

# Development of Cellulose-based Softwood Pulp Foam for the Removal of Microplastics

by

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## **Author's Declaration**

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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## Abstract

Microplastics, generated from the decomposition of large plastic products, is one of the emerging pollutants that pose tremendous risks in the aquatic environment. Although previous studies have developed various strategies for the removal of microplastics, they were found to be non-renewable and costly. Cellulose provides green and sustainable approaches in water treatment systems as it is derived from plant sources making it biodegradable and biocompatible. In this study, two cellulose derivatives, microcrystalline cellulose (MCC) and nanocrystalline cellulose (NCC), were cationically and hydrophobically modified by grafting with (3-chloro-2-hydroxypropyl)dodecyldimethylammonium chloride (QUAB 342) to the particles. The modified systems were used in the development of softwood pulp foam for microplastic capture (WFQ342MCC-0.8 and WFQ342NCC-0.8 foams)

The filtration performance of WFQ342MCC-0.8 foam was examined by analyzing its removal efficiency for polyethylene (PE) microplastics stabilized by sodium dodecyl benzene sulfonate (SDBS), polysorbate 80 (Tween 80), and hexadecyltrimethylammonium bromide (CTAB) surfactants (PE:SDBS, PE:CTAB, and PE:Tween80). The order of the removal efficiency during the filtration experiment was found to be PE:SDBS > PE:CTAB > PE:Tween80, respectively. Furthermore, WFQ342NCC-0.8 foam displayed removal efficiency of up to 99.8 %, as the addition of NCC improved the foam surface area with better microplastic capture.

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# **Chapter 1: Introduction**

## **1.1. Research Background**

The widespread use of plastics has increased in recent years, posing a potential threat in both soil and aquatic environment. From 2010, roughly 4.8 to 12.7 million metric tons of plastic waste from 198 coastal countries have been released into the ocean each year [1]. Furthermore, it was determined that the global annual output of plastic products has reached a total of 460 million tons in 2019, and it is expected to increase to 1.2 billion tons by 2060 [2]. Through UV irradiation and thermal degradation, these plastic wastes can decompose slowly into small fragments with sizes of less than 5 mm [3]. These fragments are known as “microplastics,” and they have been studied in the past decade as they are deemed harmful to both human health and aquatic organisms. Many fishes and crustaceans have consumed high amounts of microplastics, and these marine animals transferred the microplastics to human via the food chain. Recent reports revealed that Chinese consumers are exposed to 100,000 microplastics/year, and Europeans consume approximately 11,000 microplastics/year from shellfish consumptions [1], [2], [4]. Exposure to large amounts of particles can cause serious health problems to both humans and animals, such as obstructing their digestive tracts and disrupting their immune systems [4].

Microplastics are found in variety of sources, such as cosmetic products, raw industrial materials, wear of car tires, and road markings. However, the primary source originates in washing machines, where clothing and textiles release fragments and fibers, such as cotton, polyester, and nylon. Studies reported that a single garment can shed over 1900 fibers per wash [5]. Moreover, it was also discovered that the presence of detergent and softener increases the release of microfibers from the laundry machine [6].

Several existing technologies have developed to remove microplastics from water, which include coagulation, membrane bioreactor, and advanced oxidation. However, these processes exhibit many drawbacks such as high installation and maintenance costs and large environmental impact due the use of harmful substances. The focus on microplastic removal must be shifted towards the sources of microplastics and the use of green or bio-based materials in order to improve the microplastic capture and reduce the environmental impacts. Cellulose is considered as one of the most abundant natural polymers on earth and it has been widely used in many applications such as drug delivery, paper packaging, and constructions [7]. It is originated from wood, plants, and certain types of bacteria. Through acid hydrolysis, most notably hydrochloric or sulfuric acid, cellulose can be broken down into various derivatives, ranging from micro- to nano size [8]. As cellulose possesses many unique properties, such as high mechanical strength and abundance of functional groups on the surface, physical and chemical modifications can be performed on cellulose to improve the removal of microplastics in aquatic systems.

## **1.2. Research Objectives**

The main objectives of this project are to analyze the behavior of microplastics in an aqueous solution, and to develop an environmentally friendly porous material to enhance high microplastic capture for applications in water treatment. To start, understanding the microplastic behaviors in aqueous solution is critical to develop a unique design for microplastic capture. This project focuses on identifying ideal stabilizing agents to disperse microplastic particles in an aqueous solution and finding various techniques to detect particles such as Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, UV-vis spectroscopy, and Fluorescence

microscopy. Surface charges and particle sizes of microplastics are important information necessary for the design process to remove microplastic from water.

The second objective of this project is to develop a sustainable pulp foam adsorbent consisting of cellulose materials for the microplastic removal from water. Several criteria in the foam design and fabrication include strong mechanical strength, high porous structure, and excellent microplastic removal efficiency. The softwood pulp foam adsorbent was examined by its stability during and after fabrication, and this was achieved by considering different crosslinkers that possessed high mechanical strengths. Once the fabrication was completed, it was then monitored for 24 h to ensure that the structure was maintained without shrinkage or premature collapse. The next step was investigating the foam porosity to enhance better microplastic capture in aqueous solution. This was conducted by examining various approaches to cure the material, such as vacuum-drying, freezing, and freeze-drying. Different cellulose derivatives, both micro and nanostructures, were also investigated to explore if these biopolymers can incorporate high surface areas to the foam for the purpose of microplastic capture.

Finally, the removal efficiency of microplastics was analyzed to investigate the amounts of microplastic particles that were bound to the pulp foam adsorbent. Using the information on the microplastic behaviors in aqueous solution, the surface of cellulose materials was modified with different polymers to achieve higher interactions between the foam and microplastics. Zeta potentials and surface charges of the modified cellulose were analyzed to see if the interactions between the foam and microplastics were successful.

### 1.3. Thesis Outlines

The following research project is described by six chapters in the thesis, where:

- Chapter 1 focuses on the background and objectives of the research project, that provides a summary on the outline of the thesis as described above.
- Chapter 2 contains the recent literature review on the subject examined in the thesis. This chapter is organized into five sections: (1) Background of microplastics, (2) Current technologies on the microplastic removal, (3) Sustainable approach of the microplastic removal, (4) Methods for quantifying microplastics in aquatic systems, and (5) Cellulose and material selections for fabrication process.
- Chapter 3 discusses the dispersion of microplastics using three types of surfactants (anionic, cationic, and nonionic) and identifying an ideal method for quantifying microplastic particles in aqueous solution.
- Chapter 4 outlines the physical modification of cellulose derivatives, microcrystalline cellulose (MCC) and nanocrystalline cellulose (NCC), by grafting with (3-chloro-2-hydroxypropyl)dodecyldimethylammonium chloride (QUAB 342) surfactant. The modified polymers were then utilized to prepare the softwood pulp foam adsorbent.
- Chapter 5 summarizes the results of the microplastic removal efficiency using the softwood pulp foam consisting of QUAB342-MCC and QUAB342-NCC.
- Chapter 6 concludes with a summary of the overall research project and provides additional recommendations for future work.

## Chapter 2: Literature Review

### 2.1. General Introduction to Microplastic Pollution

#### 2.1.1. Formation of Microplastics

Microplastics are synthetic organic polymer particles, and they possess various shapes, colors and sizes depending on the environmental conditions. The derivations of the plastic polymer can be either beads, pellets, or fibers. The plastic particles possess diameters of less than 5 mm (Figure 2-1), and densities of approximately  $1.2 \text{ g/cm}^3$  [3]. Microplastics are divided into two categories: primary and secondary microplastics. Primary microplastics refer to micron-sized particles, and are used in by-products and industrial raw materials. Secondary microplastics are plastics resulting from the breakdown of large plastic debris through physical, biological, and chemical degradation process [9]. The degradation of plastics into microplastics are defined into two types: abiotic and biotic degradations [3].

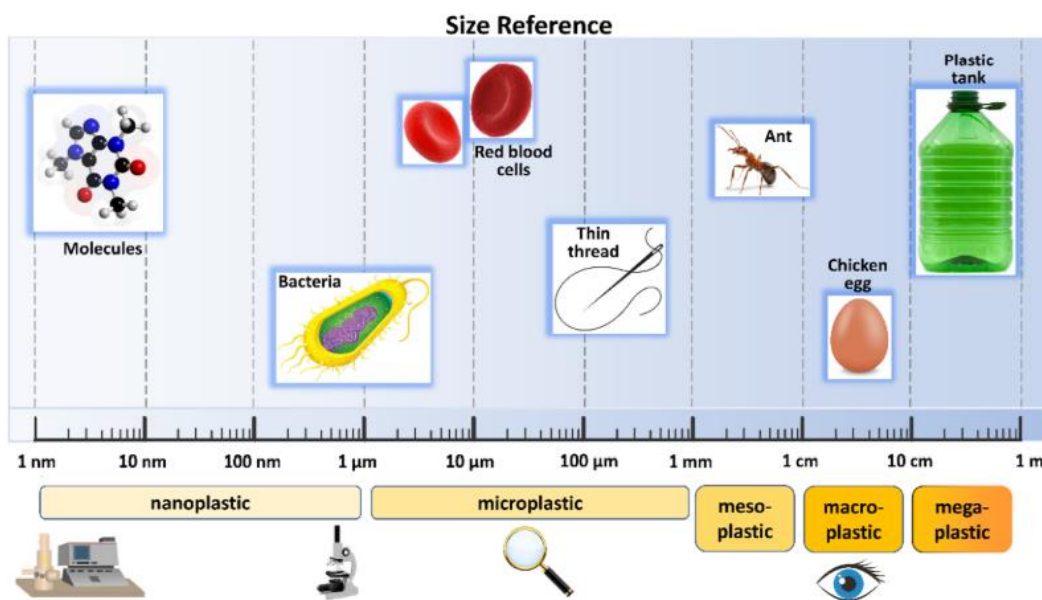


Figure 2-1: Classifications of plastic particles based on sizes (adapted from Tursi et al. [9])

#### 2.1.1.1 Abiotic Degradations

This type of degradation focuses on the change in physical and chemical properties of plastics due to abiotic factors, such as light, temperature, and wind strength. Most common types of abiotic degradation include photodegradation, thermal degradation, chemical degradation, and mechanical degradation [3], [10]. Photodegradation is regarded as the most important process in plastic degradation, since it utilizes high-energy UV radiation of wavelength ranging from 280 to 400 nm [11]. In the marine environment, the presence of UV light alters the chemical and physical structure of the plastics, such as chain scission, oxidation, and hydrolysis [12], [13], [14]. Thermal degradation is similar to photodegradation process. However, a high temperature is required to break down the carbon bonds in the long polymer chain to form free radicals [10]. An effective product temperature degradation ranges between 300 to 420 °C depending on the type of polymer [15]. Mechanical degradation involves the use of sand, wind, and waves to break down plastics into smaller fragments. Lastly, chemical degradation of plastics refers to the scission of long polymer chain by pollutants such as ozone (O<sub>3</sub>), sulfur dioxide (SO<sub>2</sub>), nitrogen dioxide (NO<sub>2</sub>), and volatile organic compounds (VOCs) [3], [10].

#### 2.1.1.2. Biotic Degradations

This type of degradation utilizes organisms to break down long polymer chain into micron-sized particles, by biting, chewing, or digestive fragmentation [3]. In both aquatic and soil systems, organisms are mainly bacteria, fungi, and insects [3], [10]. The biotic degradation is divided into two categories: biochemical and biophysical. Biochemical degradation introduces enzymes secreted by fungi or bacteria to break down long chain polymer into smaller molecules [16]. This reduces the molecular weight of the polymer and converting them to CO<sub>2</sub>, H<sub>2</sub>O,

biomass and energy [17]. Biophysical degradation involves organisms adhering to the polymer surface due to the influence of surface tension, surface structure, porosity, and environmental disturbance [16]. By hydrolysis, protonation, or ionization process, the polymers breakdown into fragments. Figure 2-2 provides a summary of the plastic degradations as discussed earlier.

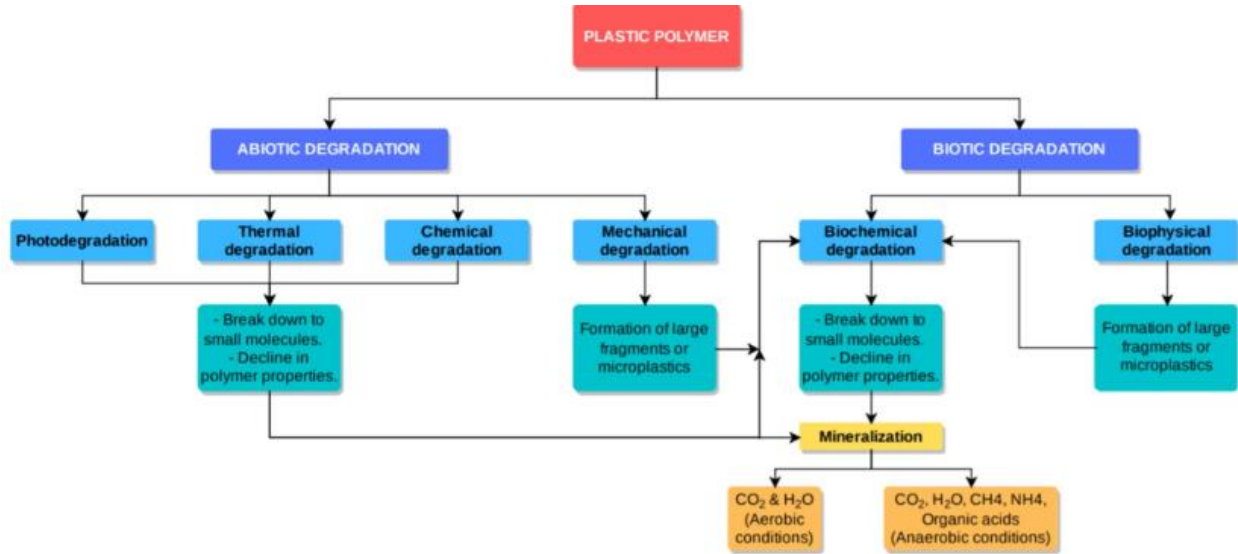


Figure 2-2: Different types of plastic degradation: abiotic and biotic (adapted from Razaviarani et al. [10])

### 2.1.2. Types of Microplastics

As explained in section 2.1.1, microplastics can be degraded into small fragments or polymers through physical, chemical, and biological methods. The common plastic polymers present in the environment are polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC) [9]. As explained in Table 1, PE is recognized as the most common plastics since it is found in variety of sources, such as cleaning products, reusable bags, food packaging, and plastic containers [9]. According to the plastic manufacturers, 36 % of the total plastic production are composed of polyethylene, followed by polypropylene (21 %), polystyrene

(12 %), polyester (10 %), and polyvinyl chloride (9 %) [18]. PE is categorized into two types: low-density polyethylene (LDPE) and high-density polyethylene (HDPE). The density of LDPE ranges between 0.910 and 0.940 g/cm<sup>3</sup>, while HDPE has density ranging from 0.93 to 0.97 g/cm<sup>3</sup> [19], [20]. The occurrence of the varying densities can be explained by the structures of the two polymers, where LDPE is highly branched while HDPE is linear [20].

Table 1: Number of studies for common types of microplastics with different densities (adapted from Hidalgo-Ruz et al. [18])

| <b>Polymer type</b>              | <b>Polymer density (g/cm<sup>3</sup>)</b> | <b>No. of studies</b> |
|----------------------------------|-------------------------------------------|-----------------------|
| Polyethylene (PE)                | 0.917– 0.97                               | 33                    |
| Polypropylene (PP)               | 0.9–0.91                                  | 27                    |
| Polystyrene (PS)                 | 1.04–1.1                                  | 17                    |
| Polyamide (nylon) (PA)           | 1.02–1.05                                 | 7                     |
| Polyester (PES)                  | 1.24–2.3                                  | 4                     |
| Acrylic (AC)                     | 1.09–1.20                                 | 4                     |
| Polyoxymethylene (POM)           | 1.41–1.61                                 | 4                     |
| Polyvinyl alcohol (PVA)          | 1.19–1.31                                 | 3                     |
| Polyvinyl chloride (PVC)         | 1.16–1.58                                 | 2                     |
| Polymethyl acrylate (PMA)        | 1.17–1.20                                 | 2                     |
| Polyethylene terephthalate (PET) | 1.37–1.45                                 | 1                     |
| Alkyd (AKD)                      | 1.24–2.10                                 | 1                     |
| Polyurethane (PU)                | 1.2                                       | 1                     |

Many studies were conducted to investigate the effect of PE in marine animals and organisms. Athulya et al. developed a study examining the structural deformities of *artemia salina* when exposed to microplastic pollution and ocean acidification [21]. When PE of 0.5 mg/mL was added under the acidified environment (pH = 8.0), the appearances of the zooplankton, which included the thoracic segments, abdomen, gut, and antennae, began to deform during stages of development [21]. Furthermore, the exposure to PE yielded a significant reduction in the hatching rate to 50 % [21]. Aside from zooplanktons and other microorganisms, fish can also be affected by the exposure of microplastics. Xiong et al. observed the behavior of goldfishes in the presence PE of varying colors, shapes, and sizes [22]. Although the fishes expel large plastic debris, they could ingest microplastics (1-3 mm) [22], and the presence of microplastics plays a negative role in the marine systems. Organisms can mistakenly identify such debris as foods, and they are ingested into their bodies. The continuous intake of microplastics can cause problems to their digestive and reproductive systems. From the information on the destructive impact of microplastics, the capturing microplastics can minimize the impact on the aquatic environment.

## **2.2. Current Technologies on the Removal of Microplastics in Aquatic Environment**

The removal of microplastics has been a major focus in many studies in order to achieve clean water supplies and maintain environmental sustainability. In recent years, large numbers of technologies have been developed for the removal of microplastics, through physical, chemical, and biological approaches. These technologies include coagulation/flocculation, bioreactors, chemical oxidation and photocatalysis treatments [23].

### 2.2.1. Coagulation-Flocculation-Sedimentation

The combination of coagulation, flocculation, and sedimentation is one of the most common techniques used to remove contamination from water sources. This process involves separating the solids and liquids by their densities. Figure 2-3 illustrates the coagulation-flocculation-sedimentation technique for microplastic removal. Coagulation is the first step of water purification, where coagulant materials, such as metal salts, are added to destabilize the suspended microplastic particles [24]. The chemicals are dispersed uniformly by a rapid mixer before transferring to flocculation tank. In the flocculation process, flocculants consisting of inorganic coagulants, synthetic organic polymers, or composites, interact with the suspended microplastic particles via electrostatic forces or Van der Waals forces [25], [26]. Slow mixing is applied for long period of time yielding large aggregates or flocs [24]. The sedimentation is the final step, where high density microplastics from the flocculation process settle to the bottom.

