Extraction of Nanocellulose from Wastepaper Using Citric Acid

A Major Qualifying Project Report
Submitted to the Faculty of
WORCESTER POLYTECHNIC INSTITUTE
in partial fulfillment of the requirements for the
Degree of Bachelor of Science
in
Environmental Engineering

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Date:
April 28, 2022

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Abstract

As interest and demand in nanomaterials continues to grow, so do environmental concerns over both the impact of the production processes and the safety of the materials. Nanocellulose, the most abundant natural nanomaterial, could prove to be a safe option for applications ranging from electronics to pharmaceuticals should an environmentally friendly extraction process be developed. Previously, most nanocellulose has been recovered from lignocellulosic materials such as agricultural wastes and plant biomass using processes involving sulfuric acid. Given that paper products are also lignocellulosic materials that have already been processed, this project seeks to understand potential opportunities and drawbacks of nanocellulose extraction from paper wastes using more environmentally friendly citric acid.

Acknowledgements

Licensure

The accreditation Board for Engineering and Technology (ABET) states that "students must be prepared for engineering practice through curriculum culminating in a major design experience based on the knowledge and skills acquired in earlier course work and incorporating engineering standards and realistic constraints that include most of the following considerations: economic; environmental; sustainability; manufacturability; ethical; health and safety; social; and political." This project completes early-stage research and preliminary designs to determine the feasibility and potential impacts of extracting nanocellulose from waste papers. Through this design, the following ABET criterion are met as follows:

- Environmental: The goal of this project was to improve understanding of a biodegradable nanomaterial and propose greener methods of acquiring it. Considerations such as environmental impact of process reagents, human health impacts of nanocellulose and other nanomaterials, and process waste disposal are included in the report.
- Health and Safety: The process uses some reagents that can pose a threat to both human and environmental health, such as highly alkaline and acidic materials, large equipment, and ultrasonic components. Regulations and best practice regarding each of these components were incorporated into the process design.

All work in this report is to be treated as preliminary, with significantly more research and the approval of a PE before finalizing plant designs. As the primary focus of the project was to identify potential benefits and issues in extracting nanocellulose from paper before future investment, any design work is focused on considering potential problems based on broad assumptions.

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Executive Summary

Background & Motivation

Stagnating paper recycling rates combined with gradually increasing demands for paper products and nanomaterials for use in fields ranging from pharmaceuticals to material reinforcement have provided a unique opportunity for paper end-of life. Nanocellulose extraction from paper could provide an economical solution to paper end-of-life while potentially providing an affordable, sustainable alternative to various man-made nanomaterials.

As nanomaterial structure impacts function, determining whether material recovered from varied paper sources still results in the same product under the same extraction process is essential to designing a pilot-scale extraction plant. If structure varies depending on source material, costly additional sorting steps could be necessary, impurities from other paper types could reduce nanocellulose product quality and value, and yield from overall paper supply could be significantly lower.

In addition, previous studies have focused on recovering nanocellulose from singular paper sources, such as newspapers, primarily using a sulfuric acid hydrolysis process. For the product to be truly sustainable, every step in its life cycle needs to minimize its environmental impact.

This project aimed to determine whether nanocellulose recovered from different paper wastes varied in structure, and whether the use of more eco-friendly citric acid in place of sulfuric acid was effective.

Extraction and Characterization Processes

Paper samples were shredded and dried prior to treatment. The process used started with caustic treatment for delignification, citric acid for hydrolysis, and ultrasonic homogenization to further mechanically break down the cellulose microfibrils. Chemical treatment steps occurred at 80C with continuous stirring. Products were characterized using FT-IR, SEM, and EDX.

Characterization Results and Analysis

Ultimately, this process failed to break the majority cellulose down past the micro-scale. Treatment did have an apparent impact on the surface of the cellulose microfibrils and removal of other impurities from the samples. Additional separations would be necessary to isolate any produced nanocellulose for analysis methods such as TEM to prevent burning. Microstructures were found to vary significantly even within some samples, but it is unknown whether the underlying nanocellulose is similarly different.

FTIR spectra also demonstrated that lignin is present in all the paper samples, and did not noticeably decrease throughout treatment. It should be noted paper products go through significant delignification during production and therefore the overall amount of lignin was low in the wastepaper examined compared to more virgin materials. Whether this amount of lignin remaining in these samples is cause for concern needs to be determined by additional methods to

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quantify lignin in samples at lower levels. Hemicellulose bonds were removed during hydrolysis. Citric acid was not successfully removed from samples through rinsing and dilution prior to FTIR, suggesting that washing the final product will be challenging in the industrial process.

