be utilized as a promising bio-sorbent for heavy metals separation from industrial effluent (Mohamed et al., 2022).

Figure 2.6 shows the synthesisation of cellulose nanofiber from OPEFB using the conventional method. In the present study, magnetic chitosan cellulose nanocomposite (Mag-Chi-CNF) were synthesized from oil palm empty fruit bunches (OPEFB) by acid hydrolysis process using sulfuric acid (H_2SO_4). Several analytical methods, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermal thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC), were utilized to determine the morphological, physicochemical, and thermal properties of the synthesized Mag-Chi-CNF. The findings of the present study will provide a theoretical foundation for the utilization of oil palm empty fruit bunches as promising raw materials for the isolation of cellulose nanofiber, as the value-added products.

There are several studies have been conducted on the isolation of cellulose fibre for various value-added application. Table 2.2 shows size dimension and percentage yield of CNF isolated from the various cellulosic sources. The isolated CNF using sulfuric acid (H_2SO_4) had a high cellulose yield and smaller nano-size, compared to cellulose pulp. The characterization of isolated CNF showed that the sulfuric acid influences the CNF lengths, where the increase the acid concentration, the smaller the CNF 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).

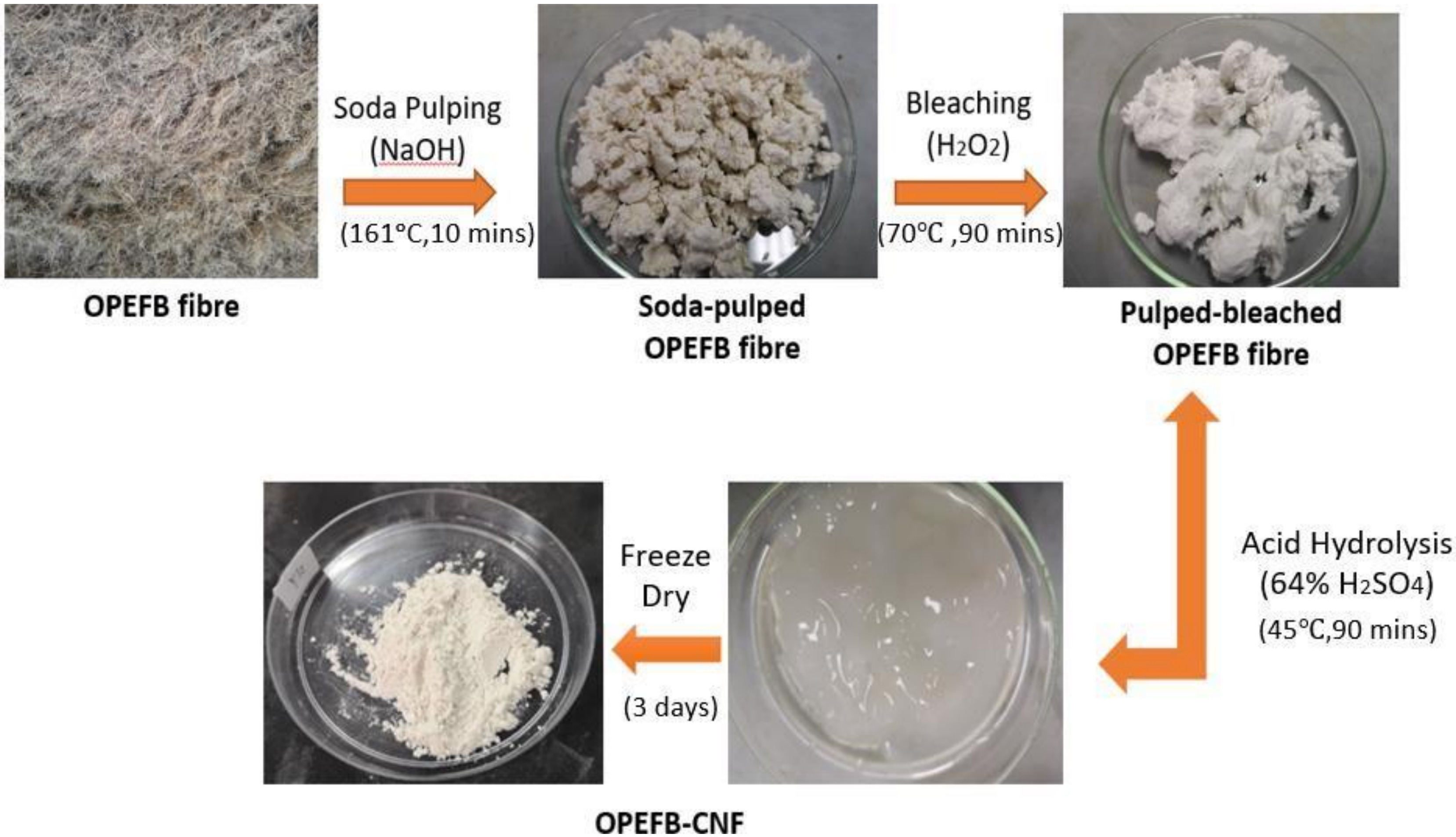

Figure 2.6 Synthesization of cellulose nanofiber from oil palm empty fruit bunches using conventional method

Table 2.2 Size dimension and yield of cellulose nanofiber isolated from lignocellulose biomass for various applications