Multiple types of coagulants have been implemented to optimize the removal efficiency of microplastics. Currently, aluminum-based and iron-based coagulants are widely used in the wastewater treatment [23]. However, these materials display low removal efficiencies of microplastics due to different factors, such as microplastic sizes and pH variations. Based on the studies by Ma et al., it was found that the use of  $\text{Al}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  resulted in removal efficiencies of less than 8.3 and 12.7 % for PE with the size range of 0.5 – 5 mm [27]. This was due to the fact that the low density of PE could suspend on the water surface making it difficult for the treatment process, and the average size of the flocs was smaller than the PE particles. Furthermore, another study reported the PE removal efficiencies decreased from 60 to 39.7 % for Al-based coagulant and 33.5 to 13.5 % for Fe-based coagulant when the pH was increased from 6 to 8 [28]. These results revealed that the low pH activates the positively

charged cations, such as  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ , to interact with the negatively charged PE particles. The removal efficiency of microplastics was improved to 92 % when anionic polyacrylamide (PAM) was added to the alum coagulant [29], [30]. This was because the positively charged alum interacted with the negatively charged PAM forming a large floc that could capture large amounts of microplastics.

Although the approach of coagulation-flocculation-sedimentation has advantages such as simple operation and better capture of microplastics, it has several drawbacks and limitations. For example, high dosages of metal-based coagulants generate significant amounts of sludge, which can lead to potential risks to aquatic organisms when release to the environment [23]. This also increases the cost of sludge treatment and equipment maintenance. Another limitation of this treatment is the poor removal efficiency of microplastics. Depending on the size of the microplastics or the use of coagulants, this process was reported to obtain a low removal efficiency for large-sized microplastics.

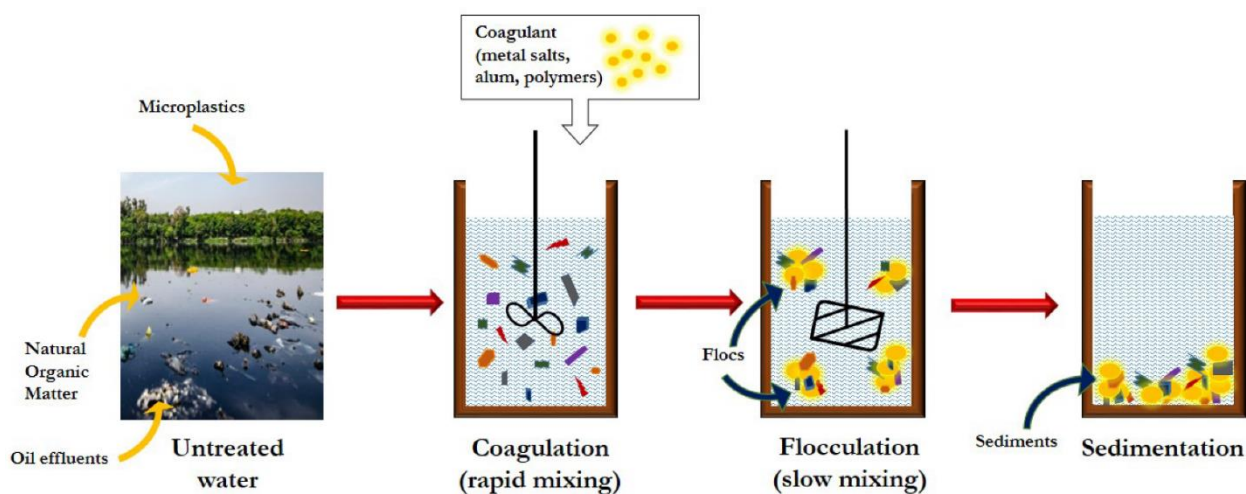


Figure 2-3: Removal of microplastics using the combination of coagulation, flocculation, and sedimentation process (adapted from Pandey et al. [24] )

### 2.2.2. Membrane Bioreactors (MBR)

This treatment process has become an innovative technology in industrial wastewater treatment, and it involves the combination of pretreatment, bioreactor, and membrane filtration. MBR is divided into two configurations: submerged and side-stream [31]. Submerged MBR is membrane placed inside the reactor, while side-stream MBR is membrane located outside the tank. Polyvinylidene fluoride (PVDF) membrane is widely used in the system, as it exhibits excellent mechanical strength, good adsorption capacity for better capture of microplastics, and desirable pore size [32]. MBR has many advantages, which includes eliminating secondary settling tank, producing less sludge, and minimizing hydraulic retention time [31], which displays high removal efficiency. It is reported the MBR process had a slightly better removal efficiency of microplastics (99.4 %) compared to the conventional activated sludge (CAS) process (98.3 %) [33]. This is due to the fact that the microplastics could not settle well in the settling tank of CAS, resulting in the inefficient removal of the microplastics particles [31]. Despite many advantages of MBR, it has many drawbacks, and membrane fouling is one of the most common problems in the MBR process, where suspended particulates are adsorbed onto the membrane surface clogging the pore and reduced the permeate flux [34]. This results in high operating costs and energy consumption due to the need to clean the membrane. Although PVDF membrane is widely used in the treatment process, the addition of hydrophilic polymers or inorganic oxides nanoparticles is enhanced to improve its antifouling properties. Polyvinylpyrrolidone (PVP), a hydrophilic polymer, is implemented as a pore forming agent and a hydrophilic modifier to control the pore size distribution that mitigate membrane fouling [35]. Among many nanoparticles,  $\text{TiO}_2$  and  $\text{SiO}_2$  are also used to modify PVDF membrane due to their

low costs and good stability, and they played a remarkable role in improving water flux and enhancing antifouling properties [35], [36].

### **2.2.3. Advanced Oxidation Process**

In comparison with the current technologies, the method of advanced oxidation process (AOP) involves the decomposition of microplastics into small fragments using appropriate light energy sources. It demonstrates promising results in the environmental approach, as it removes microplastics and other inorganic pollutants without producing sludges and the need for frequent cleanings [37]. The AOP process undergoes both Fenton and photocatalytic reactions to decompose microplastics into small molecules. This reaction involves the generation of  $\text{OH}\cdot$  and  $\text{SO}_4\cdot$  radicals by reacting  $\text{H}_2\text{O}_2$  with a solid catalyst, such as ferric ions, in an acid medium [23], [38]. The radicals possess high reactivity, which has the capability to break down carbon chains of microplastics and achieve degradation. The Photo-Fenton process is implemented by applying UV radiation to enhance the rate of reaction and increase the production of radicals [39].

Photocatalytic reaction involves the use of semiconductor oxides acting as photocatalysts and the implementation of UV light to remove microplastics from water [40]. Titanium dioxide ( $\text{TiO}_2$ ) and zinc oxide ( $\text{ZnO}$ ) are the most common photocatalysts in microplastic degradation since they provide several properties including low toxicities, high reactivities, and efficient removal efficiencies of pollutants [41].  $\text{TiO}_2$  and  $\text{ZnO}$  possess appropriate bandgap energy of 3.2 eV and 3.4 eV respectively when interacted by light sources [39]. The interaction between the UV light and photocatalysts excites electrons from the valence band to the conduction band, and generates electron-hole ( $\text{e-h}^+$ ) pairs (Figure 2-4a) [38], [39], [41]. The  $\text{e-h}^+$  pairs react with  $\text{O}_2$  and  $\text{H}_2\text{O}$  and produce  $\text{OH}\cdot$  and  $\text{O}_2\cdot$  radicals, which are utilized for microplastic degradation.

Although  $\text{TiO}_2$  and  $\text{ZnO}$  photocatalysts play a key role in microplastic degradation, they possess several limitations. When bare photocatalysts are used in the process, they can only absorb small fractions of UV light making the removal efficiency low. In addition, they operate at high temperatures, which increase the energy cost in the wastewater treatment [39]. As a result, the degradation efficiency is improved by combining the photocatalyst with metal dopants that reduces the bandgap energy, hence increasing the optical absorption and maximizing the degradation process [42]. The addition of Fe dopant to the  $\text{ZnO}$  photocatalyst produced a modified photocatalyst that reduces the bandgap energy from 3.4 eV to 3.25 eV (Figure 2-4b) [41], [43]. This effect allows the material to absorb high amounts of light compared to the undoped  $\text{ZnO}$  photocatalyst. Furthermore, the catalytic performance of  $\text{Ag-TiO}_2$  photocatalyst showed promising results, as it decreased the bandgap energy (3.11 eV to 2.66 eV), and increased the degradation rate compared to the unmodified  $\text{TiO}_2$  [44]. This is due to the Ag ions acting as an electron acceptor to reduce the  $e^-h^+$  pair recombination which further improves the photocatalytic activities [44].

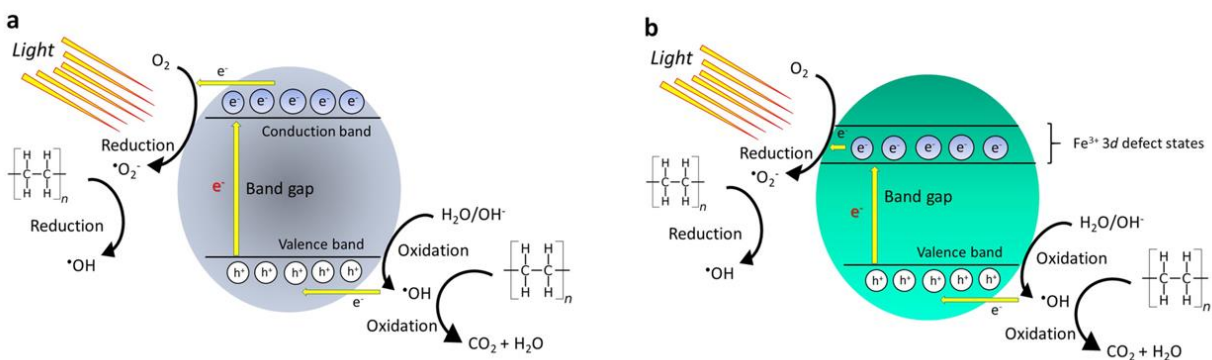


Figure 2-4: Photocatalysis process of PE using a)  $\text{ZnO}$  catalyst and b)  $\text{Fe-ZnO}$  photocatalyst (adapted from Ebrahimbabaie et al. [41])

### **2.3. Sustainable and Bio-based Approach for Microplastic Removal**

With the many limitations in the existing technologies, the rapid growth of nanotechnology and the incorporation of nanomaterials in many substrates have drawn attention to many industries worldwide. Covering the scale ranging from 1 to 100 nm, this technology provides potentials to address complex problems in engineering fields. The research on green nanotechnology and nanomaterials has mainly focused on water treatments that promote environmental sustainability. Several bio-based materials, such as biochar and biopolymers, have been used as membrane filtration, ultrafiltration, and adsorption processes for the microplastic removal from water.

#### **2.3.1. Biochar Material for Microplastic Removals**

The utilization of biochar has gained attentions in water treatment processes, since it derives from the pyrolysis of biomass and uses less energy [45]. Furthermore, the porous structure and active sites of biochar provides high interactions with polymers or composites making the material more attractive [45].

Recent researchers have studied the use of biochar to improve the removal efficiency of microplastics. Wang et al. introduced corn straw and hardwood biochar to integrate with sand filtration systems to remove polystyrene microbeads [46]. The results demonstrated the removal efficiency exceeding more than 95 % compared to an efficiency of 60 – 80 % when utilizing only conventional sand filtration systems [46]. The mechanism explained that the pore structure of the biochar allowed the microbeads to be bound, trapped, and entangled allowing only water molecules to pass through the filtration system (Figure 2-5).

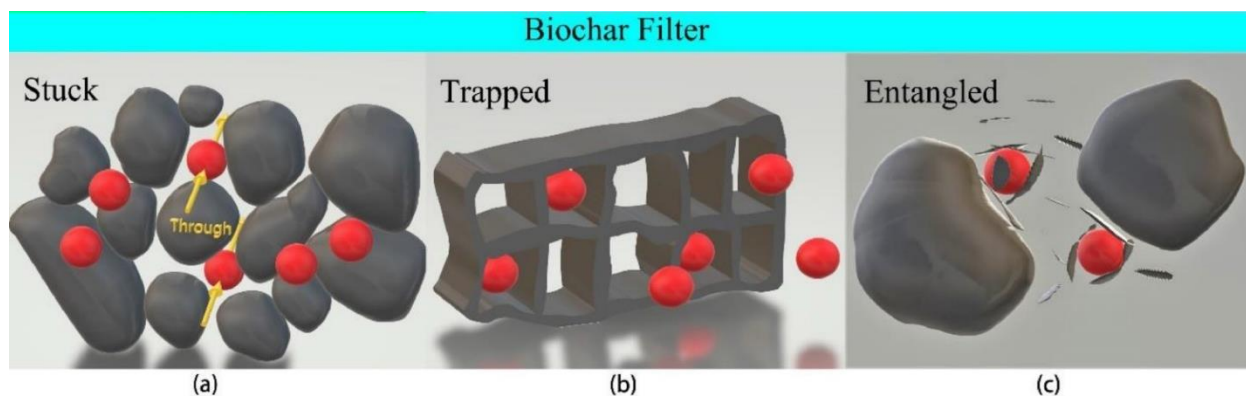


Figure 2-5: Three mechanisms for microplastic capture: a) stuck, b) trapped, and c) entangled (adapted from Wang et al. [46] )

The modification of biochar is crucial for the microplastic adsorption, since raw biochar can produce low recovery rate and generate secondary pollutions [47], [48]. Using transition metals or metal oxides, biochar can be converted to magnetic biochar by impregnation or liquid precipitation method [48], [49], [50]. The results demonstrated an improvement in the microplastic adsorption, as the addition of metals to the biochar achieved removal efficiencies ranging from 94 to 99 % (Figure 2-6a). Furthermore, the microplastic removal efficiencies was investigated for the adsorption-regeneration cycles. It was observed that three magnetic biochar materials maintained removal efficiencies between 94 and 96 % after 5 cycles (Figure 2-6b) indicating the adsorbents were stable over time. The mechanism was due to the high electrostatic interactions between the negatively charged microplastics and positively charged biochar [50]. Overall, the use of biochar as a bio-based adsorbent can be a viable option for microplastic removal in water treatment system.

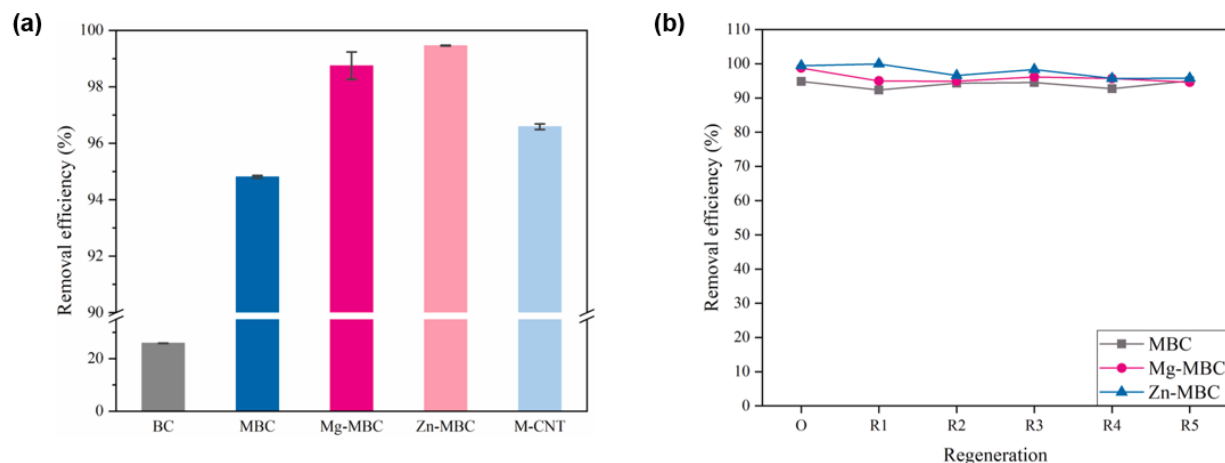


Figure 2-6: a) Removal efficiencies of magnetic biochar composed of various transition metals, and b) removal efficiencies after 5 cycles of regeneration (adapted from Wang et al. [50])

### 2.3.2. Natural Biopolymers for Microplastic Removals

Besides using biochar, biopolymers have also been explored for the microplastic removal in aquatic systems. These materials possess many advantages since they are renewable, cost-effective, and biodegradable. Notable biopolymers like chitosan, starch, polycaprolactone, and cellulose have been investigated for the removal of microplastics from aquatic systems.

Chitosan is the second most abundant natural biopolymer after cellulose, and it is extracted from chitin of shrimps and crustacean shells through a deacetylation process [51]. Its molecular structure consists of a glycosidic residue of hydroxyl and amino groups, yielding a polycationic polymer [52]. The positively charged chitosan, due to the protonation of the amino groups will interact with negatively charged microplastics via electrostatic interactions. Zeng et al. fabricated a magnetic chitosan aerogel with polydopamine (PDA-MCS) to achieve high adsorption capacity and improve the microplastic removal efficiency in aqueous systems [53]. Using the PDA-MCS aerogel, the removal efficiencies of PE, PET, and PS microplastics reached 97.3%, 94.6%, and 92.3% [53]. The mechanisms can be explained by zeta potentials of

microplastics and aerogels indicating the electrostatic interactions were achieved (Figure 2-7a). Furthermore, PDA-MCS aerogels showed better adsorption performance in aqueous solution at pH 6, as the removal efficiency of microplastics was 92 % (Figure 2-7b). However, the increase in the pH in the aqueous solution reduces the efficiency, mainly due to the presence of hydroxide ions [54]. Overall, chitosan as adsorbent displayed promising results in capturing microplastics in aquatic systems. However, it must be optimized to enhance the adsorption performance under basic conditions.