Design Considerations

Preliminary design suggestions for a pilot scale process are also included with recommended reactor types and a basic model to determine sizes based on mass of paper processed, bath concentrations, and residence times. As more information is required to determine optimal concentrations, temperatures, and flow rates, the model allows most process parameters to be adjusted.

Two Continuous Stirred Tank Reactors (CSTRs) are recommended for the chemical treatment. Washing steps between treatment are necessary to prevent changes in the pH of the citric acid bath and purification of the final product. Additional processes may be necessary after to adjust the functional groups of cellulose to tailor it to specific applications. Recycling some of the caustic and citric bath can greatly reduce material costs for the process.

Neither the low concentration of caustic nor the citric acid are of environmental concern. The pH of the citric acid bath will need to be increased to at least 6.5 prior to disposal. By mixing both the spent caustic and citric acid, much of this neutralization can be accomplished without any additional cost. Additional analysis is necessary to determine what impurities in paper waste may end up in discharge.

Conclusions and Recommendations

A more rigorous process is necessary to fully break down paper wastes into nanofibrils. It is possible that the ultrasonic system used in this work was not powerful enough to break the microfibers down significantly. A higher-powered ultrasound system, or other methods (e.g., ball milling), would be of intrest for further work. This could also be accomplished through additional mechanical steps, longer residence times in the bath, or the use of sulfuric acid in place of citric. While citric acid has the benefit of being less environmentally taxing, it may not be sufficient to break down cellulose microfibrils.

Additional work is also necessary to optimize the process, should nanofibril structure be similar enough across paper sources to produce a valuable product. Once an extraction method has been optimized, the created model can provide preliminary design information such as reactor size and material requirements to allow for a more sophisticated pilot plant design.

1.0 Introduction

Given stagnating paper recycling rates combined with increasing demand for paper products, additional solutions are needed to tackle paper end-of-life. According to the EPA, paper recycling has stayed just under 70% since 2015, with 17,220 tons landfilled in 2018 (US EPA, 2021). Meanwhile, estimates of paper production and consumption continue to gradually increase, with the world's largest producer, China, producing well over 100 million tons per year (China Paper Association, n.d.; Mordor Intelligence, n.d.). Finding additional, more profitable uses for paper waste could encourage higher recovery rates and reduce the amount landfilled.

One potential high-value use of wastepaper is as a source of nanocellulose. Nanocellulose is a nano-scale material derived from cellulose, which makes up the majority of plant-based biomass. Cellulose makes up the majority of tree material (with lesser amounts of hemicellulose and lignin), which is then processed to form paper. Previous research has demonstrated the viability of recovering nanocellulose directly from trees or agricultural waste (Rajinipriya et al., 2018). Given that paper has already undergone some of the needed processing steps to remove other natural polymers from the cellulose, it is possible that recovering nanocellulose from paper could be simpler and more cost-effective.

Nanocellulose itself is a valuable resource with a variety of applications ranging from drug delivery to reinforcing composites. It provides a sustainable alternative to other nanomaterials: where environmental and human toxicity remain major concerns for many anthropogenic nanomaterials, plant-product-derived nanocellulose is generally benign and naturally degradable (Endes et al., 2016).

In order to determine if extracting nanocellulose from paper is feasible, nanocellulose derived from different products need to be characterized and compared. Nanomaterial function is heavily dependent on structure, so determining whether nanocellulose extracted using the same process from different sources has similar structures is an essential first step in designing a pilot-scale process.

The process used impacts the overall sustainability and feasibility of this end-of-life option for paper. While most current extraction processes use sulfuric acid hydrolysis, sulfuric acid has a high negative impact on the environment. To make the process greener, organic acids are suggested instead. This project proposes and tests the use of citric acid for use in hydrolysis due to its lower impact.

This project aims to qualitatively characterize cellulose extracted from seven different common paper wastes using caustic treatment, acid hydrolysis, and ultrasonic homogenization. Considerations for the design of a theoretical pilot-scale production plant are also included.