Length (nm)	Diameter (nm)	CNF yield (%)	Methods	Applications	References
180 ± 60	10 ± 1	91	H_2SO_4 hydrolysis	PVA film	Thambiraj and Shankaran (2017)
111 ± 38	11 ± 2.33	90	H_2SO_4 hydrolysis	Soy-protein film	Huang et al. (2020)
161-193	10-13	80	H_2SO_4 hydrolysis	Anti-inflammatory	Morais et al. (2013)
130 ± 25	10±4	52	H_2SO_4 hydrolysis	Antioxidant	de Morais Teixeira et al. (2010)
135 ± 50	14 ± 4	65	H_2SO_4 hydrolysis	Aerogels	de Morais Teixeira et al. (2010)
150 ± 50	14 ± 5	60	H_2SO_4 hydrolysis	Bio-composites	Martins et al. (2011)
76-159	15	53	H_2SO_4 hydrolysis	Bio-composites	Yue et al. (2012)
100	8	50	H_2SO_4 hydrolysis	Bio-sorbent	Mohamed et al. (2022)

2.4 Pulping processes

Pulping process is commonly utilized to isolate cellulose nanofiber from lignocellulose fibre, including biomass, and food crops. The pulping process may increase the cellulose porosity and surface area, thus increase the digestibility of cellulose fibre (Mohamed et al., 2022). Cellulose, lignin, and hemicellulose are the main component existing in the plants primary cell walls. Both lignin and hemicellulose component acting as the binding agents to hold the cell walls together to create a rigid structure for the plants (Ang et al., 2010). The isolation of cellulose nanofiber from OPEFB requires various processing steps. It includes delignification of lignocellulose for the extraction of cellulose (pulping process), and the conversion of cellulose pulp to CNF (acid hydrolysis). The existing process for the extraction of cellulose from OPEFB is the combination of alkaline pulping and bleaching processes (Fatah et al., 2014). The mechanism of pulping process includes hydrolysing both lignin and hemicellulose component which binding the cellulose fibre, using alkali treatment. The alkali treatment has been widely utilized for the isolation of nanofiber from biomass, such as cotton fibres, bagasse, rice husks, and oil palm empty fruit bunches (OPEFB).

Soda pulping is one of the most common pulping techniques to isolate the cellulose nanofiber from biomass. The technique utilized the caustic soda or sodium hydroxide (NaOH) as the cooking liquor to dissolve the lignin and hemicellulose component in the biomass, leaving only cellulose component in nano-size (cellulose nanofiber) (Mohamed et al., 2021). Soda pulping technique involves cooking at a high temperature up to 170 °C for 3 h of treatment time. The isolated cellulose nanofiber (CNF) from biomass using pulping process is also known as the pulp fibre. The fibre produced is in nano-size ranging between 100 nm to 200 nm in diameter, with a spiral and entangled network structure (Huang et al., 2020; Ding et al., 2017). The fibre has a flexible shape, consisting of both amorphous and crystalline region of cellulose component. In addition, bleaching process serves as a pre-treatment technique with purpose to remove pigment in the biomass such as oil palm empty fruit bunches (OPEFB). Wherein, the pigment of yellowish-brown in the OPEFB fibre can be bleached out by bleaching process using hydrogen peroxide (H_2O_2). Besides, bleaching process helps in remove unwanted impurities and increase the isolated cellulose purity (Wang et al., 2017; Zhang et al., 2014).

2.5 Heavy metals removal from wastewater

2.5.1 Sources of heavy metals ion in wastewater

Heavy metal contamination in the aquatic ecosystem poses severe environmental pollution concerns worldwide. The main sources of heavy metals in the aquatic ecosystem are industrial activities such as tannery, textiles industries, pigment and paint production, and glass manufacturing processes (Carolin et al., 2017). Although some heavy metals in a micronutrient concentration are essential for many biological activities, heavy metals in higher concentrations can cause toxicity effects due to their non-biodegradable nature and accumulation tendency with living organisms (Peng et al., 2014). Hexavalent chromium [Cr(VI)] is a highly toxic heavy metal ion. It is mutagenic and carcinogenic to living organisms. Cr(VI) is a notorious environmental pollutant. The presence of Cr(VI) in the aquatic ecosystem may pose a severe threat to the aquatic plants and animals (Sun et al., 2014). Meanwhile, copper metal ion [Cu(II)] and lead metal ion [Pb(II)] have widespread application in manufacturing various products, such as building construction materials, household products, electronic products, electroplating, battery manufacturing process, pharmaceuticals machinery, and automotive parts (Peng et al., 2014). However, these Cu(II) and Pb(II) are toxic elements for the aquatic organisms. An excessive amount of Cu(II) and Pb(II) in the aquatic environment poses a life threat to the fish, algae, and invertebrates (Carolin et al., 2017). Therefore, removing these heavy metals from the aquatic ecosystem is crucial to preserve human health, aquatic life, and the environment.

2.5.2 Existing removal techniques of heavy metals ion from wastewater

Several technologies have been utilized for the separation of heavy metals from industrial effluent, including adsorption, precipitation, flotation, ion-exchange, and membrane filtration (Zhao et al., 2020; Selvaraj et al., 2018). Among these techniques, adsorption is considered the most promising method to remove heavy metal from effluent owing to its distinct advantages over other technologies, including easy to operate, cost-effective, and element trace metals ion (Mnasri et al., 2019; Tighadouini et al., 2018). Several materials are utilized as the adsorbent for the separation of heavy metals from industrial effluents, including clay, bentonite, activated carbon, chelating materials, and natural polymer (Shahrokhi et al., 2021; Yao et al., 2019). However, the low sorption efficiency of these adsorbents has limited their application for the adsorption of heavy metals (Peng et al., 2014; Sun et al., 2014). Meanwhile, an ideal adsorbent for removing heavy metals from industrial effluent contains a large surface area, high thermal and mechanical stability, high selectivity, easy accessibility, cost-effectiveness, biodegradable, and environmentally friendly (Peng et al., 2017).

There is increasing interest of utilizing bio-based materials from the natural resources in various industrial and environmental applications due to the rapid depletion of global petrochemical-based resources and environmental pollution