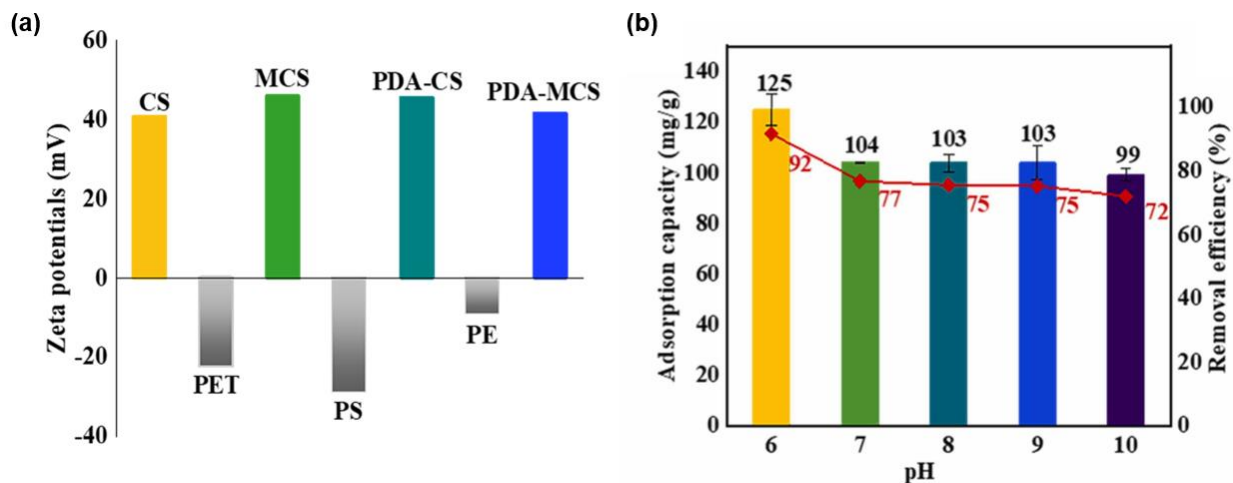


Figure 2-7: a) Zeta potentials for modified chitosan aerogels and microplastics, and b) adsorption effect of PDA-MCS aerogels on PET microplastics at different solution pH (adapted from Zheng et al. [53] )

Starch is another natural biopolymer that has been researched for water treatment process. Mainly originated in corn, rice, and wheat, it has many advantages such as low-cost, resource renewability, and biocompatibility [55]. The structure can be classified into two types: amorphous linear amylose and crystalline branched amylopectin [55]. Despite their differences in terms of structures and properties, they contain free hydroxyl groups capable of absorbing

water. However, starch displays poor mechanical strength which possesses many disadvantages during the filtration or adsorption process. Hence, it must be crosslinked with other polymeric crosslinkers to enhance its mechanical strength. Fu et al. introduced gelatin, another biopolymer, to crosslink with corn starch to develop an ultra-light sustainable sponge for microplastic removal [56]. The results demonstrated high removal efficiency of 90%, due to the strong hydrophobic and electrostatic interactions between the sponge and microplastics [56]. The combination of two biopolymers can benefit in the use of sustainable materials for microplastic removals that reduce the environmental impact.

Polycaprolactone (PCL), a non-toxic, biodegradable polymer, has been studied by researchers as a potential biodegradable polymer for microplastic removal in aquatic systems. Due to its hydrophobic characteristics, the polymer has been employed as an adsorption agent to eliminate organic dyes and heavy metal ions from aquatic solution [57]. Han et al. incorporated PCL with diatomite to produce an adsorbent-based filtration for the microplastic removal from aquatic environments [58]. This enhances hydrophobic properties on the filtration device, where the plastic polymers can adhere to the surface by hydrophobic interactions. Using the fabricated filter, the removal efficiency of the 1.1  $\mu\text{m}$  microplastics achieved 92.23 % and 94.18 % for concentrations of 10 and 100 ppm, respectively [58].

Lastly, cellulose is the most abundant polymer on earth, and it is obtained from various resources, such as plants, trees, and bacteria. As a renewable and biocompatible material, it features many different sizes and shapes, ranging from fibers to crystalline structures [8]. Additionally, it possesses abundant surface functional groups that can be used for physical and chemical modifications on the surface. With its unique properties, cellulose has played an essential role in many industrial applications. Several studies on cellulose have been conducted

to optimize the removal efficiency of microplastics from water. Liu et al. introduced cellulose nanofiber (CNF) to coat delignified wood for the purpose of removing PS microplastics [59]. The removal efficiency of PS microplastics was evaluated for the CNF-coated delignified wood membrane. In comparison to raw wood and delignified wood that possessed removal efficiencies of 24.7 % and 23.57 %, the addition to the CNF yielded a high removal of 96 % (Figure 2-8a). The varying CNF concentrations were also investigated, and the results revealed that the use of 0.5 wt% CNF achieved the highest removal efficiency (Figure 2-8b).

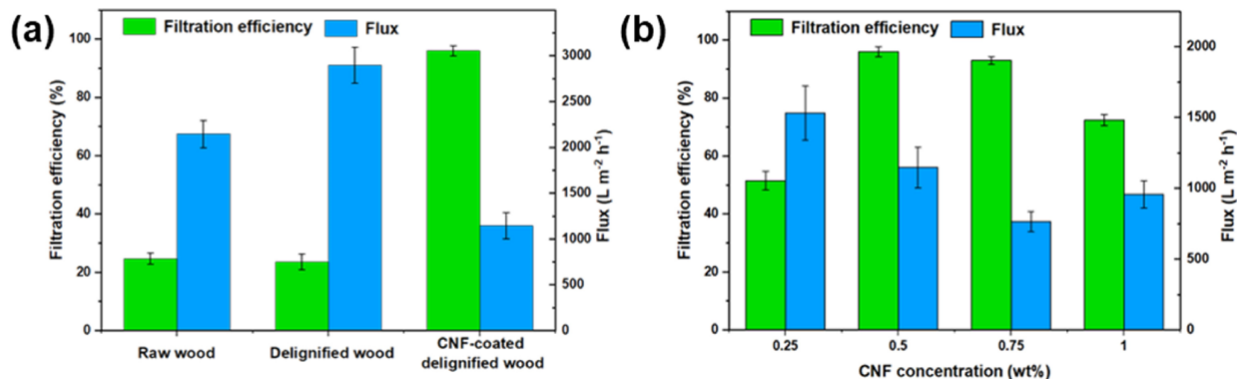


Figure 2-8: a) Microplastic removal efficiencies of raw wood, delignified wood, and CNF-coated delignified wood, and b) microplastic removal efficiencies of different CNF concentrations (adapted from Liu et al. [59])

Bio-based materials, such as biochar and natural biopolymers are promising alternatives to existing technologies since they are low-costs, renewable, and biocompatible and display lower environmental impacts on water sources. They also display remarkable results in removing contaminants and organic pollutants from water due to their unique properties and characteristics. However, further improvements on the biomaterials must be considered since the variety of microplastics possess different structures and properties. Additionally, studies on the

removal of polyethylene microplastics must be addressed, as these are common polymers that can be found in several plastic products. For further optimization of microplastic removal from water, cellulose is the ideal method for water treatment process since its abundant surface functional groups can attract many polymers or substances to modify the surface of the cellulose to be hydrophobic.

## **2.4. Sampling Detection of Microplastics**

The quantification and identification of microplastics are essential requirements to analyze the removal efficiency in water purification process. Recent analytical techniques have been used to characterize the morphological features of microplastics, and quantify the number of particles in a collected sample. The following methods used during the water treatment process include fluorescence staining method, Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, and UV-vis spectroscopy.

### **2.4.1. Fluorescence Staining Method**

The fluorescence staining technique is a simple method that incorporates fluorescent dye to study the morphological characteristics of microplastics. Typically, Nile red (NR) has been widely used as a fluorescent dye since it possesses lipophilic properties that binds to the plastic polymer chains via Van der Waal and additional dipole interactions [60]. Although several dyes have been studied, such as Evans blue and Calcofluor white, NR is the most attractive due to its high adsorption to plastics and better fluorescence intensity [10], [60]. In this technique, the NR stock solution is prepared in various solvents, such as acetone, n-hexane, or chloroform [61].

Next, microplastics are stained with 1 mL of NR dye, and incubated for 24 h at temperatures (30 – 60 °C) [60], [61], [62]. The dried samples are placed under a green fluorescence microscope to visualize their structure and size (Figure 2-9). Although the staining method is simple to implement and inexpensive, the NR dye can co-stain with other organic materials leading to discrepancies in quantifying the microplastics. To mitigate the issue, lipids and from organic particles must be removed [61]. Furthermore, some plastic polymers show weak fluorescence when exposed to light. As explained in Figure 2-9, it was observed that HDPE particles showed strong fluorescence, while the PVC and PP displayed weak fluorescence. As a result, the fluorescence staining technique is not the ideal method of quantifying microplastics for water applications.

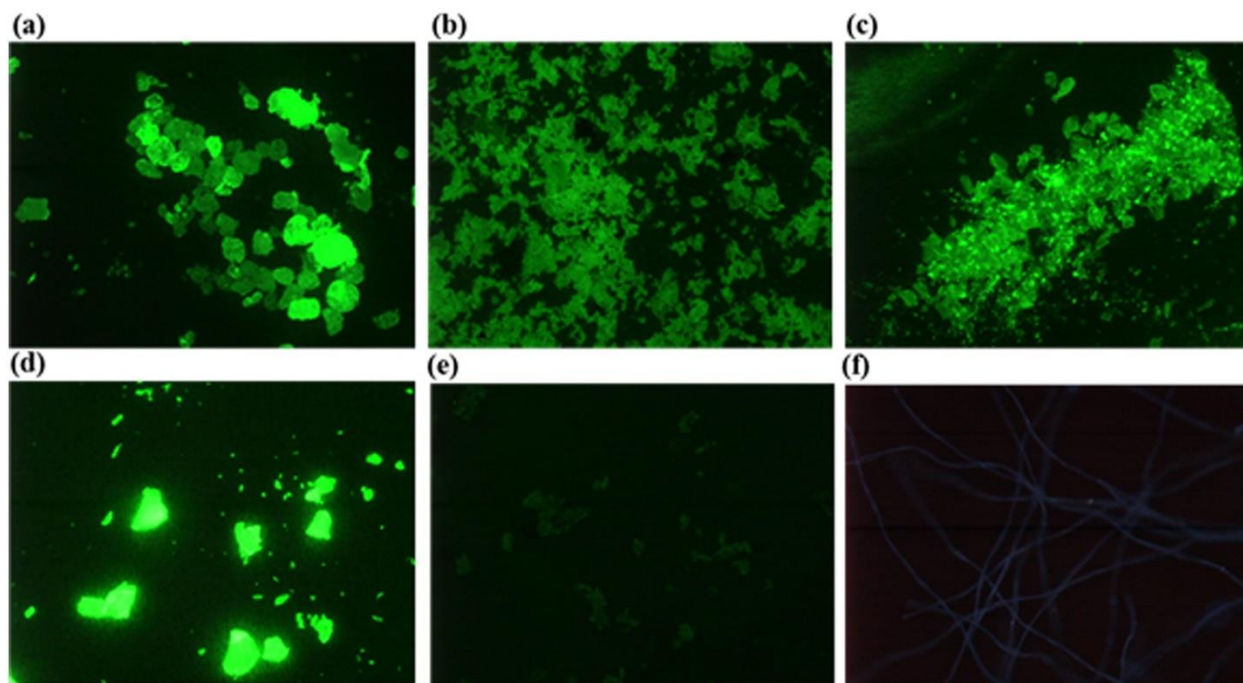


Figure 2-9: Images of a) high density polyethylene (HDPE), b) polycarbonate (PC), c) polyurethane (PU), d) poly(ethylene-vinyl acetate) (PEVA), e) polyvinyl chloride (PVC), and f) polyester (PES) stained with NR dye under green fluorescence microscope (adapted from Shim et al. [62] )

#### 2.4.2. Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy has been widely used to identify and quantify microplastics in several water treatment processes. This technique has become a valuable tool to provide quick and non-destructive detection of organic materials, as well as determining their chemical compositions [63], [64]. In this method, microplastic samples are irradiated with infrared light, and their chemical bond structures (carbonyl, hydroxyl, and carbon-oxygen bond) can be determined based on the absorption peak at a corresponding wavenumber ranging from 4000 to 500  $\text{cm}^{-1}$  [64]. The FTIR spectroscopy has two different settings:  $\mu$ -FTIR and attenuated total reflection (ATR)-FTIR spectroscopy.  $\mu$ -FTIR spectroscopy is extensively used to study small particles (10  $\mu\text{m}$ ), while, ATR-FTIR spectroscopy is implemented to study large particles ( $> 500 \mu\text{m}$ ) [65]. Automatic FTIR imaging, such as focal plan array (FPA) coupled to the  $\mu$ -FTIR provides fast acquisition of chemical imaging and generates high resolution for particles ranging from 10 to 500  $\mu\text{m}$  [65], [66].

Lee et al. utilized  $\mu$ -FTIR spectroscopy to evaluate the removal efficiency of PE microplastics using in-situ ferrate coagulation process [67]. In this study, 10 mg/L of the PE sample (40  $\mu\text{m}$ ) was placed into the FTIR imaging, and the number of particles was counted (Figure 2-10a). After the treatment process, the number of particles were determined for the effluent sample to determine the removal efficiency (Figure 2-10b). Approximately 96.7 % of PE microplastics was removed after the coagulation process, and very few particles were visible based on the FTIR imaging [67]. Furthermore, IR spectrum of PE before and after treatment was examined, and a significant reduction in the intensity was achieved after coagulation (Figure 2-10c). Although the FTIR spectroscopy provides a quantitative information on the microplastics, however the identification of very small particles ( $< 10 \mu\text{m}$ ) can be challenging. Since

microplastics can be broken down into small fragments due to environmental conditions, these small particles cannot be identified under the FTIR imaging since the machine has a detection limit of 10  $\mu\text{m}$  [65], and this leads to errors in the quantitative analysis. In addition, FTIR techniques can be affected by other organic pollutants which can alter absorption peaks in the IR spectrum.

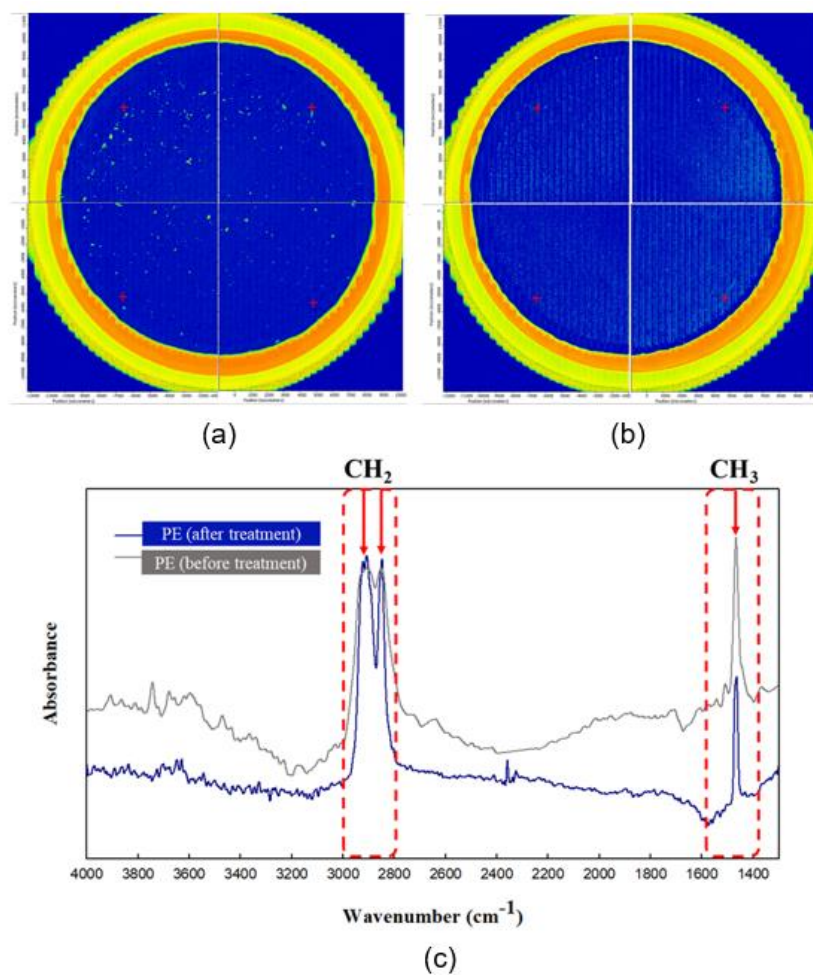


Figure 2-10:  $\mu$ -FTIR imaging of a) PE before treatment and b) PE after treatment, and c) IR spectrum of PE before and after treatment (adapted from Lee et al. [67] )

### **2.4.3. Raman Spectroscopy**

Raman spectroscopy is another common technique used to quantify microplastics in water samples. This method is a promising tool compared to the FTIR spectroscopy, since it can detect very small particles (1  $\mu\text{m}$ ) with high resolutions making the quantification more accurate and precise [68]. Furthermore, it can be employed for wet sample analysis since it has less interference with water molecules [69]. The principle behind Raman spectroscopy involves the use of laser that interacts with a sample generating scattered lights [65]. These scattered lights, containing different frequencies and vibrational properties can be captured by the Raman spectrum to give information about the structure of the sample. The Raman spectroscopy has several limitations despite being an effective quantification of microplastics. The use of laser as a light source can generate heat, which can destroy the sample by particle burning or melting [70]. Secondly, the presence of fluorescence due to the impurities from the sample can interfere with the Raman spectra, hence it can lead to discrepancies in the quantification [68]. To reduce the fluorescence signal, the method can be optimized by altering the substrate. Cabernard et al. introduced gold-coated polycarbonate substrates to improve the reflection-absorption in the spectra [71]. As a result, it was revealed that a total of 10,550 particles (1 – 10  $\mu\text{m}$ ) were identified compared to 5,243 particles (10 – 500  $\mu\text{m}$ ) by Raman spectroscopy [71].

### **2.4.4. UV-Vis Spectroscopy**

The approach of UV-vis spectroscopy involves the implementation of UV light absorbed by a sample producing an absorbance peak at a corresponding wavelength [72]. Based on the Beer-Lambert law, the absorbance peak is directly proportional to the concentration of the substance [72]. The UV-vis spectroscopy plays an essential role in evaluating the quality of water

and detecting any contaminant that can damage the aquatic environment. For example, the technique was used to study the concentration of organic dyes, such as methyl orange and methylene blue, present in water bodies. The absorption peak of methyl orange and methylene blue can be observed at a wavelength of 464 nm and 644 nm [73].

Several studies have reported the quantification of microplastics using the UV-vis adsorption technique. Since microplastic particles are insoluble in water, several organic solvents have been considered for preparing the dispersions. Batool et al. prepared the microplastic particles from PMMA, PVC and PVAc by encapsulating with a fluorescent dye, perylene tetraester (PTE) [74]. When the solution was placed in the UV-Vis spectrophotometer, the absorption peak was observed at a wavelength of 454 nm [74]. Fan et al. dissolved PET microplastics in 10 M sulfuric acid, and the peak appeared at a wavelength of 266 nm [75]. An increase in the absorbances was displayed when increasing the PET concentration (Figure 2-11a). The calibration curve was generated illustrating the UV absorbances as a function of concentration (Figure 2-11b). Although the UV-vis spectroscopy showed potential result in microplastic quantification, limitations can occur in this approach. The use of solvents for microplastic dispersion can interfere with the plastic particles, which can lead to discrepancies in the quantitative analysis. Hence, the absorption peak obtained from the instrument might not represent the actual concentration of microplastics. Additionally, the correct solvent use for microplastic dispersions is very crucial since unstable suspensions cannot be identified by the UV-vis spectrometer. Hence, it is considered that an alternative technique must be required to quantify the accurate number of particles.