2.0 Background

2.1 Life Cycle of Paper Products

Paper products include a diverse range of materials, ranging from newsprints and glossy magazines to coated cartons and corrugated cardboards. While some types of paper products are starting to disappear, the paper market is overall continuing to grow. As a result, it is imperative to find sustainable solutions for the products at their end-of-life. Recycling has prevailed as the most sustainable option when done properly. However, paper recycling rates in the United States

have stagnated over the past decade at around 67%, with a significant portion of paper products still ending up landfilled or incinerated (US EPA, 2021). Figure 1 shows the material flow of various paper products throughout their lifecycles.
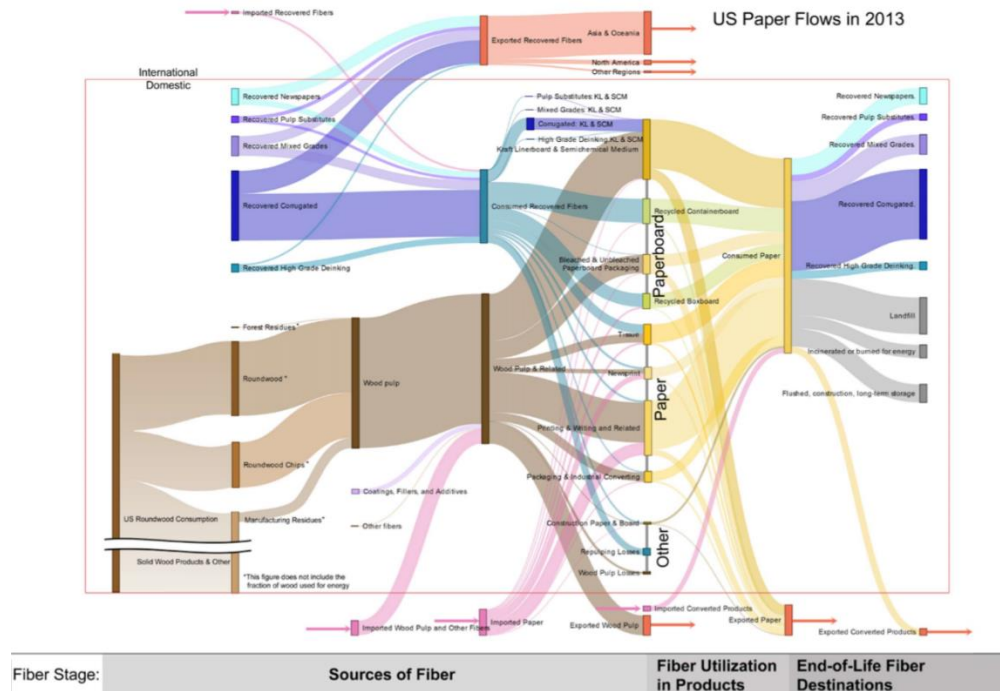
Figure 1: U.S. Paper flows in 2013. Figure from American Forest & Paper Association.

2.1.1 Demand for Paper Products and Packaging

The market for paper and related products has continued to increase over the past few decades ("Pulp and Paper Industry," 2022). While some sectors of the paper market, such as newsprint and other graphic papers, have faced a sharp decline due to digitization, other sectors such as tissue, kraft paper, and wood pulps continue to see growth (Berg & Lingqvist, 2019). Consumption in the two largest producers of paper products – China and the United States – was over 107 and 74 million metric tons, respectively (Berg & Lingqvist, 2019; Mordor Intelligence, n.d.). An overview of paper production and consumption in China, the world's leader in paper production, can be seen in Figure 2, while a breakdown of what paper products are being produced by China is shown in Figure 3.

These figures show that production in China alone has remained at over 100 million metric tons per year with an overall increase since 2009. Over 40% of the paper produced was corrugating medium and linerboard, which is used to produce cardboard. These categories have seen overall increases in the past decade, and are likely to continue increasing as demand for cardboards for use in e-commerce markets and shipments increase (Mordor Intelligence, n.d.).

Other categories, such as newsprint and printing papers, have been trending downwards. While they previously had larger market shares, digitization has been pushing these out of fashion (Mordor Intelligence, n.d.).
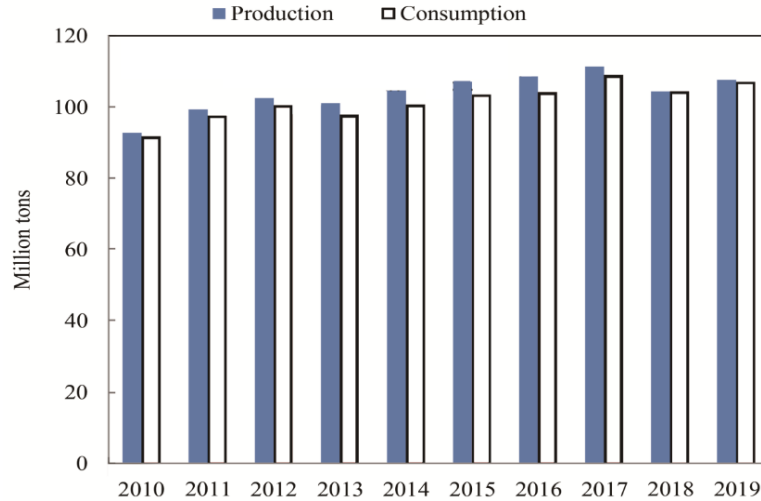
Figure 2: Annual production and consumption of paper in China from 2010 to 2019. China is the world's largest paper producer. Figure from China Paper Association (2020).
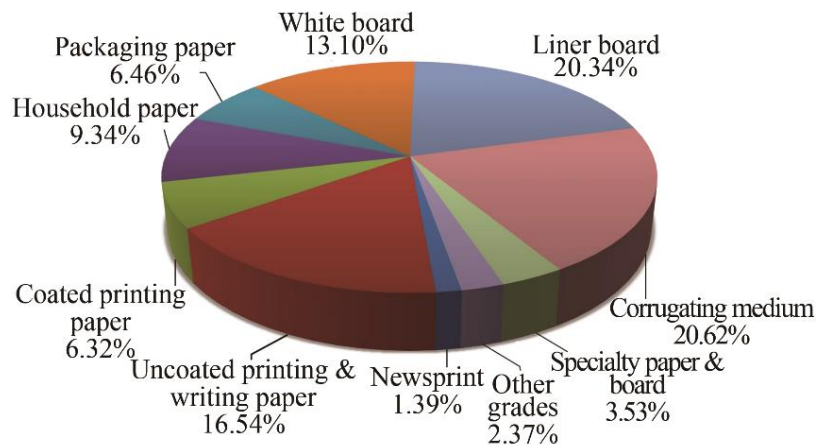
Figure 3: Paper production by product type in China in 2019. Figure from China Paper Association (2020).

Understanding what paper products are being produced and in what quantities is essential to understanding what resources are being spent on paper production and what end-of-life options these products face. Given that this already large market continues to grow, sustainable and economically sensible plans for these resources are necessary.

2.1.2 Raw Material Collection and Processing

In order to produce paper, wood is chemically processed into pulp. This pulp undergoes different manufacturing processes depending on the final product, resulting in different compositions and properties. Paper can also be recycled into new paper products, often of lower quality due to further breakdown of its cellulose fibers.

The paper pulp and production process is outlined below, in Figure 4:
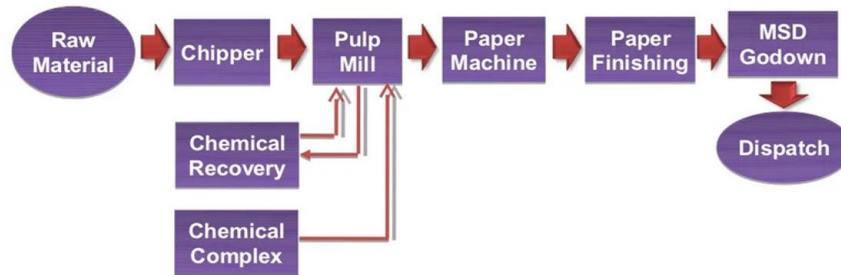
Figure 4: Paper production process. Figure from Vashist, 2012.

The chemical pulping of the raw material, or wood, results in delignification. Lignin, as will be discussed later, forms a matrix around cellulose fibrils and provides additional structure that improves plant fiber tensile strength significantly. However, as it also makes processing into paper difficult, reducing the amount of lignin is key to most paper products. The finishing step varies.

2.1.3 Paper End-of-Life

After paper products have been used, they are typically either landfilled, incinerated, or recycled. Studies of paper life cycles determined that recycling paper has the least negative environmental impact (Villanueva & Wenzel, 2007). However, even as paper production continues to rise, paper recycling has stagnated. From 2015 to 2018, the EPA reported an increase of only 1% in recycling rates, as shown in Table 1. As of 2018, roughly 68% of paper products were recycled. This leaves the remaining 32% to be landfilled or incinerated.