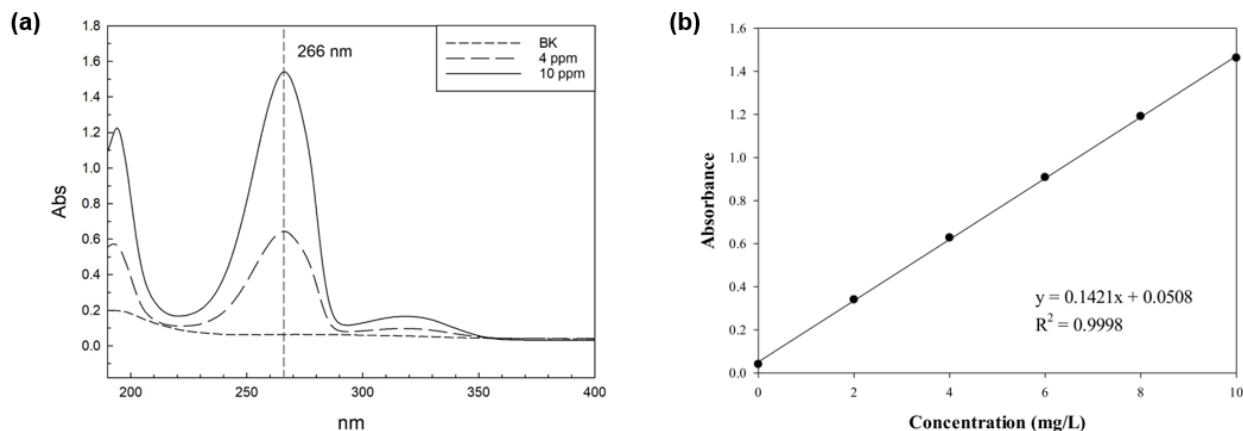


Figure 2-11: a) UV spectra and b) calibration curve of PET dissolved in 10 M sulfuric acid  
(adapted from Fan et al. [75] )

## 2.5. Cellulose and Material Selections

### 2.5.1. General Introduction to Cellulose

Cellulose is the most promising biopolymer and it has attracted increasing attentions from various industries due to its excellent mechanical strength, low density, biodegradability, and biocompatibility. The annual biomass production of the material is estimated between  $7.5 \times 10^{10}$  and  $1.5 \times 10^{12}$  tons [7], [8]. Derived from the primary cell walls of plant materials, cellulose molecules are packed together in millions of microfibrils, aligned in parallel, by Van der Waals forces and inter- and intramolecular hydrogen bonding [76]. The cellulose microfibrils consist of diameters ranging from 2 to 35 nm, and they composed of both amorphous and crystalline regions (Figure 2-12) [76]. The molecular structure of cellulose is composed of repeating anhydroglucose units (AGU) covalently linked together by  $\beta$ -1,4-glycosidic bonds (Figure 2-12). Each AGU unit contains three reactive hydroxyl groups on C<sub>2</sub>, C<sub>3</sub>, and C<sub>6</sub>, and these groups play an important role in surface modification through various chemical processes. The degree of

polymerization (DP) of cellulose ranges from 100 to 20,000, depending on the length of the chain [76], [77].

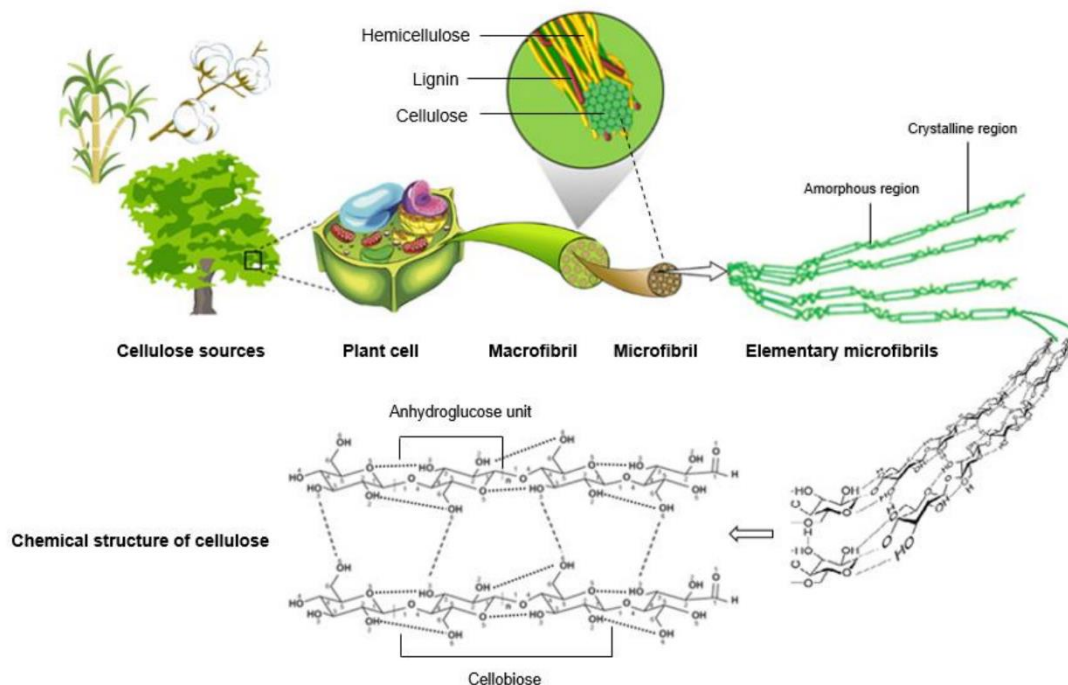


Figure 2-12: Schematic representation of the hierarchical structure of cellulose fibers and the chemical structure of cellulose (adapted from Casanova et al. [7] )

### 2.5.2. Extraction Techniques of Cellulose from Natural Resources

Over the years, different techniques and methods have been explored for the extraction of cellulose from lignocellulosic biomass in order to meet high demands for green materials in various engineering fields. The selection of cellulose extraction method depends on the plant sources, desired fiber dimensions, required purity, and yield [7]. The extraction of cellulose occurs in two stages (Figure 2-13): (1) pretreatment of source materials, and (2) production of cellulose derivatives as micro and nanostructures [78]. The pretreatment process is first carried out by dewaxing the biomass to eliminate impurities such as wax, resins, and oily substances. A mixture of organic solvents with different polarity, which are either benzene/methanol,

hexane/ethanol, ethanol/toluene, is applied to the material to interact with the polar and nonpolar contaminants [79]. Next, alkali treatment involves the decomposition of hemicellulose and lignin from the material using NaOH or KOH under high temperatures between 50 and 210 °C [80], [81], [82]. After the alkalization process, successive bleaching finalizes the removal of excess hemicellulose and lignin purifying cellulose by adding H<sub>2</sub>O<sub>2</sub>, CaClO<sub>2</sub>, or NaClO<sub>2</sub> substance [81].

After the purification process, the second stage involves depolarization of cellulose into various derivatives consisting of both micro and nano-sized materials. Three basic approaches, namely, acid hydrolysis, enzymatic hydrolysis, and mechanical treatment have been used to break down amorphous or crystalline region to produce the desired morphology (Figure 2-13). Acid hydrolysis is the most commonly used technique where the acid eliminates the amorphous region of cellulose microfibrils forming a crystalline structure [82]. Typical acids for cellulose extraction are sulfuric acid, hydrochloric acid, and phosphoric acid [82]. However, sulfuric acid is determined to be more effective as it produces a negative surface charge on the surface of the cellulose resulting in more stable suspensions [78], [79]. Although studies have used hydrochloric acid in the extraction process, the resulting product displays poor colloidal stability in aqueous solution due to the lack of ionic interactions between crystalline particles and water molecules [83]. Enzymatic hydrolysis is another extraction technique, where the cellulose chains are broken down into small molecules by the enzymes. This biological process contains low toxicity and uses less energy consumption thereby reducing the environmental impact [84]. The most common types of enzymes used in the extraction process are endoglucanase, cellobiohydrolases, and  $\beta$ -glucosidases [84]. However, enzymatic processes are typically slow making the extraction less efficient. As a result, catalysts must be added to improve the hydrolysis process. Aside from chemical and biological treatments, mechanical processes, such

as ultrasonication, high-pressure homogenization, and grinding, have been used to extract cellulose fibrils from the plant sources [78]. The methods break down the crystalline region of the cellulose microfibril forming a cellulose nanofiber [79]. Once the cellulose has been extracted to yield the desired morphologies, the final stage involves sonication, freeze-drying, and centrifugation to obtain commercial grade products [78], [79], [82].

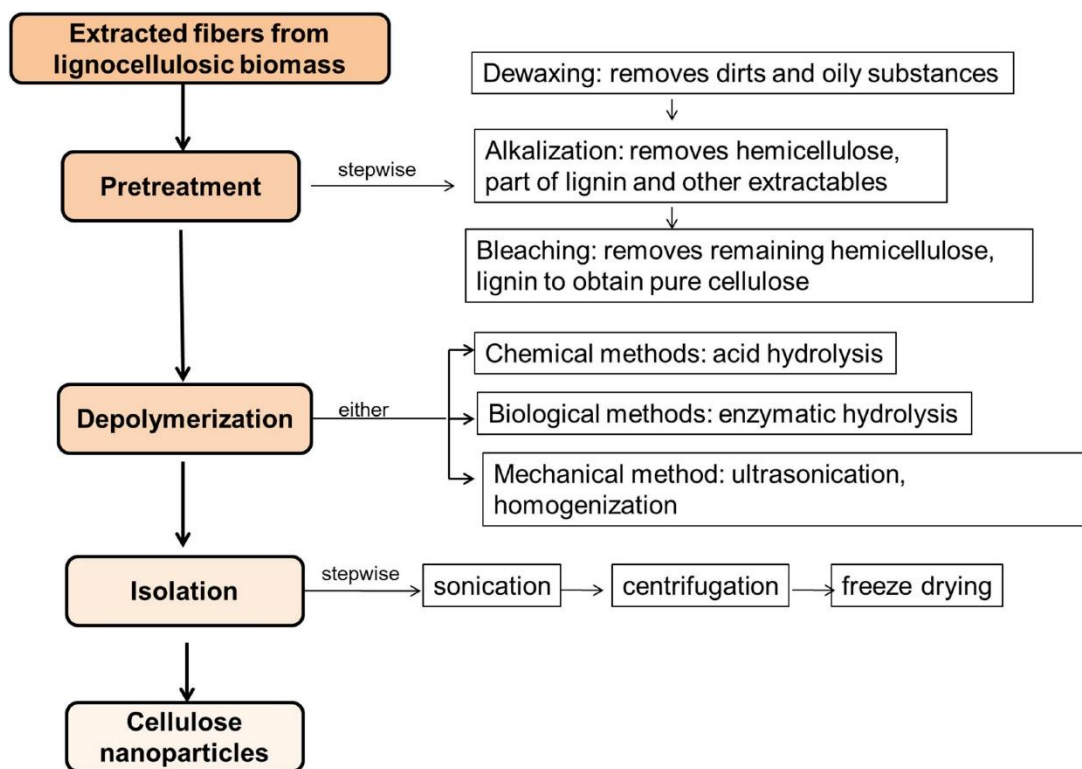


Figure 2-13: Schematic diagram of the chemical process involving cellulose extraction from lignocellulose biomass (Owonubi et al. [79])

### 2.5.3. Type of Cellulosic Derivatives

The extraction of cellulose using chemical, biological, and mechanical techniques have demonstrated promising results in producing desired morphologies for industrial applications. Among the derivatives, microcrystalline cellulose (MCC), nanofibrillated cellulose (NFC), and

nanocrystalline cellulose (NCC) are widely studied since these three materials showed promising tools in several engineering fields (Figure 2-14).

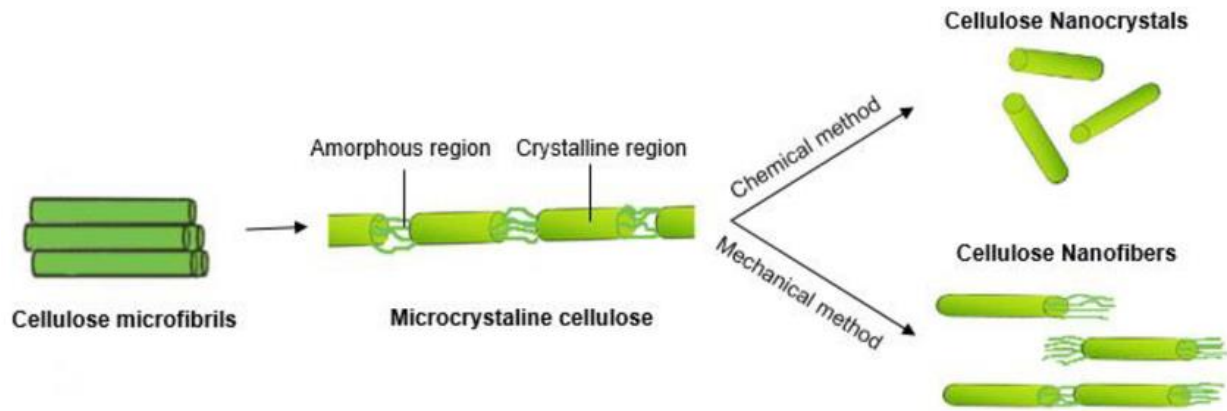


Figure 2-14: Microcrystalline cellulose (MCC) and nanocellulose (NFC and NCC) production from cellulose microfibrils (adapted from Casanova et al. [7] )

#### 2.5.3.1 Microcrystalline Cellulose (MCC)

MCC is a white powdered material that is mainly used in pharmaceuticals and food packaging. It can be synthesized by acid hydrolysis to break down the amorphous region of the cellulose microfibrils forming a short crystalline fragment [82]. The resulting product has a diameter ranging from 10 to 50  $\mu\text{m}$  with a high cellulose content [78]. However, dispersing MCC is a challenge since the cellulosic molecules can agglomerate. Due to the presence of hydroxyl groups in each repeating glucose units, they can interact with each other by hydrogen bonding resulting in poor dispersibility in water.

#### 2.5.3.2 Nanofibrillated Cellulose (NFC)

NFC is one of the common types of nanocellulose derived from the microfibrils. It has been studied for various biomedical applications including drug delivery, wound healing, and tissue engineering [85]. The difference between nanofibrillated cellulose and microfibrillated cellulose (MFC) is that NFC produced using chemical pretreatment followed by a high-pressure homogenization to remove the crystalline region of microfibrils, while MFC is produced via chemical treatment [86]. The structure of NFC consists of repeated glucose molecules bound together by hydrogen bond network. This produces unique properties, which include exceptional mechanical strength, high aspect ratio, and low thermal expansion [87]. The parameters of NFC are approximately 20 – 50 nm in diameter and 200 nm in length [86], [88]. With its unique structures and properties, NFC can benefit in water purification process as adsorbents or filtration devices to capture organic pollutants.

#### 2.5.3.3 Nanocrystalline Cellulose (NCC)

The cellulose microfibrils can further be enhanced by breaking down into nano-scale region using extensive acid hydrolysis. This modification produces a rod-like shape, known as nanocrystalline cellulose (NCC) or cellulose nanocrystals (CNC). The structure of NCC composed of 5 – 20 nm in diameter, and 5 – 500 nm in length [78], [82]. Depending on the acid type for the hydrolysis, the surface functional groups vary on the NCC molecule. For example, the use of  $\text{H}_2\text{SO}_4$  results in the formation of NCC comprised of negative sulfate groups ( $-\text{OSO}_3^-$ ) groups on the surface [7]. In comparison with the MCC and NFC, the NCC displays high crystallinity, large surface area, and excellent mechanical strength. In addition, the amount of surface functional groups on the NCC provides sites for surface modification making the

material more compatible [78]. Over the years, there have been increasing interests from several industries in the production of NCC due to its sustainable approach for engineering applications. CelluForce Inc., one of Canada’s leading manufacturers, produced NCC at a capacity of 1 tons/day, while Blue Goose Biorefineries Inc. produced NCC a capacity of 100 kg/day [89], [90]. However, they both use different plant sources and incorporate different extraction techniques for NCC productions. Table 2 shows the production of NCC from different global companies throughout the years.

Table 2: Lists of global companies in NCC production from lignocellulosic biomass (adapted from Haldar et al. [82] )

| <b>Companies</b>              | <b>Locations</b> | <b>Raw materials</b>                          | <b>Extraction processes</b>                    |
|-------------------------------|------------------|-----------------------------------------------|------------------------------------------------|
| CelluForce Inc.               | Canada           | Wood pulp                                     | Acid hydrolysis using $H_2SO_4$                |
| Cellulose Lab                 | Canada           | Cotton, kraft pulp, sisal, tunicate cellulose | Acid hydrolysis ( $H_2SO_4$ , HCl, $H_3PO_4$ ) |
| Blue Goose Biorefineries Inc. | Canada           | Pulp from lignocellulosic biomass             | Metal catalytic oxidation                      |
| American Process Inc.         | USA              | Bamboo                                        | Chemical treatment using acid and alcohol      |
| ICAR-CIRCOT                   | India            | Cotton and cotton linters                     | Enzymatic and mechanical treatments            |

## 2.6. Conclusions

The chapter provides a general description of microplastics and strategies for removing the microplastics from aquatic systems. While numerous publications have been investigated on existing technologies for the microplastic removal, many sustainable materials have gained increasing attentions from researchers due to their low-cost, biodegradability, and biocompatibility. Cellulose is a promising candidate for biomaterial, as its unique properties can maintain a stable structure in aqueous solution and capture high amounts of microplastics. Using both micro and nanocellulose materials, their abundant functional groups can be reacted with different polymers or substances to modify their surfaces for the purpose of microplastic removal.

## Chapter 3: Development of Microplastic Detection and Analysis

### 3.1. Introduction

Over the years, there have been many research studies on the microplastic behaviors in aquatic environments. PS microplastics have been mainly focused since they are capable of suspending in aqueous solution due to their high density. However, PE microplastics contain hydrophobic properties and have low density making the particles float in water, which pose challenges during the quantification process. Surfactants are widely used as dispersants in laboratory research and industrial applications [91], and due to their amphiphilic characteristics associated with the polar hydrophilic head and non-polar hydrophobic tail, they can be adsorbed at the particle/water interface and yield a well-dispersed suspension [91]. Surfactants are classified into three categories, depending on the surface charges on their head groups: anionic, cationic, and nonionic surfactants [92]. These variety of surfactants can be found in laundry detergents and fabric softeners, which can adsorb onto textile fibers of clothings [93]. A recent study by Sun et al. revealed that PE microplastics disperse easily in three types of surfactants: sodium dodecyl benzene sulfonate (SDBS), polysorbate 80 (Tween 80), and hexadecyltrimethylammonium bromide (CTAB) [94]. These dispersions can alter the surface charge of the microplastics which are important characteristics to note when designing a filtration system for microplastics.

Quantification of PE microplastics is another step to evaluate the particle concentration in an aqueous solution. Regarding the techniques reported by many researchers for quantifying the microplastic particles, many disadvantages have been noted that lead to discrepancies in the results. To mitigate the issue, the detection system must be simple and possess fast detection in

order to obtain a precise quantification of the particles. Coulter counter offers an attractive method for microplastic quantification, as it is an apparatus for counting and sizing particles in an electrolyte solution. The method applies a metering pump to draw the suspended particles into a small cylindrical aperture with two electrodes. The passage of each individual particle induces a change in the electrical resistance that produces a voltage pulse [95], [96]. With each pulse, the number and size distributions of particles are determined. Modern coulter counters are capable of detecting particles smaller than 1  $\mu\text{m}$  [97], which can be beneficial to count number of microplastics with size less than 10  $\mu\text{m}$ .

In this chapter, PE microplastics were stabilized with SDBS, CTAB, and Tween80 surfactants in order to suspend these particles in an aqueous solution. Since Coulter counter was the ideal apparatus for microplastic quantification, sodium chloride solution was selected as the conductive liquid due to its high conductivity. The optimal mass ratio between the PE and the surfactant were investigated to determine the ideal concentration of surfactant for better dispersion stability. Afterwards, zeta potentials and particle sizes of three PE dispersions were analyzed to obtain information for the design of the pulp foam. Finally, calibration curves of the three PE dispersions were created to determine the particle's concentrations.

## **3.2. Materials and Methods**

### **3.2.1. Materials**

Polyethylene microparticles (PE, powder) were purchased from BASF, USA. Sodium dodecylbenzenesulfonate (SDBS, powder,  $\leq 100\%$ ), hexadecyltrimethylammonium bromide (CTAB, powder,  $\geq 99\%$ ), and Tween<sup>®</sup>80 (Tween 80, viscous liquid) were purchased from Sigma Aldrich. Sodium chloride (ACS reagent, 99%) was purchased from Fisher Scientific.

### **3.2.2. Preparation of PE Microplastics using Three Stabilizing Agents**

320 mg of PE powders were measured and injected into the 40-mL NaCl solution (1 wt%). A stock solution of SDBS (2.5 wt%) surfactant was prepared in 1% NaCl solution, and was diluted to achieve specific PE:SDBS mass ratios (1:0.001 to 1:0.1). Then, each sample was bath sonicated for 3.5 hours to produce a well-dispersed microplastic suspension (pls show the picture before and after the addition of surfactant). The particle sizes of PE:SDBS samples were measured using the Anton Paar PSA 1190. Using the information from the PSA, the ideal mass ratio was used for PE dispersed in two other surfactants: CTAB and Tween80. Figure 3-1 shows the schematic representation of the PE microplastics dispersed in three different surfactants.

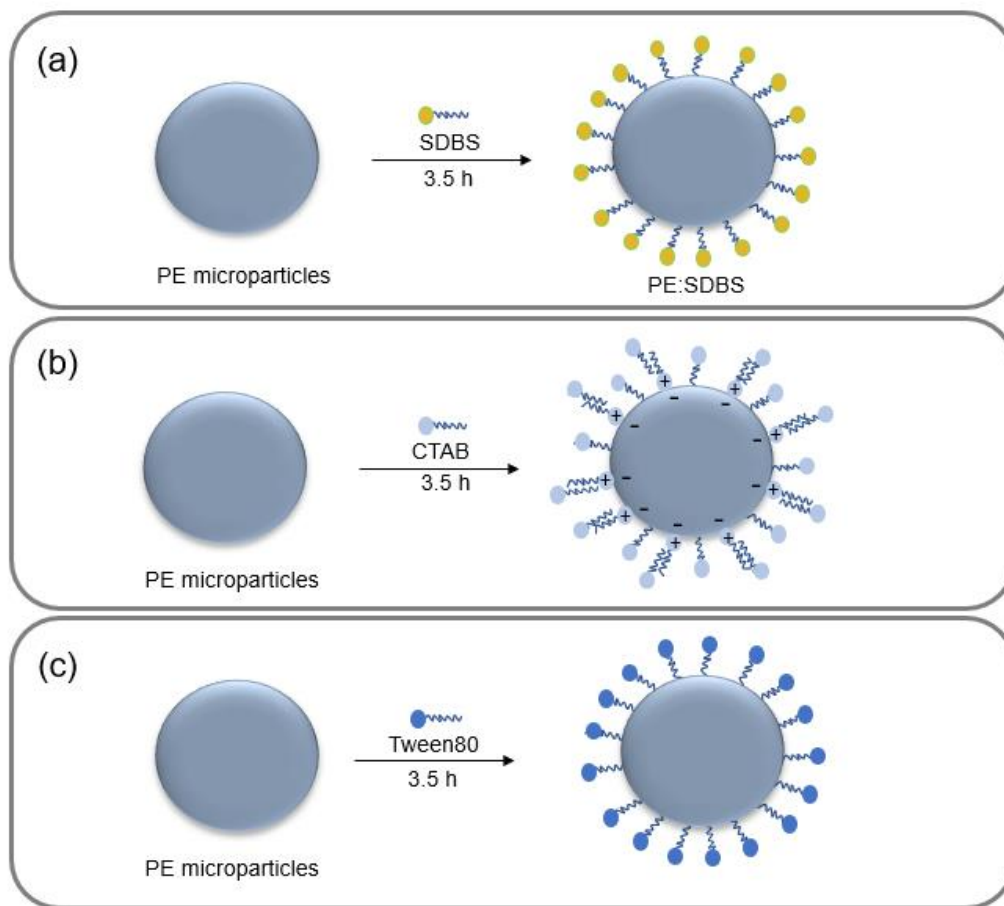


Figure 3-1: Schematic illustration of polyethylene microparticles dispersed in: (a) SDBS, (b) CTAB, and (c) Tween80

### 3.2.3. Particle Sizes and Zeta Potentials

The PSA was used to determine the size of the PE microparticles and estimate the optimal surfactant concentrations for the PE dispersion. In the PSA quantification, 8 mg/mL concentrations of PE:SDBS, PE:CTAB, and PE:Tween80 were prepared, and 2.5 mL of each sample was added to the particle analyzer. For the zeta potential measurement, the samples were diluted to 100 mg/L in 1% NaCl solution and bath sonicated for one minute. The measurements of each sample were performed using the Malvern Nano-ZS90 Zetasizer, and averages were calculated by obtaining the average of six measurements of 10 runs.

### **3.2.4. Coulter Counter**

The objective of utilizing the coulter counter was to identify the number of microplastics suspended in an aqueous solution. The equipment was filled with 1% NaCl solution, and the detection limit was set to 4.72  $\mu\text{m}$ . PE-SDBS, PE-CTAB, and PE-Tween80 stock solutions with concentration of 800 mg/L, were prepared in 1% NaCl solution. The solutions were then diluted to 12 different concentrations (0.1– 60 mg/L), and they were bath sonicated for 5 minutes before they were introduced to the Beckman Coulter<sup>®</sup> Z Series to determine the number of particles for each concentration that was used to prepare a calibration curve.

## **3.3. Results and Discussions**

### **3.3.1. Particle Sizes and Zeta Potentials Results**

As previously discussed in section 3.2.2, the ideal mass ratio of PE:SDBS was selected by analyzing their particle sizes. Figure 3-2 displays the PSA results of varying PE:SDBS mass ratios. At PE:SDBS mass ratios of 1:0.001 and 1:0.005 the PE microplastics were not well-dispersed after bath sonicating for 3.5 hours due to the insufficient amount of SDBS surfactants added to the suspensions. As a result, the PE particles could not be dispersed in an aqueous solution leading to larger particle sizes. At PE:SDBS mass ratio of 1:0.001, the initial particle diameter was determined to be 29.0  $\mu\text{m}$ , and when the mass ratio PE:SDBS was further increased to 1:0.01, the diameter decreased to 7.6  $\mu\text{m}$ . After further increase in the surfactant concentration, the sizes remained constant. This was due to the fact that between the PE:SDBS mass ratio of 1:0.01 to 1:0.10, the PE microplastics were well-dispersed in water representing.

the actual diameter of the microplastics. To determine the optimum mass ratio, PE:SDBS = 1:0.02 was selected since the dispersion time was lower than PE:SDBS = 1:0.01.

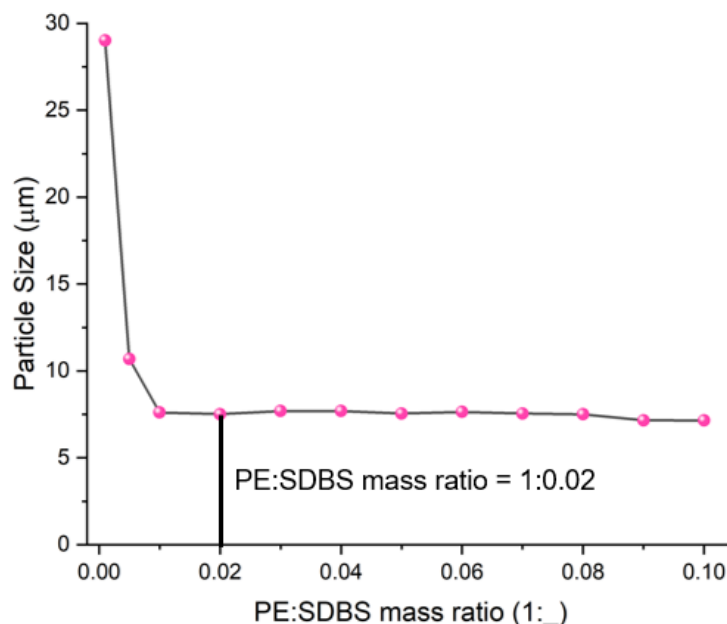


Figure 3-2: PSA results of various mass ratios of PE:SDBS

Once the optimum PE:SDBS mass ratio was chosen, it was then used to prepare PE dispersion of PE:CTAB and PE:Tween80. The particle sizes were measured for all three suspensions, and it was determined they were all within the range between 7.5 and 9.1 μm. The slightly larger particle size for PE:Tween80 was due to slightly longer carbon chains on Tween80.

After analyzing the particle sizes of the three suspensions, the next step was to determine their zeta potentials. As explained in section 3.2.2., it was expected the PE stabilized by the three surfactants would display different surface charges. When zeta potentials were examined for each dispersion, it was determined the PE:SDBS, PE:CTAB, and PE:Tween80 were -46.13, +12.33, and -3.36 mV (Table 3). As shown in Figure 3-1, the long carbon chains of the surfactant

molecules interacted with the PE particles through hydrophobic interaction leaving the hydrophilic heads of the surfactants with different surface charges. As expected, PE:SDBS and PE:CTAB displayed negative and positive zeta potentials. When PE was stabilized by Tween80, a nonionic surfactant, it exhibited a slightly negative zeta potential that was consistent with the small amounts of carboxylate groups on the PE microplastics. The information on the PE surface charge can benefit for the foam production.

Table 3: Particle sizes and zeta potentials of PE dispersions

|                                                  | <b>PE:SDBS</b> | <b>PE:CTAB</b> | <b>PE:Tween80</b> |
|--------------------------------------------------|----------------|----------------|-------------------|
| <b>Particle sizes (<math>\mu\text{m}</math>)</b> | 7.51           | 8.91           | 9.08              |
| <b>Zeta potentials (mV)</b>                      | - 46.13        | +12.33         | - 3.36            |

### 3.3.2. Coulter Counter Calibration Curves

The purpose of utilizing the Coulter counter was to quantify the number of microplastics in an aqueous solution. As explained in section 3.2.4, twelve PE concentrations (0.1 – 60 mg/L) stabilized by SDBS, CTAB, and Tween80 surfactants were prepared and quantified by the particle counter, and the calibration curve was plotted based on the results for each PE concentrations. From Figure 3-3a all three PE dispersions displayed similar slopes with coefficients ranging between 2760 and 2810. In addition, all three curves showed strong correlations between the # of particles/mL and PE concentrations. The particle count was recorded as 3,804 for 2 mg/L of PE. At 4 mg/L of PE, the particle number doubled to a value of 7,147. The results confirmed that the Coulter counter provided a precise quantity of microplastic in an aqueous solution. With this information, the average calibration curve was plotted (Figure

3-3b), which could be used to determine the unknown concentrations during the filtration experiments.

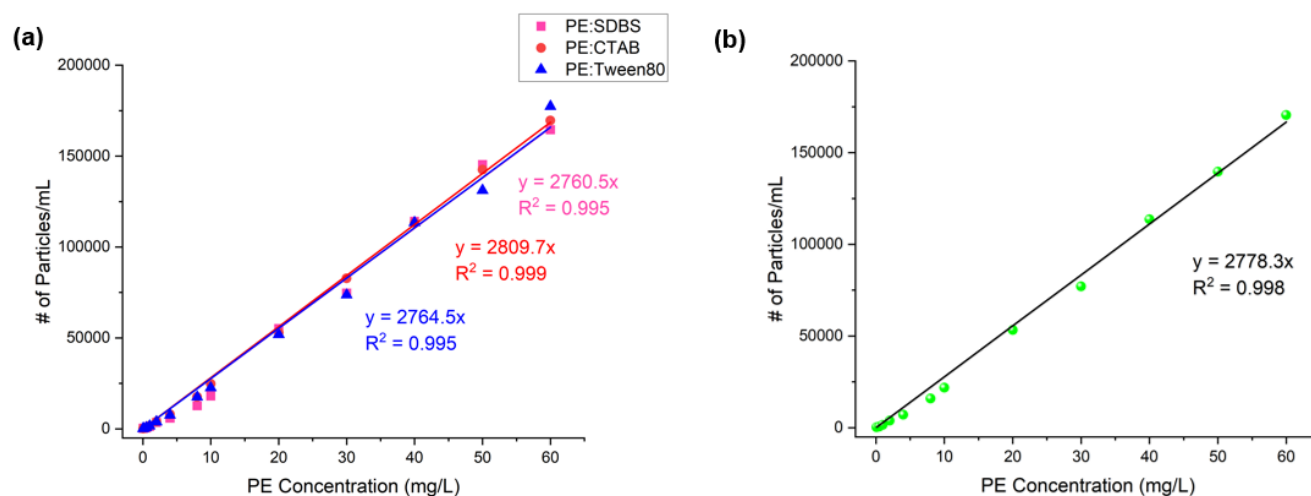


Figure 3-3: a) Coulter counter calibration curves using three PE dispersions and b) average calibration curve of PE

### 3.4. Conclusions

This chapter summarizes the preparation and quantification of the PE microplastic dispersion in three different stabilizing surfactants, SDBS, CTAB, and Tween80, to enhance the hydrophilicity of the microplastics in an aqueous solution. The ideal mass ratio of the PE and the surfactant was investigated to identify the optimal particle stability in water. At a mass ratio of 1:0.02 PE:SDBS, the particle size measurements approached a constant value indicating the hydrophilicity of PE has been stabilized in water. This optimal mass ratio was selected for the other two stabilizing agents. Furthermore, the PE:SDBS, PE:CTAB, and PE:Tween80 dispersions showed promising results, as their zeta potentials were determined to be -46.13, +12.33, and -3.36 mV, respectively. These representations demonstrated the modifications of PE microplastics were successful.

The utilization of Coulter counter to determine the PE microplastic concentration confirmed that this apparatus was capable of precisely detecting the number of particles suspended in an aqueous solution. This was further confirmed by the calibration curve, as it displayed a strong linear relationship between the number of particles per milliliter and the concentrations of PE microplastics. With this curve, it could be used for analyzing the filtration performance of the pulp foam during the filtration tests, as will be discussed in Chapter 5.

## **Chapter 4: Cellulosed-based Softwood Pulp Foam for Microplastic Capture Removal**

### **4.1. Introduction**

Current technologies, namely coagulation-flocculation and membrane bioreactors, provide disadvantages in the water purification process due to their high energy consumptions, installation costs, and environmental risks. Furthermore, their abilities of removing microplastics from large bodies of water shows discrepancies in the results since these microplastics existed in various sizes and shapes. To mitigate the issue, a low-cost and environmentally friendly filter must be developed and installed in the discharge end of a washing machine to capture the microplastics released from the washing of clothes.

Cellulose has become an attractive candidate for water treatment applications due its unique properties and features. With their abundant surface functional groups and excellent mechanical strength, this natural biopolymer has been implemented to produce multiple solid materials, such as aerogel or hydrogel. A lightweight pulp foam based on cellulose has drawn significant attentions due to its low density and high porosity [98]. It has used in many applications, such as thermal insulation, material packaging, and water filtration [99]. The production of solid pulp foam is achieved by the introduction of air bubbles in the material, which improves the porous structure [99]. To generate bubbles, surfactants is added under a vigorous stirring. Sodium dodecyl sulfate (SDS) have been widely for the preparation of foam, since it is cost-effective and possesses high foam stability [100], [101]. However, there are some limitations since the pulp foam can be destabilized due to drainage, coalescence, and coarsening

[102]. To mitigate the problem, Pickering emulsions was introduced to stabilize the air bubbles inside the foam [102]. Once the wet foam has been produced and transferred to a mold, the final product can be formed using various freezing and drying protocols. These include freeze-drying, vacuum/oven-drying, and supercritical carbon dioxide drying [98], [101].

In this chapter, microcrystalline cellulose (MCC) and nanocrystalline cellulose (NCC) were selected as naturally derived materials for the preparation of softwood pulp foam. Since MCC and NCC contain large amounts of negative functional groups, electrical repulsions between the cellulose derivatives and microplastics are present. Thus, the surface of the cellulose materials must be modified to introduce both cationic and hydrophobic functionalities. Hydrophobic modification of cellulose can be achieved by coating with surfactants. Being an amphiphilic molecule, the head of the surfactant electrostatically interacts with the surface of the MCC and NCC, where the microplastic's surface charge comprises that of the hydrophilic head groups of the surfactant. SDS surfactant displays high foamability and foam stability. However, for anionic surfactant, where interacting with the negatively charged cellulose surface can be promoted by modifying the surface of the cellulosic materials. Hence, 3-chloro-2-hydroxypropyldimethyldodecylammonium chloride (QUAB 342) surfactant was deemed to be the ideal solution since it is a cationic surfactant with dodecyl hydrocarbon ( $C_{12}$ ) chains. Also, QUAB 342 surfactant contains one hydroxyl group which can be activated to produce an epoxide ring that will readily react with the hydroxyl groups on the surface of MCC or NCC. With this approach, the cationic and hydrophobic features could be introduced to the cellulosic materials. The cellulose-based softwood pulp foam must possess excellent mechanical strength and high stability to withstand the higher flow rate during the filtration experiments. Hence, (3-

glycidyloxypropyl)trimethoxysilane (GPTMS) and branched poly(ethyleneimine) (PEI) were selected to crosslink with softwood pulp fiber for the foam preparation [103].

## **4.2. Materials and Methods**

### **4.2.1. Materials**

Softwood pulp fibers (WF) were supplied by Suzano, Brazil. Microcrystalline cellulose (MCC), and (3-glycidyloxypropyl)trimethoxysilane (GPTMS,  $\geq 98\%$ ), were purchased from Sigma Aldrich. Nanocrystalline cellulose (NCC) were supplied by CelluForce Inc. Poly(ethyleneimine) (PEI, 50 wt%) solution was purchased from Supelco. 3-chloro-2-hydroxypropyldimethyldodecylammonium chloride (QUAB 342, 40 % chlorohydrin) was purchased from QUAB Chemicals. Milli-Q water was used as a solvent for all procedures.