1960	1970	1980	1990	2000	2005	2010	2015	2017	2018
17%	15%	21%	28%	43%	50%	63%	67%	66%	68%

Table 1: Percent of paper and paperboard recycled per generation. Data from U.S. Environmental Protection Agency

As shown in Figure 5, paper and paperboards make up a significant portion – over 11% - of total landfilled waste as of 2018. To complicate the issue, in 2019, China implemented new restrictions on imported waste. Prior to 2019, the majority of U.S. paper and plastics were sent overseas for recycling. While the process of transporting waste added significant emissions to the material lifespan and sustainability practices in overseas recycling varied, this shift forced the U.S. to either pay more for recycling or start landfilling previously "recyclable" waste. The overwhelming response was to landfill; as a result, recycling rates have likely declined in the past four years (Semuels, 2019).
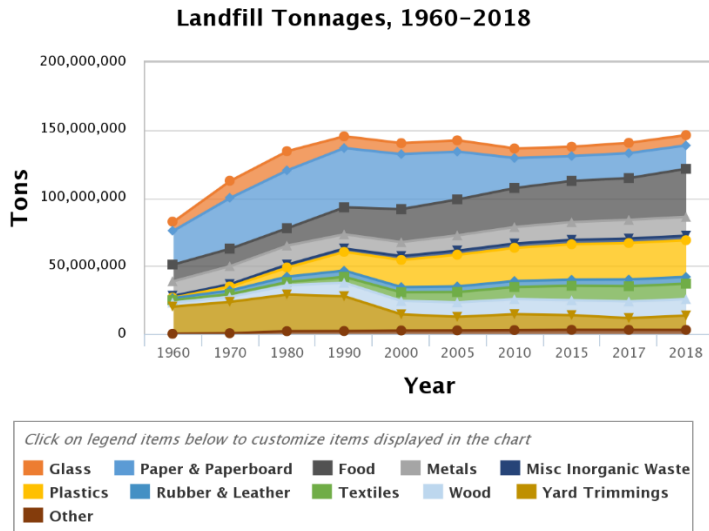
Figure 5: Landfill waste by category from 1960-2018. In 2018, paper and paperboard made up over 11% of landfill waste by mass. Figure from EPA

Incineration has also emerged as another potential end-of-life solution. The EPA reports that, in 2018, around 4.2 million tons of paper waste went to incineration (US EPA, 2021). While incineration provides some benefits over landfilling, such as energy production, numerous human and environmental health impacts have been associated with waste incineration (Tait et al., 2020). This leaves recycling as the preferred method of paper waste management.

In order to increase these recycling rates, better economic incentives are necessary to counteract the rising prices of domestic recycling. One potential method of increasing profitability of paper recycling is by upcycling paper waste into a more valuable material: nanocellulose.

2.2 Push for Nanomaterials

Nanomaterials are a rapidly growing field of interest, and the potential to recover nanocellulose from paper waste could address many of the challenges surrounding paper waste end-of-life options. This section explains what nanomaterials are and why nanocellulose specifically matters through exploring nanomaterial properties, structures, and challenges.

2.2.1 Nanomaterial Overview

In 2011, the European Commission adopted the following definition of nanomaterials:

"A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm."

In short, nanomaterials are materials developed and used on the molecular scale, as illustrated in Figure 6:

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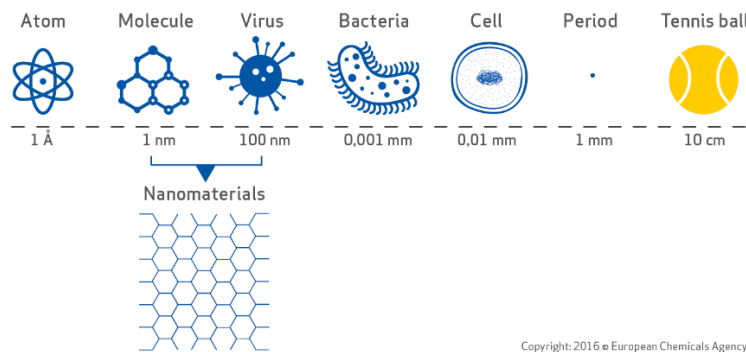
Figure 6: Nanomaterial scale: Nanomaterials have at least one dimension that is within the 1-100nm range. Figure from European Chemicals Agency.