### **4.2.2. Synthesis of QUAB342-MCC/NCC**

As described earlier, QUAB 342 surfactant was grafted onto the surface of MCC producing both hydrophobic and cationic properties. The reaction mechanisms and the schematic illustrations of the QUAB342-MCC synthesis are shown in Figure 4-1a and 4-1b. In the synthetic process, 833 mL of QUAB 342 was pre-heated to 45 °C. Next, a pre-activation process was conducted where 151.2 mL of 6 M NaOH were added to the heated QUAB 342 solution at a mole ratio of QUAB 342:NaOH = 1:1, and the solution was mixed for 13 minutes. This produced an epoxide ring on the end of the QUAB 342 molecule (Figure 4-1a). 150 g of MCC powder was weighed and placed onto a metal bowl, and 18.45 g of NaOH pellets were ground, and mixed with the MCC powder to yield a mass ratio of MCC:catalytic NaOH of 1:8.13. The pre-activated QUAB 342 was slowly added to the MCC-NaOH mixture and stirred for 5h at a temperature of

between 42 – 45 °C. The QUAB342-MCC synthesis was examined every 30 minutes to ensure no color change occurred during the reaction. Simultaneously, the reaction temperature was monitored.

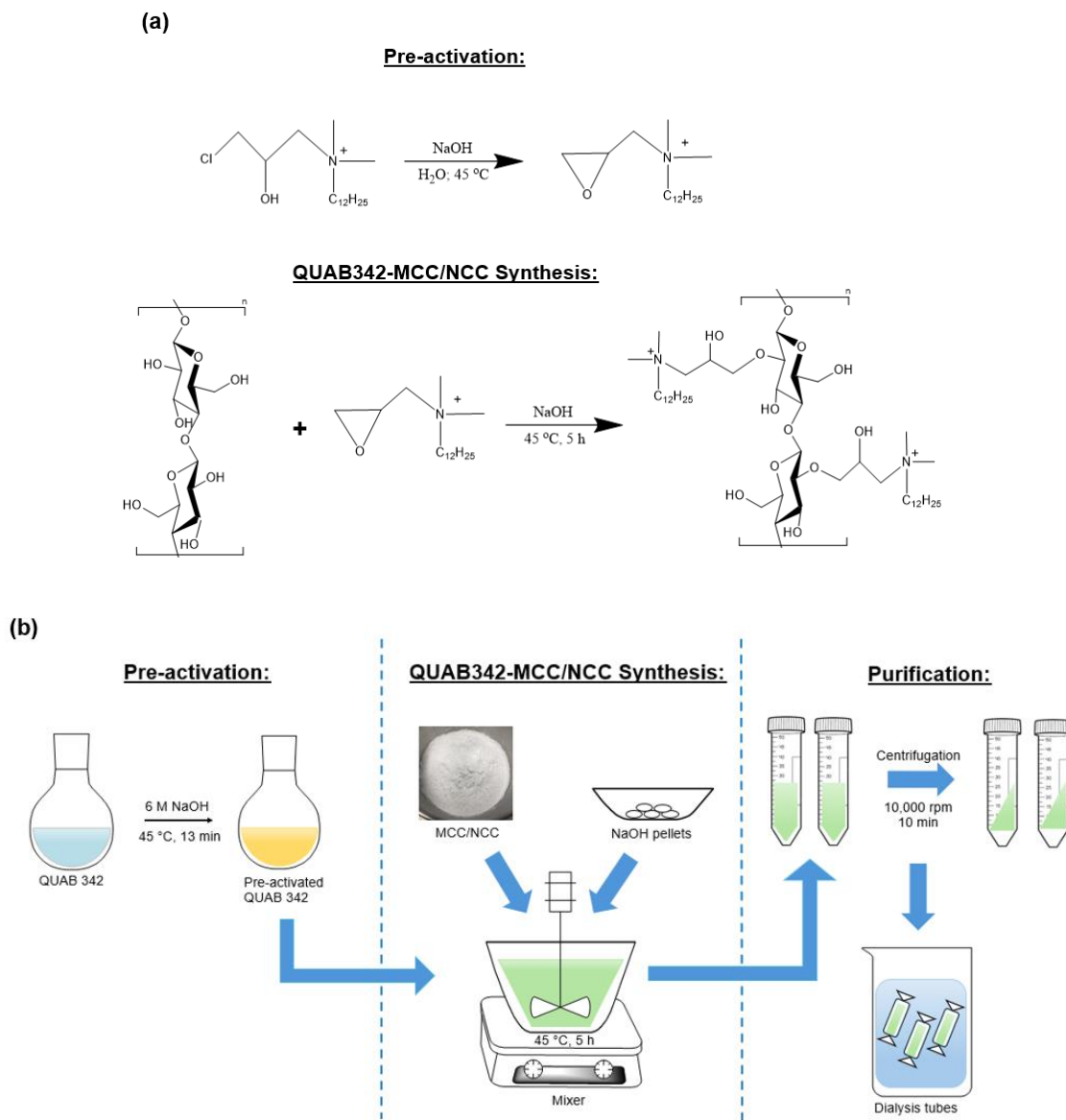


Figure 4-1: a) Reaction mechanism and b) experimental procedures for QUAB 342-MCC/NCC synthesis

After 5-h of reaction, the mixture was cooled to room temperature, and centrifuged to purify the product as at 10,000 rpm for 8 minutes. After the centrifugation, the impurities were removed and the solid QUAB342-MCCs were recovered. A certain amount of Milli-Q water was added to minimize the viscosity of QUAB342-MCC, and the QUAB342-MCC was dialyzed in a bucket of deionized water for 3.5 days to remove unreacted NaOH and QUAB 342. After dialysis process, the sample was collected, and gravimetric analysis was performed to determine the concentration. Similar procedures were conducted for the synthesis of QUAB 342-NCC (Figure 4-1b).

#### **4.2.3. Preparation of WFQ342MCC Foam**

30 g of softwood pulp fibers (WF) were soaked in 1-L of distilled water at room temperature for 3 days. The soaked fibers were then placed into a fiber beater and subjected to 700 beats to produce 3 wt% WF suspensions. 200 g of WF suspensions were weighed and transferred to a 400-mL glass beaker. 6 g of GPTMS were added to the suspensions at a mass ratio of WF:GPTMS=1:1, and stirred for 30 minutes. A certain amount of QUAB342-MCC (225 mg/mL) was added to the suspensions and pre-stirred for 5 minutes to achieve a homogeneous dispersion. After the pre-mixing process, the mixture was transferred to the 10-speed blender (name the model and type) and mixed for 5 minutes at a speed setting of 6. After 5-minute of blending, 30 g of PEI (20 wt%) was added to the mixture at a mass ratio of WF:GPTMS:PEI=1:1:1 (Figure 4-2a). The blending process was continued for another 5 minutes to produce a pulp foam, which was then transferred to the 1” cylindrical mold containing polyester mesh attached to the bottom. Seven samples were produced, each weighing 26 g, and they were kept in a freezer overnight. The samples were removed from the freezer and dried

under ambient condition for 12 h. Figure 4-2b provides a schematic illustration of softwood pulp foam preparation process.

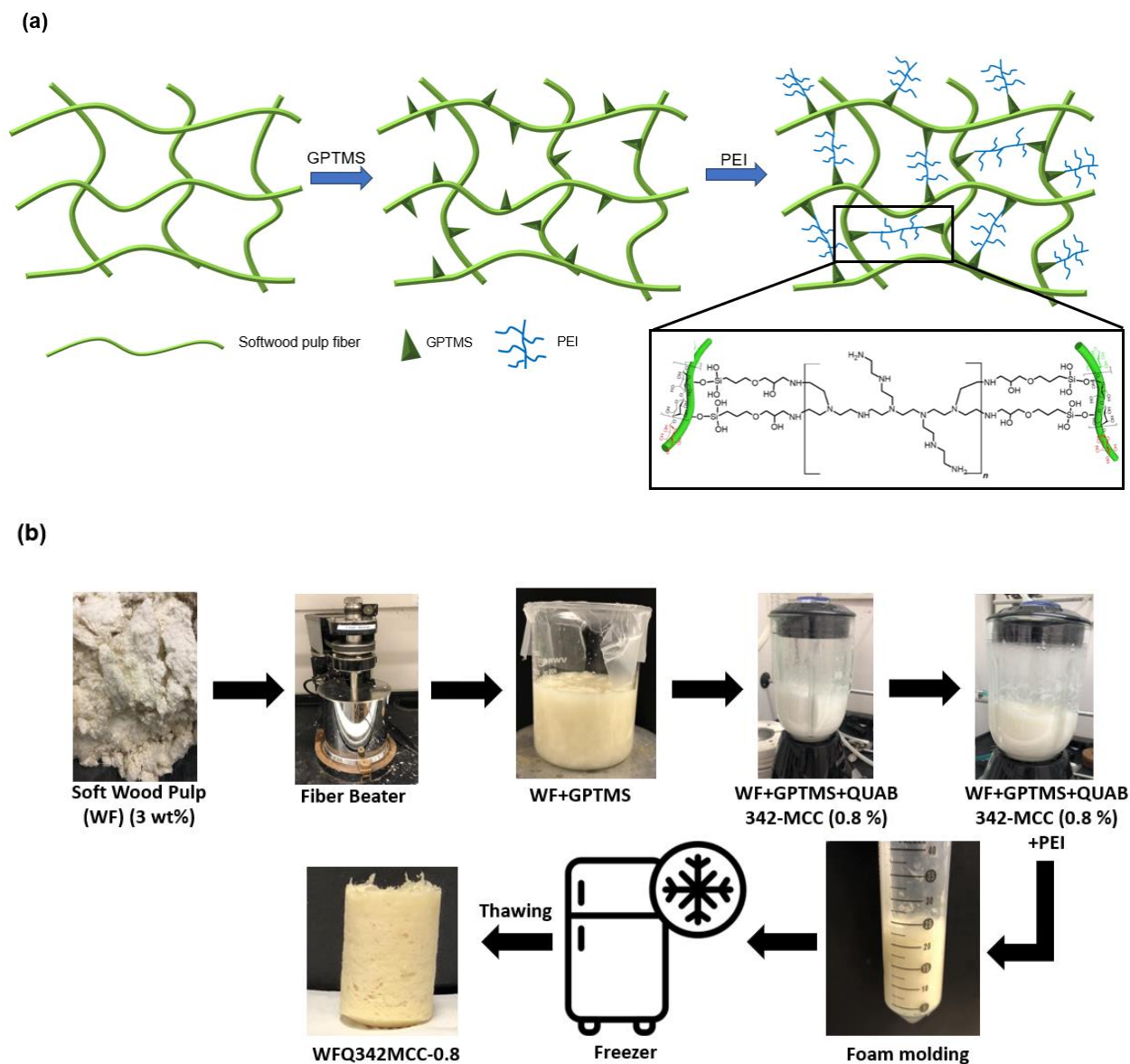


Figure 4-2: a) Schematic illustrations of softwood pulp crosslinking with GPTMS and PEI (adapted from Tang et al. [103]), and b) experimental procedures of softwood pulp foam preparation

#### 4.2.4. Foam Porosity

WFQ342MCC-0.8 and WFQ342NCC-0.8 foams were soaked in Milli-Q water in a beaker, which were placed in a vacuum oven for 3.5 h at a pressure of 25 kPa. This technique removed all air bubbles trapped inside the foams. The soaked WFQ342MCC-0.8 and WFQ342NCC-0.8 foams were then transferred to the VWR M-Series moisture analyzer to remove all the water present in the pulp foam at a drying temperature and time of 70 °C for 3.5h respectively. The pore volume was calculated from the difference of wet and dried mass of the foam and the density of water (1.0 g/cm<sup>3</sup>) (Eq. 1). Since the foam was a cylindrical shape, volume of the foam could be easily determined from the height and diameter.

$$P(\%) = \frac{V_{pore}}{V_{foam}} \times 100 \quad (\text{Eq. 1})$$

where  $V_{pore}$  represents the pore volume, and  $V_{foam}$  represents the foam volume.

#### 4.2.5. Particle Sizes and Zeta Potentials

The Anton Paar PSA 1190 was used to determine the size of QUAB342-MCC and QUAB342-NCC. For the zeta potential measurement, the two samples were diluted to 0.05 %, and bath sonicated for 5 minutes. The measurements of each sample were performed using the Malvern Nano-ZS90 Zetasizer, and averages were determined from the average of 10 runs.

#### 4.2.6. Silver Nitrate (AgNO<sub>3</sub>) Titrations

QUAB342-MCC and QUAB342-NCC samples were diluted to 0.3 wt%, and 30-mL of the sample was titrated with 10 mM AgNO<sub>3</sub> to determine the amounts of quaternary ammonium groups. The titration curve was obtained by measuring the conductivity of the solution as a function of the titrant volume. The quaternary ammonium group (QAG) was calculated using Eq. 2.

$$QAG = \frac{V_{AgNO_3} \times C_{AgNO_3}}{m_{sample}} \quad (\text{Eq. 2})$$

where  $V_{AgNO_3}$  is the equivalence point where the conductivity begins to increase,  $C_{AgNO_3}$  is the concentration of AgNO<sub>3</sub> titrant, and  $m_{sample}$  is the mass of the QUAB342-MCC and QUAB342-NCC.

### 4.3. Results and Discussions

#### 4.3.1. Physical Characterization of Cellulosed-based Softwood Pulp Foams

In the previous section, QUAB342 surfactant was grafted onto the MCCs imparting both cationic and hydrophobic functionalities to the MCC. The modified MCCs were added to the softwood pulp foam for the capture of microplastics. After the blending process described in section 4.2.3, 26 g of WFQ342MCC-0.8 foam was weighed and poured into the mold. As shown in Figure 4-3, the foam was filled to the 25-mL mark on the centrifuge tube. Plastic mesh was placed inside the tube for the excess water to drain from the tube leaving only the pulp foam, which led to a shrinkage in the volume by approximately 5 mL. The solid foam was placed

inside the freezer for curing and it was thawed for 24 h at room temperature to generate a high porous structure.

Different drying methods were investigated during the foam preparation steps. Before the freezing method, vacuum oven drying was first examined with the pressure and temperature were set to 2 kPa at 50 °C respectively. The foam was dried overnight, however gaps occurred on the surface of the foam resulting in leakages on the walls of the tube. The freezing and ambient drying conditions were compared based on their physical properties. In this experiment, two foams with different curing conditions were placed for 5 minutes in liquid nitrogen and freeze-dried for 3 days.

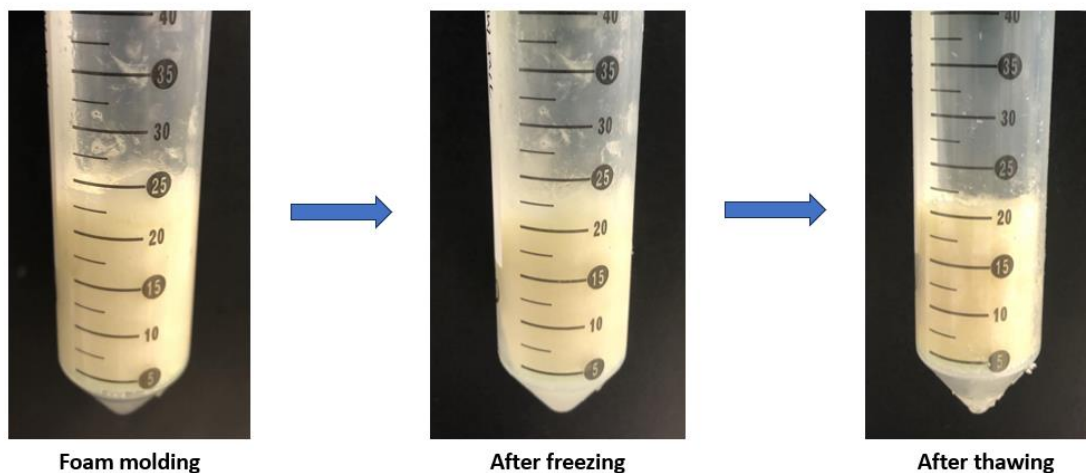


Figure 4-3: Schematic representations of softwood pulp foam curing process

The foams were cut in half, and the interior microstructure of the foam was examined and quantified. Based on the physical characterization, it was observed the foam with the freezing condition was stable as indicated by its smooth surface. This implies the GPTMS and PEI successfully crosslinked with the softwood pulp fibers. While the foam with the ambient condition displayed gaps in the middle of the foam, as well as concave profile on the top surface,

indicating there were very little crosslinking reactions in the material (Figure 4-4). From the two approaches, the freezing method maintained the crosslink within the foam, which was beneficial and contributed to the good mechanical strengths and high porous structure. Furthermore, the two foams were compared by pouring 30 mL of Milli-Q water into the material. Based on the observation, the foam prepared at the ambient conditions inhibited the flow of water, hence the freezing method found to be the most suitable method for the pulp foam preparation.

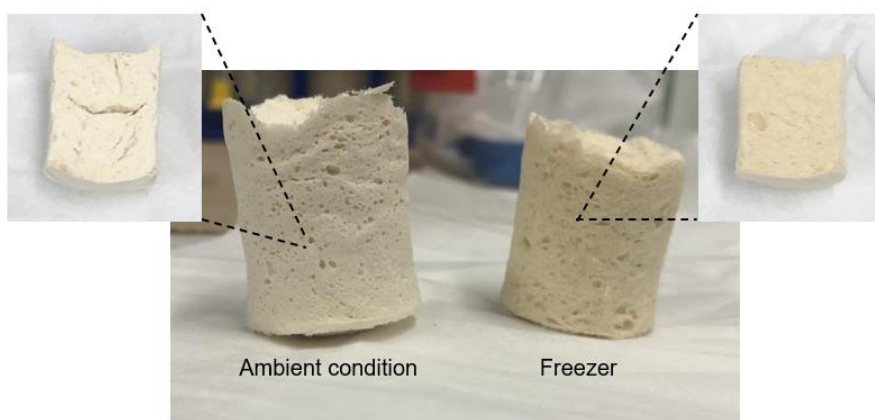


Figure 4-4: Visual representations of softwood pulp foam with different drying conditions

#### 4.3.2. Foam Stability Analysis

Different concentrations of QUAB342-MCC were considered in the study on the foam stability. WF foams containing QUAB342-MCC concentrations between 0.8 to 1.0 % were prepared by blending and pouring into graduated cylinders (Figure 4-5a). The foam volumes were measured from 0 to 24 h to examine the possible separation from the solid to liquid (Figure 4-5b). We determined that the cellulose foam containing 0.8 % QUAB342-MCC concentration was the most stable, while increasing the surfactant concentration resulted in the observed phase separation after 24 h (Figure 4-5a).

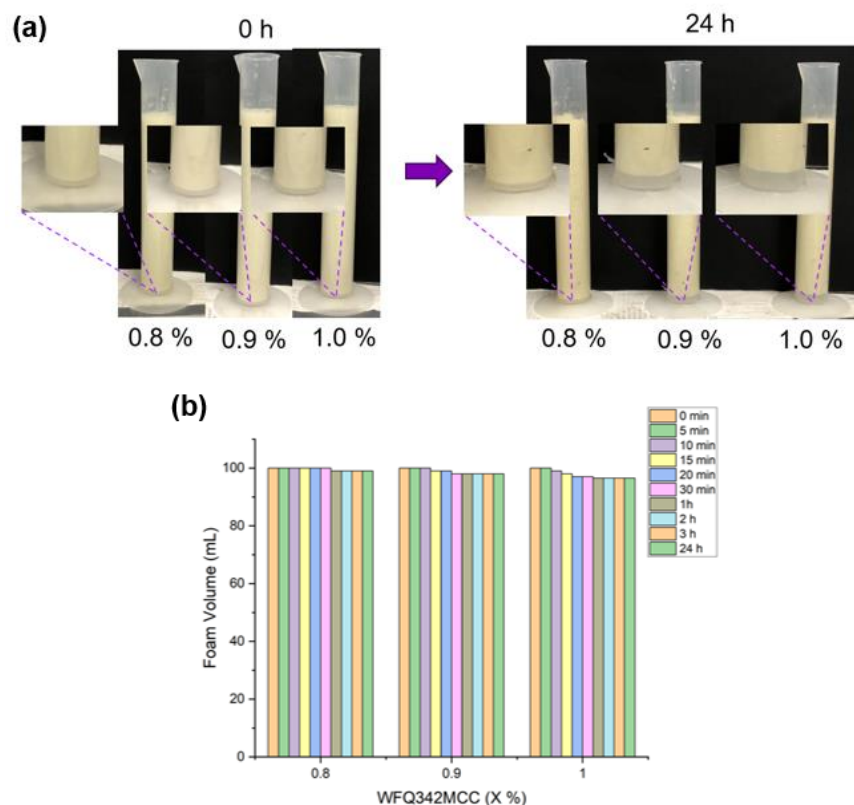


Figure 4-5: a) foam stability tests after 0 and 24 h, and b) foam volumes of different QUAB342-MCC concentrations

#### 4.3.3. Particle Sizes and Zeta Potentials Analysis

The zeta potentials and particle size of QUAB342-MCC and QUAB342-NCC samples were measured to examine the surface charge. Both QUAB342-MCC and QUAB342-NCC displayed positive zeta potentials ranging from +30 to +40 mV (Figure 4-6). Furthermore, the particle sizes for the two were ranged between 16 and 18  $\mu\text{m}$ . These results demonstrated the two systems were successfully modified, and they could capture the microplastics.

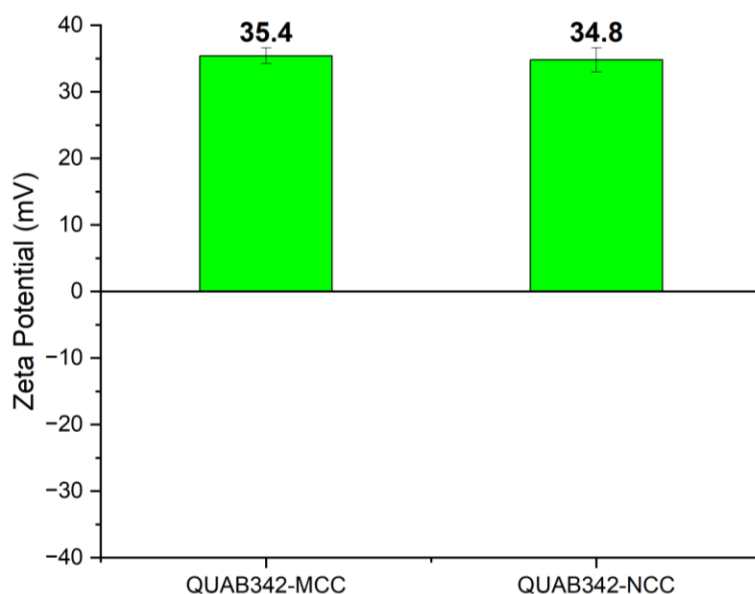


Figure 4-6: Zeta potentials of QUAB 342-MCC and QUAB 342-NCC

#### 4.3.4. $\text{AgNO}_3$ Titrations

As previously explained in section 4.2.6, the QAGs of QUAB342-MCC and QUAB342-NCC were determined using 10 mM  $\text{AgNO}_3$  as the titrant. Figure 4-7a shows the two solutions before and after reacting with  $\text{AgNO}_3$ . After the experiment, the titration curves of QUAB342-MCC and QUAB342-NCC were plotted to determine the QAG values for the two foams (Figure 4-7b). In the first stage, the addition of  $\text{Ag}^+$  interacted with the counter-ion  $\text{Cl}^-$  to form insoluble  $\text{AgCl(s)}$  that contributed to the reduction in the conductivity. The second stage occurred when all the  $\text{AgNO}_3$  reacted with all the counter ions, as well as the excess  $\text{Ag}^+$  and  $\text{NO}_3^-$ . This led to an increase in the conductivity of the solution, and the two samples began to form cloudy appearances. The equivalence points of the two samples were identified, and using Equation 4.2, the QAGs for QUAB342-MCC and QUAB342-NCC were determined to be 0.46 mmol/g and 0.52 mmol/g, respectively.

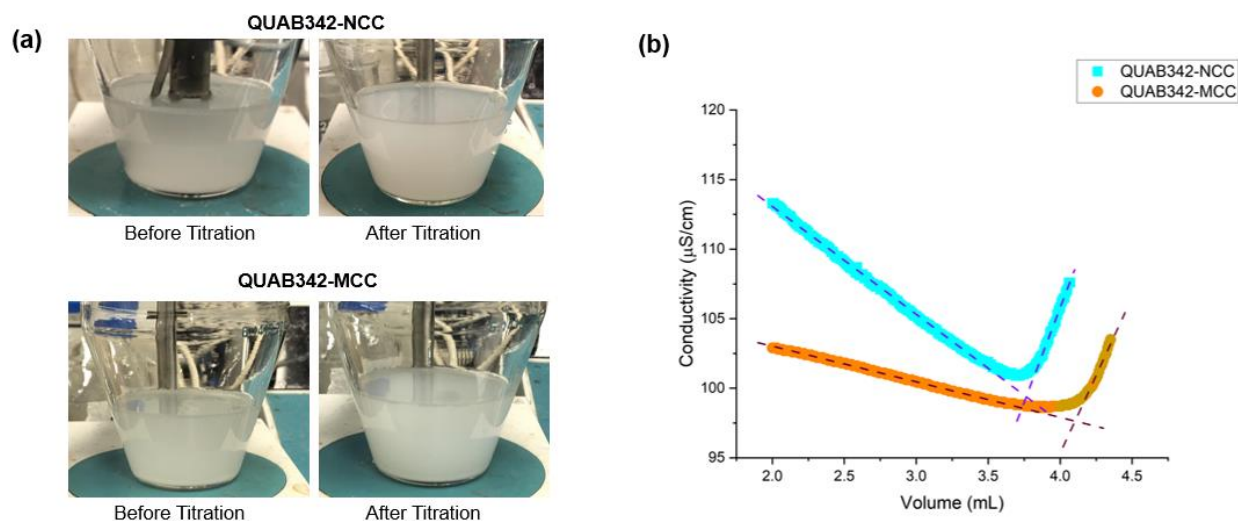


Figure 4-7: a) Visual images of QUAB342-MCC and QUAB342-NCC before and after titrations, and b) titration results of QUAB342-MCC by 10 mM  $\text{AgNO}_3$

#### 4.3.5. Foam Porosity Results

As described in section 4.2.4, the porosity of the WFQ342MCC-0.8 and WFQ342NCC-0.8 foams were determined from the difference in the weight of the sample using the moisture analyzer. The use of NCC to prepare the pulp foam, a high porosity was expected since nanomaterials could enhance the adsorbent surface area. Before performing the porosity analysis, different drying temperatures ranging from 70 to 100 °C were performed. This reduced the drying time when the test was conducted at higher temperatures. However, it was observed that the fibers turned brownish when temperatures were set to 90 or 100 °C. As a result, 70 °C was selected as the preferred drying temperature for the porosity measurements. In the first phase, each soaked softwood pulp foam was placed inside the moisture analyzer, and their initial masses were obtained from the instrument. During the heating process, a reduction in the mass was observed over time, indicating removal of water inside the foam by evaporation. In the second

phase, the mass of softwood pulp foam remained stable demonstrating every water droplet absorbed in the foam and the wood fibers was completely evaporated. The final dried foam was determined by the point of intersection of the two curves (Figure 4-8a). Using Equation 1, the porosity of WFQ342MCC-0.8 and WFQ342NCC-0.8 foams were calculated. As displayed in Figure 4-8b, the porosity of WFQ342MCC-0.8 foam was determined to be 83.4 %. While WFQ342NCC-0.8 showed a porosity of 78.8 %, which corresponds to a foam containing MCC adsorbed with higher amounts of water content compared to the foam containing NCC. The comparison of the two foams will be further examined in the filtration performance.

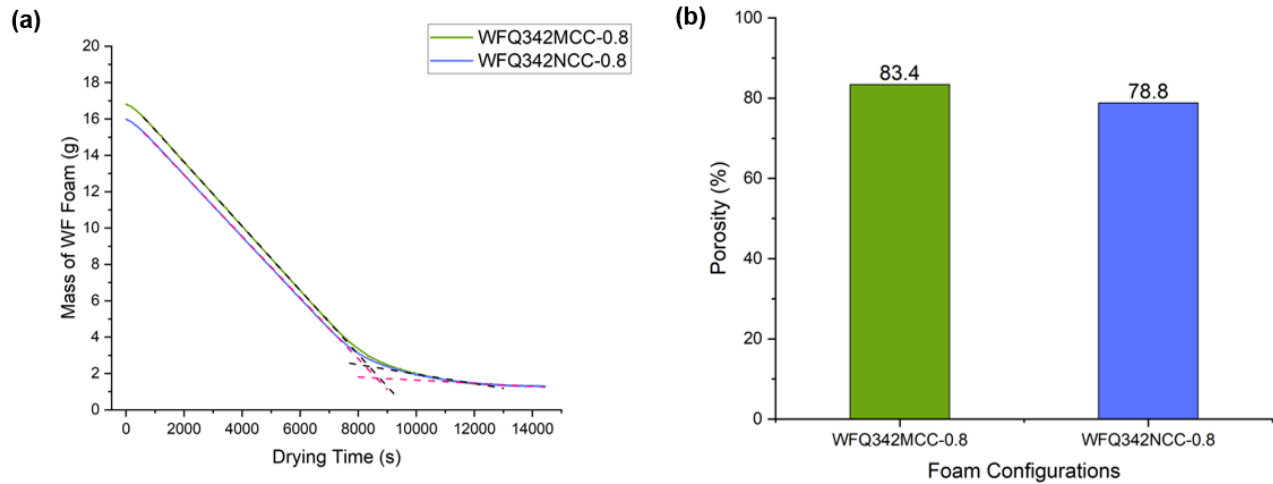


Figure 4-8: a) Moisture analyzer results and b) porosity results of the two foam configurations

#### 4.4. Conclusions

This chapter focuses on the development of softwood pulp foam containing cellulose-based materials to act as a sustainable filtration device for microplastic removal. QUAB 342 surfactant was grafted onto both surfaces of MCC and NCC to produce cationic and hydrophobic functionalities to the foam. The grafting process displayed remarkable results, as the modified cellulosic materials generated positive surface charges ranging from +30 to +40 mV. In addition, the amounts of quaternary ammonium groups for QUAB342-MCC and QUAB342-NCC were determined using the  $\text{AgNO}_3$  titration, which were calculated to be 0.46 mmol/g and 0.52 mmol/g, respectively.

The modifications of MCC and NCC were then incorporated into the two foam configurations (WFQ342MCC-0.8 and WFQ342NCC-0.8) for the purpose of removing microplastics from water. Two crosslinking agents, GPTMS and PEI, were added to the softwood pulp foams to produce higher mechanical strength and excellent pore structures. Different dosages of QUAB342-MCC were added to evaluate the stability of the foam during the production process. It was determined that the increase in the QUAB342-MCC concentrations decreased the foam stability, as phase separation occurred after 24 h. The porosity analysis of WFQ342MCC-0.8 and WFQ342NCC-0.8 foams was conducted using a moisture analyzer. After the calculations, it was concluded the WFQ342MCC-0.8 foam possessed a higher value of 83.4 %, compared to the value of 78.8 % for WFQ342NCC-0.8 foam, and foam containing MCC was capable to obtain high amounts of water molecules than the foam with the NCC.

## **Chapter 5: Optimization of Microplastic Removal using Softwood pulp Foam**

### **5.1. Introduction**

After the successful development of WFQ342MCC-0.8 and WFQ342NCC-0.8 foams, the final step was to examine their filtration performances using PE microplastics. Since many studies demonstrated promising results in the removal of PS microplastics, few studies had been conducted to evaluate the removal efficiency of PE microplastics due to their low density and hydrophobic properties. By dispersing PE using anionic, cationic, and nonionic surfactants, the removal efficiency of the microplastics was examined.

WFQ342MCC-0.8 foam was analyzed for the removal of various concentrations of PE:SDBS, PE:CTAB, and PE:Tween80 microplastic dispersions. Due to its cationic and hydrophobic properties, it is likely the material could interact with the microplastics via electrostatic and hydrophobic interactions. Next, WFQ342MCC-0.8 foam was further investigated by analyzing its capacity to capture microplastics during the filtration test. This experiment focused on pouring multiple passes of different concentration of PE suspensions onto the foam to evaluate the removing efficiency of PE microplastics. Aside from microplastic filtration experiment, methyl orange dye was used for the filtration experiment to examine if the electrostatic interactions between the anionic organic dye and cationic foam were successful. Lastly, the filtration performance for WFQ342NCC-0.8 was optimized for microplastic removal.

## 5.2. Filtration Experiments

### 5.2.1. Experimental Procedures of PE Filtration Experiment

WFQ342MCC-0.8 foam was placed in a vacuum filtration system, where vacuum was applied for 75s to remove excess liquid trapped inside the tube. This ensured that the fluid could pass through the pulp foam. The foam was rinsed four times with 1% NaCl solutions, and the vacuum filtration process was applied to remove excess NaCl trapped inside the tube. 30 mL of PE dispersions were poured onto the foam and the effluents were collected from the bottom of the tube (Figure 5-1), and the filtration time was measured. The collected samples were analyzed by the Coulter counter to determine the final concentration, and the removal efficiency can be calculated from Eq. 3:

$$R.E.(%) = \frac{C_0 - C}{C_0} \times 100 \quad (\text{Eq. 3})$$

where  $C_0$  and  $C$  represent the inlet and outlet PE concentrations.

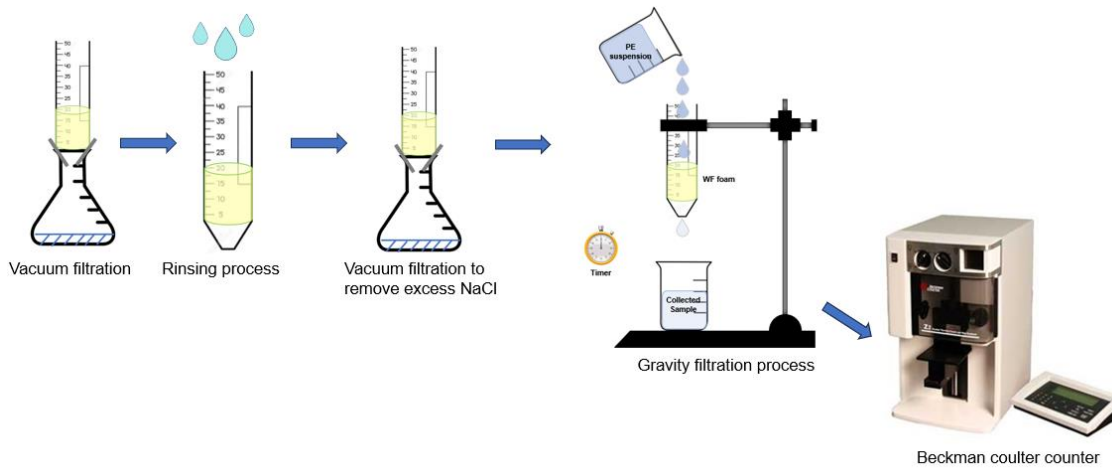


Figure 5-1: Experimental procedures of PE gravity filtration test

### 5.2.2. Capture of Microplastic Analysis Test

The objective of the experiment was to investigate the amounts of microplastics that could be captured by the softwood pulp foam. In this experiment, three PE:SDBS concentrations (50, 200, and 500 mg/L in 30-mL volume) were poured onto the foam 10 times, and 10 effluent concentrations were collected from the bottom. Simultaneously, the filtration times were obtained for every cycle. The collected samples were analyzed by the Coulter Counter to identify the unknown concentrations. The total mass of PE microplastics loaded into the softwood pulp foam was determined using Eq. 4:

$$m_{load} = C \times V \times R.E._{avg} \quad (\text{Eq. 4})$$

where C corresponds to the PE concentrations, V the total volume poured onto the foam, and R.E.<sub>avg</sub> represents the average removal efficiency over multiple passes.

### 5.2.3. Methyl Orange Dye Filtration Test

Aside from the microplastic solutions, further investigation was conducted by examining the removal efficiency of methyl orange dye by the pulp foam. Prior to the filtration experiment, the foam was rinsed five times with Milli-Q water. Next, two methyl orange concentrations (10 and 500 ppm in 30-mL volumes) were poured onto the foam, and the filtered liquids were collected. The samples were analyzed by the Cary 100 UV-Vis Spectrophotometer to determine the concentrations.

### 5.3. Results and Discussions

#### 5.3.1. Removal Efficiencies of PE Dispersed in Three Stabilizing Agents

The filtration performances of the WFQ342MCC-0.8 foam were observed by analyzing the removal efficiencies of PE stabilized by three surfactants: SDBS, CTAB, and Tween80 with the three suspensions possessing negative, positive, and neutral charges, respectively. As explained in section 5.2.1, three different concentrations (20, 100, and 500 mg/L) of PE microplastics in a 30-mL volume were passed through the foam and the effluents were collected. Particle counter was to determine the number of particles in the effluents, and the final concentration was determined using the calibration curve (Figure 3-3b) and Equation 3. During the filtration process, the time of filtration was recorded for each sample. As evident from Table 4, the time increased when high PE concentrations were passed through the foam. When 20 mg/L of PE was poured into the foam, the filtration time ranged from 54 to 56 s, and it increased to between 83 and 103 s at high concentrations. The higher amounts of microplastics were trapped by the foam and reduced the flow through the porous foam.