This results in unique structures with high ratios of surface atoms to interior atoms. As a result, nanomaterials can exhibit novel and enhanced properties in comparison to their macroscale counterparts, such as electronic and ionic conduction, variable optical properties, and many others. Due to this, the potential applications for nanomaterials reach across all branches of science and industry. Already, nanomaterials and nanostructures are used in fields ranging from semiconductors and quantum computers to enhanced drug delivery and water filtration (Dahman, 2017).

Within this wide field of applications are incredibly diverse nanomaterials made up of anything from pure carbon to metal oxides, formed into structures ranging from tubes and spheres to more complex geometries. They can either be naturally occurring, like DNA, incidental, such as fullerenes, or synthetically produced and engineered, such as carbon nanotubes.

Naturally occurring inorganic nanomaterials such as mineral oxide and volcanic ash nanoparticles have always existed on Earth, while more complex viruses and organic bionanomaterials like DNA evolved much later. These nanomaterials serve important functions in biological and environmental processes (Hochella et al., 2019).

Incidental nanomaterials, like soot particles and some nanoplastics, are unintentional results from human action, and generally started appearing around the time of the industrial revolution. These are mostly produced in areas used for agricultural, industrial, and mining, and can form in combustion, smelting, and similar reactions before being carried out into the environment as exhaust (Hochella et al., 2019). These nanomaterials are generally known to have toxic impacts on the environment and human health (Taghavi et al., 2013).

Meanwhile, synthetic and engineered nanomaterials were purposefully developed through human action for specific applications. These intentional nanomaterials are a far more recent development than the naturally occurring and incidental nanomaterials; modern interest in the subject can be traced back to the discovery of fullerenes in the 1980s, and in 1999 the National Nanotechnology Initiative was founded (Dahman, 2017).

Due to how recent most of these developments are, little is understood about the impact of these engineered nanomaterials on the environment (Nowack & Bucheli, 2007; Taghavi et al., 2013). Developing and implementing consistent, effective regulations has proven a challenge due to this lack of knowledge and the incredible diversity of nanomaterials (EUON, n.d.). As a result, improving this understanding of their potentially toxic effects on the environment has been an increasingly essential field of research (Nowack & Bucheli, 2007; Taghavi et al., 2013).

Some of the potential positive and negative impacts of nanomaterials specifically are shown in Figure 7:
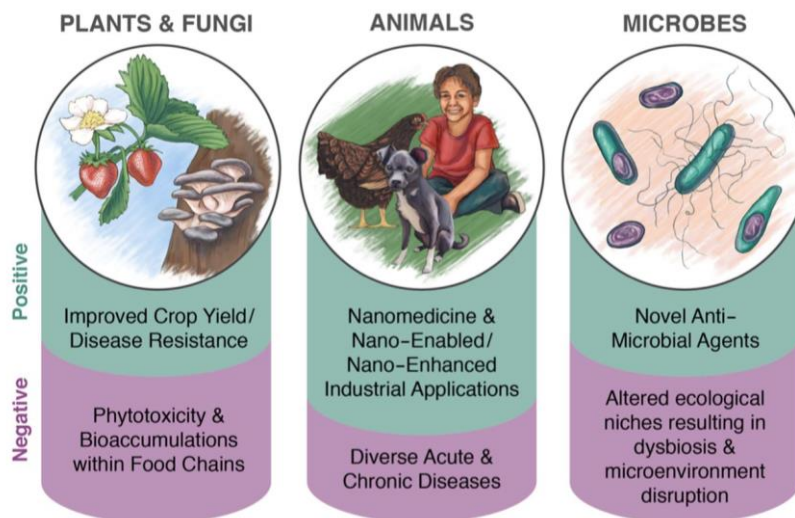
Figure 7: Positive and negative impacts of nanomaterials on different kinds of organisms. Figure from Hochella, et al. (2019).

In addition to needing a better understanding of various nanomaterials' environmental impact, it is also imperative to consider the impacts of their production processes. Greener processes can be developed through implementation of the principles of green chemistry: namely, prevention of hazardous waste and designing for degradation (*12 Principles of Green Chemistry*, n.d.).

As the field of nanomaterials continues to develop, it is imperative that these considerations are taken into account. Natural nanomaterials offer a unique opportunity as they often have a number of these sustainability concerns already addressed. They are often renewable, inherently biodegradable, and relatively environmentally benign (Endes et al., 2016). Additional engineering processes can modify and adapt them to various applications while maintaining the sustainable base.

These natural nanomaterials can be recovered through top-down production techniques; while synthetic production techniques vary greatly along with their material types and uses, they can typically be generalized into one of two categories: top-down or bottom-up production. In top-down production, the process begins with a bulk material that eventually is "whittled" down to the nanoscale components. The properties of the nanomaterial are already determined by the bulk material, though can be impacted by the methods used for recovery. In bottom-up synthesis, the building blocks are individual atoms or molecules, synthesized into a material. The properties in bottom-up synthesis are then limited by the ability to bond different pieces together, as opposed to handling what was already present in top-down methods (Wilson et al., 2002).

The main focus for sustainable development, regardless of production method, is ensuring that each step of the process adheres to green principles and results in a product that can be responsibly managed at its end-of-life.

2.2.2 Nanocellulose Structure

Nanocellulose is the most abundant natural nanomaterial in the world, existing as a key component in all forms of lignocellulosic biomass (Lee et al., 2014). Lignocellulosic biomass makes up plant cell walls in all plant mass, ranging from live hardwood trees to food scraps. This renewable carbon source consists of three main components – lignin, hemicellulose, and cellulose – combined in a complex carbohydrate with the structure shown below:
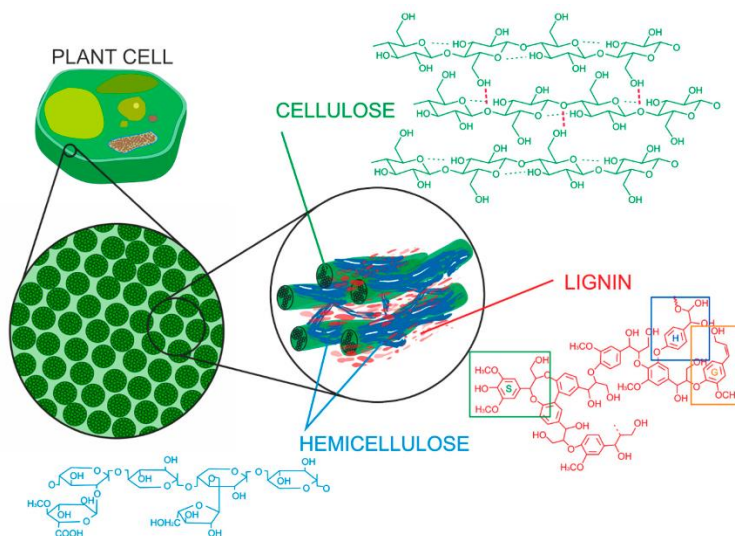
Figure 8: Structure of lignocellulosic biomass. Plant cell walls consist of three main components: cellulose (shown in green), hemicellulose (shown in blue), and lignin (shown in red). Figure from Hasanov, Raud, & Kikas 2020.

Lignin and hemicellulose create an outer matrix around the cellulose fibrils through hydrogen bonding with the hydroxyl and ether groups of the cellulose, improving rigidity (Smith, 2019). The exact proportions and structures of each vary greatly between plant matter, determining each plant's material properties.

Cellulose acts as the backbone, making up the innermost portions of each lignocellulose fibril. It is the most abundant of the three components, making up anywhere from 40-80% of the overall matrix (Rajinipriya et al., 2018). As opposed to the heteropolymers lignin and hemicellulose, cellulose consists of long homopolymers (Smith, 2019). The monomer of cellulose is shown below:
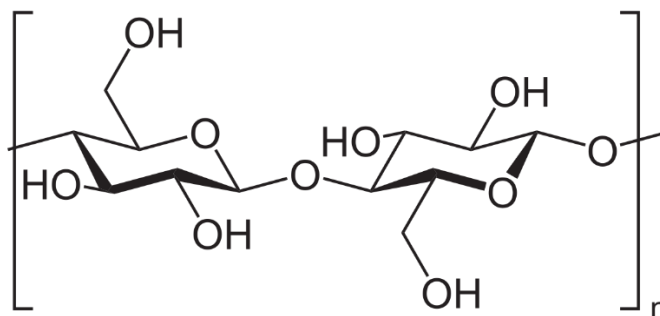
Figure 9: Structure of cellulose monomer, also known as D-glucopyranose. Figure from Smith (2019).