Table 4: Time of filtrations for three PE dispersions

|                                      | <b>PE:SDBS</b> |            |            | <b>PE:CTAB</b> |            |            | <b>PE:Tween80</b> |            |            |
|--------------------------------------|----------------|------------|------------|----------------|------------|------------|-------------------|------------|------------|
| <b>Initial concentrations (mg/L)</b> | <u>20</u>      | <u>100</u> | <u>500</u> | <u>20</u>      | <u>100</u> | <u>500</u> | <u>20</u>         | <u>100</u> | <u>500</u> |
| <b>Filtration time (s)</b>           | 54.18          | 59.46      | 83.58      | 56.73          | 67.63      | 73.49      | 54.58             | 64.19      | 102.91     |

As the time of filtration was recorded, the removal efficiencies of the PE were analyzed for the three microplastic concentrations. Figure 5-2a shows the visual images of the PE suspensions before and after the filtration. It was revealed the WFQ342MCC-0.8 foam displayed better filtration when the PE was stabilized by SDBS surfactant, since the collected sample was clear and transparent. However, the filtration was poor when the PE stabilized by Tween80 surfactant was studied, and a cloudy suspension was observed in the effluent stream. The filtrate samples were analyzed by the particle counter to determine the final concentrations, and the removal efficiencies were calculated. Figure 5-2b shows the removal efficiencies of PE stabilized by the three different surfactants. As shown, the WFQ342MCC-0.8 foam possessed the best removal efficiencies for all three PE:SDBS concentrations ranging between 98.5 and 99.5 %. This is due to the large electrostatic interactions between positively charged QUAB342-MCC and negatively charged PE particles. The foam also displayed promising results when filtering the PE:CTAB suspension. Although the particles possessed positive surface charges, it was possible that the positive-charged head of the CTAB surface electrostatically interacted with the negative-charged PE particles imparting hydrophobic properties to the PE microplastics, as shown in Figure 3-1. Hence, the microplastic particles interacted with the foam via hydrophobic interactions. High removal efficiency of 91 % was achieved when 20 mg/L of PE:CTAB was poured into the foam. However, the efficiency decreased to 53.8 % when filtering 500 mg/L through the foam. Lastly, the filtration performance for the PE:Tween80 displayed low removal efficiency; 67.4 % for 20 mg/L and 32.7 % for 500 mg/L. Due to the Tween80 surfactant being non-ionic, negligible electrostatic and hydrophobic interactions were present between the foam and PE:Tween80. As a result, the WFQ342MCC-0.8 foam had better performance removing the PE stabilized by SDBS and CTAB.

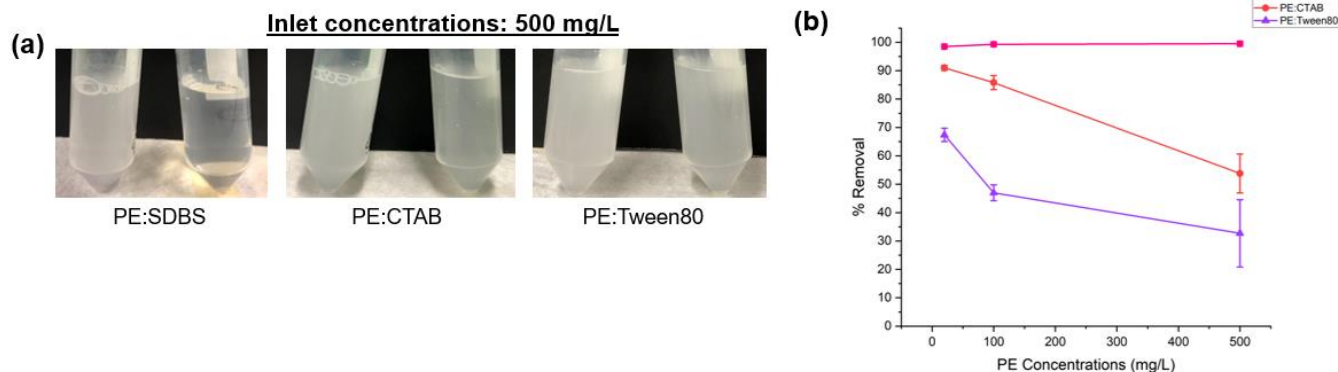


Figure 5-2: a) Schematic illustration of inlet and outlet PE concentrations, and b) removal efficiencies of three PE dispersions

### 5.3.2. Analysis of Microplastic Capture

50, 200, and 500 mg/L of PE:SDBS concentrations were passed through the WFQ342MCC-0.8 foam 10 times, and the collected samples were quantified using the Coulter counter. The final concentrations were calculated using Equation 3. The graph of removal efficiency as function of the total mass of PE particles loaded inside the foam was plotted (Figure 5-3a). It was determined the WFQ342MCC-0.8 foam displayed high removal efficiencies ranging from 95 to 99 % when 50 mg/L PE:SDBS was passed through the foam 10 times. However, the removal efficiency decreased from 85.8 % to 67.7 % when 500 mg/L PE was passed through the foam multiple times. When the flow rate was examined for the WFQ342MCC-0.8 foam, a rapid decrease occurred when high PE concentrations were passed through the foam, suggesting that the microplastics were trapped inside the foam (Figure 5-3b). However, since the foam had limited capacity to hold large amounts of microplastics, the particles trapped inside the material could be dislodged due to the pressure from the inlet concentration producing a low removal efficiency during the process.

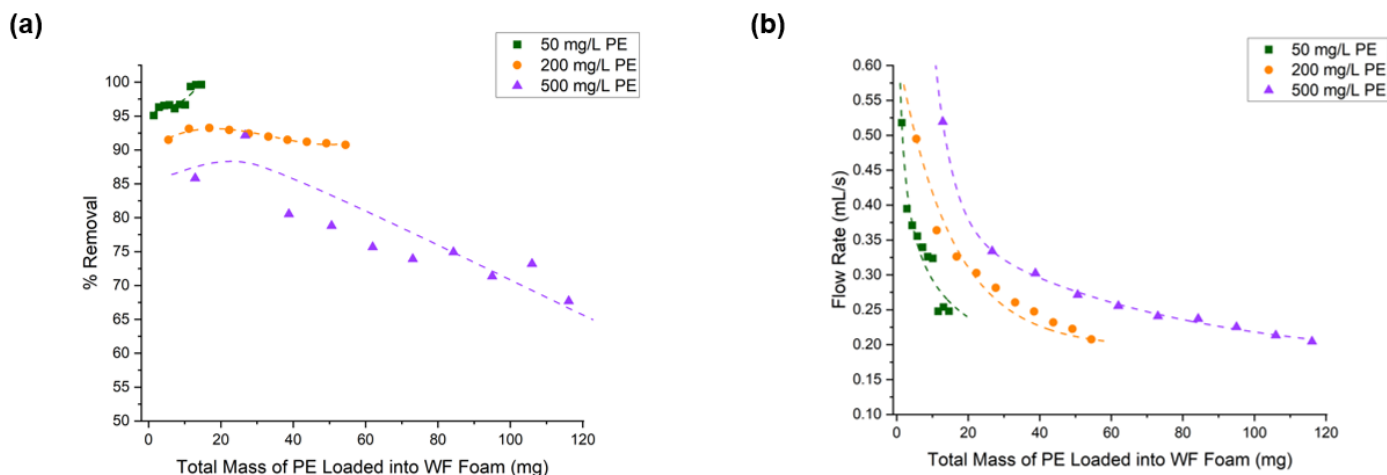


Figure 5-3: a) Removal efficiencies, and b) flow rates of softwood pulp foam at various PE loadings

### 5.3.3. Methyl Orange Dye Filtration Test

UV-Vis spectroscopy was used in this experiment to determine the final concentrations of methyl orange dye. A stock solution of 2500 ppm was prepared in Milli-Q water, and was diluted to six concentrations (2 to 12 ppm). The concentrations were quantified by the Cary 100 UV-Vis Spectrophotometer and a clear absorbance peak at 464 nm was observed (Figure 5-4a). The calibration curve was plotted, and the equation of the linear fitting was used to calculate the methyl orange concentration (Figure 5-4b).

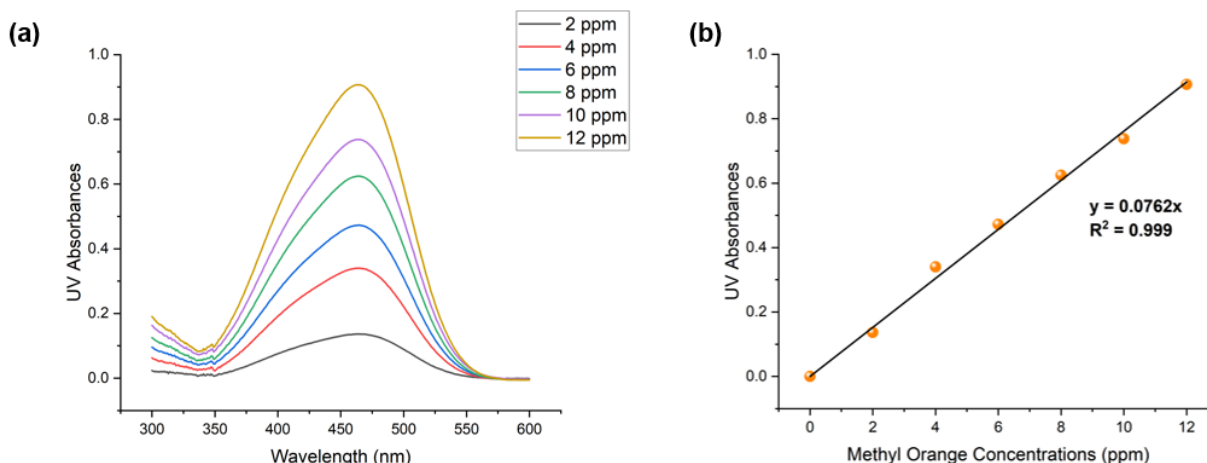


Figure 5-4: a) UV spectra, and b) Calibration curves of methyl orange dye concentrations

After the filtration experiment, the collected samples were analyzed by the spectrophotometer to obtain the UV absorbances. Using the calibration curve, the concentrations were identified, and the removal efficiencies were calculated using Equation 3. Figure 5-5a shows the visual representations of methyl orange dye before and after the filtration experiments, where the transition from bright orange to colorless was observed. When analyzing the removal efficiency, it was revealed the WFQ342MCC-0.8 foam displayed high efficiencies ranging between 95 and 100 % when 10 and 20 ppm were passed through the foam (Figure 5-5b). When 500 ppm of methyl orange were treated by the pulp foam, 85 % of the dye was removed (Figure 5-5b). Since methyl orange dye possessed negative charges, they were bound strongly to the cationic MCC via electrostatic interactions, which also confirmed that the grafting of QUAB 342 surfactant onto the surface of MCC was successful.

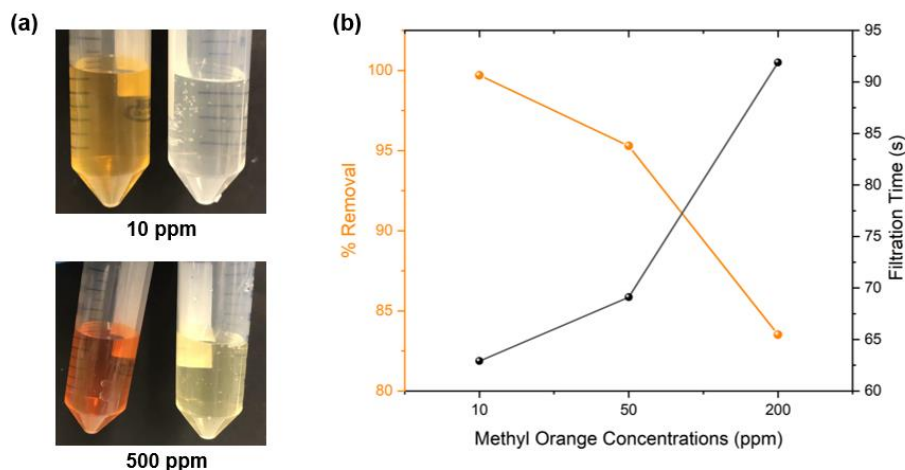


Figure 5-5: a) Influent and effluent samples of methyl orange dye, and b) removal efficiencies

#### 5.3.4. PE Filtration Performance between WFQ342MCC-0.8 and WFQ342NCC-0.8 Foams

As the WFQ342MCC-0.8 foam could remove PE stabilized by SDBS, the removal efficiency of WFQ342NCC-0.8 foam was analyzed and compared. The objective of this experiment is to determine whether the modified nanocellulose could capture higher amounts of PE due to its high surface area. In this experiment, 20 mg/L and 500 mg/L of PE:SDBS concentrations were introduced to the two pulp foams, and the filtrate samples were analyzed by the particle counter to determine the concentrations. Table 5 shows the filtration results of both WFQ342MCC-0.8 and WFQ342NCC-0.8 foams. When analyzing the removal efficiencies of the PE:SDBS, it was concluded the foam containing QUAB342-NCC displayed higher removal efficiency compared to the foam containing QUAB342MCC. Since the particle size of the NCC was smaller compared to MCC, it possessed a higher surface area of the softwood pulp foam leading to higher capture of microplastics. The removal efficiency of QUAB342-NCC was not significantly higher since the QUAB342-NCC was aggregated as revealed by the particle size.

Table 5: Comparison of PE filtration performances between two foam configurations

|                                      | <b>WFQ342MCC-0.8</b> |            | <b>WFQ342NCC-0.8</b> |            |
|--------------------------------------|----------------------|------------|----------------------|------------|
| <b>Initial concentrations (mg/L)</b> | <u>20</u>            | <u>500</u> | <u>20</u>            | <u>500</u> |
| <b>Removal efficiency (%)</b>        | 97.8                 | 89.4       | 99.8                 | 93.5       |
| <b>Filtration time (s)</b>           | 72.88                | 76.40      | 92.26                | 146.91     |

#### 5.4. Conclusions

This chapter presents the analysis of microplastic filtration experiments using WFQ342MCC-0.8 and WFQ342NCC-0.8 foams. The removal efficiency of WFQ342MCC-0.8 foam was analyzed for the filtration studies using PE:SDBS, PE:CTAB, and PE:Tween80, where the foam displayed higher removal efficiencies of 98.5 and 91 % with PE:SDBS and PE:CTAB. The mechanism is mainly due to the electrostatic and hydrophobic interactions between the microplastics and QUAB342-MCC. Despite the promising result, WFQ342MCC-0.8 foam displayed lower removal efficiency of 67.4 % for PE:Tween80. In another experiment, the WFQ342MCC-0.8 foam displayed higher stability in the removal efficiency when 50 mg/L of PE:SDBS were introduced to the pulp foam 10 times. However, its stability decreased at high concentrations due to the limited capacity inside the foam. Aside from microplastic filtration experiment, methyl orange dye adsorption test showed excellent results as the color transition from orange to clear was observed. The incorporation of NCC into the foam system increased the surface area, which improved the capture of microplastics. The result demonstrated an increase in the removal efficiency to 99.8 % compared to the 97.8 % for the WFQ342NCC-0.8 foam.

## Chapter 6: Conclusions and Recommendations for Future Works

In summary, the objectives of this research are to investigate the behavior of microplastics in an aquatic environment and to develop a renewable bio-based material to enhance high microplastic capture for applications in water treatment. While numerous publications have addressed the removal of PS microplastics, limited studies have been conducted on PE microplastics since these particles have low density and carry hydrophobic properties making them float on top the water surface. Hence, their behavior in water poses challenges during the water treatment process.

PE microplastics was dispersed using three stabilizing agents, SDBS, CTAB, and Tween80, to enhance their dispersibility in an aqueous solution. A mass ratio of 1:0.02 PE:SDBS revealed a stable dispersion in an aqueous solution due to the constant particle sizes of  $\sim 8 \mu\text{m}$ . The optimal mass ratio was similarly applied to both PE:CTAB and PE:Tween80. In addition, the PE:SDBS, PE:CTAB, and PE:Tween80 dispersions displayed different characteristics, as their zeta potentials were -46.13, +12.33, and -3.36 mV, respectively. Quantification method was another crucial step to determine the concentration of PE microplastics. The Coulter counter was found to be effective, as it provided accurate measurements at a fast detection rate.

Following the transformation of PE microplastics to be hydrophilic in water, softwood pulp foam containing cellulose-based materials were developed as a sustainable filter for the removal of microplastics. QUAB 342 surfactant was grafted onto both surfaces of MCC and NCC to impart cationic and hydrophobic properties to the cellulosic materials. The grafting process displayed remarkable results, as the modified cellulosic materials produced positive surface charges (+30 to +40 mV). The modifications of MCC and NCC were then incorporated into the two foam configurations (WFQ342MCC-0.8 and WFQ342NCC-0.8) to remove

microplastics from water. Two crosslinking agents, GPTMS and PEI, were added to the softwood pulp foams to enhance the high mechanical strengths and pore structures. The porosity of the two foams were investigated, and WFQ342MCC-0.8 foam displayed a removal efficiency of 83.4 %, compared to 78.8 % for the WFQ342NCC-0.8 foam. This represents the foam containing MCC obtained a better water absorption capacity than the foam prepared with the NCC.

With the development of WFQ342MCC-0.8 and WFQ342NCC-0.8 foams, the final step was to examine the foams' filtration performances and their removal of microplastics from water. The removal efficiency of WFQ342MCC-0.8 foam was analyzed in the filtration test using PE:SDBS, PE:CTAB, and PE:Tween80. The results showed that the foam achieved high removal efficiencies of 98.5 and 91 % for PE:SDBS and PE:CTAB due to the strong electrostatic and hydrophobic interactions between the microplastics and the foam. However, very low interactions occurred between the PE:Tween80 and the foam resulting in a low efficiency of 67.4 %. Furthermore, the stability of WFQ342MCC-0.8 foam was analyzed on whether the filter could maintain the removal efficiency through introduction of multiple batches of PE microplastics. Despite the foam being able to maintain its efficiency for 50 mg/L PE, a decrease in the removal efficiency occurred for 500 mg/L PE suggesting that the capacity of capturing microplastics was limited. Lastly, WFQ342NCC-0.8 foam optimized the removal efficiency to 99.8 %, as the incorporation of NCC improved the foam surface area resulting in a higher microplastic capture.

In future studies, it is recommended to optimize the softwood pulp foam to increase its removal efficiency during the filtration process. In this scenario, a double-layered softwood pulp foam containing anionic and cationic properties can be produced to remove both cationic and anionic contaminants. For the purpose of treating laundry effluent, it is suggested to study the

behaviors of softwood pulp foam under different water temperatures. This information is crucial since consumers alter the water temperature during the laundry process. Lastly, further studies on water pressure can be investigated to see whether the foam can withstand under high settings.

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