Hydrogen bonding between the hydroxyl groups and ethers within these monomers creates the cellulose macrostructure in plants, forming fibrils that the lignin and hemicellulose attach to. Within the fibril are smaller bundles of cellulose nanofibrils (CNF). This structure can be seen in the figure below:
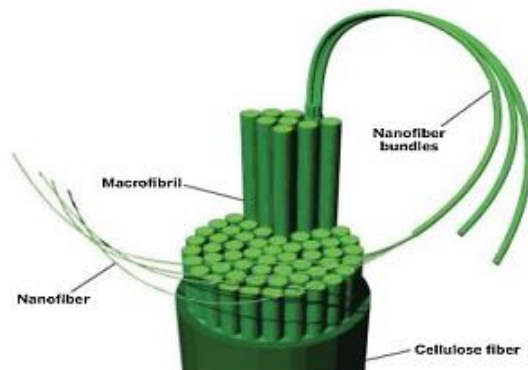
Figure 10: Cellulose fiber structure without lignin and hemicellulose. Cellulose tends towards long fiber structures, with hydrogen bonds between hydroxyl groups and ethers creating each level of fiber. Figure from Kumar, Pathak & Bhardwaj (2019)

CNFs typically range from 3-35nm wide with lengths reaching up into the micrometers (Rajinipriya et al., 2018). These nanofibrils contain both crystalline and amorphous regions, as shown in the figure below:
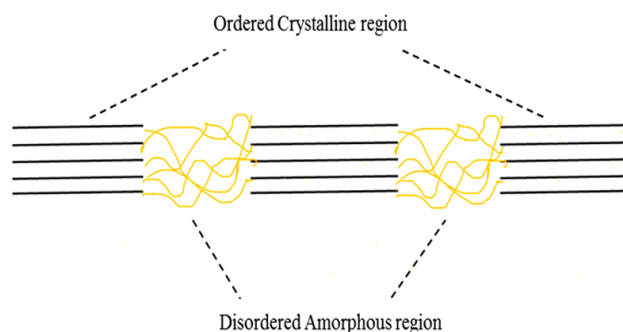
Figure 11: Crystalline and amorphous regions of CNF. These regions are created by the hydrogen bonds and determine the crystallinity of the cellulose

Through extracting and processing, the amorphous regions of the nanocellulose can be dissolved. This produces cellulose nanocrystals (CNC), which only consist of the ordered crystalline regions. As a result, CNC lengths are limited to a few hundred nanometers (Xu et al., 2013).

Outside of lignocellulosic biomass, cellulose can also be produced by bacteria, producing bacterial nanocellulose (BNC). The structure of bacterial nanocellulose also varies in accordance to the type of bacteria (Zinge & Kandasubramanian, 2020). In general, BNC has a higher degree of crystallinity than the CNCs produced by plants, as well as other unique physiochemical processes, but is prohibitively expensive with low yields (Gupta et al., 2019).

The properties of nanocellulose vary with form, source, and extraction methods, but it generally has high transparency, flexibility, low thermal expansion, tunable rheology, and

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intrinsic biodegradability (Tayeb & H. Tayeb, 2019). Furthermore, the surface groups of nanocellulose can be modified for a wide range of applications.

2.2.3 Nanocellulose Benefits and Applications

Interest in nanocellulose has skyrocketed over the past decade; according to the Web of Science, the number of papers published per year on the subject has increased from 148 in 2009 to over 1,055 in 2018 (Bacakova et al., 2019). A number of factors contribute to this, both relating to its properties and applications.

First, as established, nanocellulose's structure allows for a wide variety of applications. It has various hydroxyl groups, which can be relatively easy to modify for addition of other functional groups or to adjust new shapes and structures. Common examples include acetylation and silylation. These processes introduce hydrophobic groups, which can allow for better dispersion in non-polar substances such as polymers. TEMPO-mediated oxidation has also been used to produce nanocellulose and impart negative charges to improve their stability in aqueous solutions. This process can be followed with sulfonation for further control of surface charges. These are just a handful of examples; the processes to chemically modify nanocellulose are extensive and allow for a range of final properties (Ghasemlou et al., 2021).

Due to the fact that it is entirely carbon, hydrogen, and oxygen and produced by plants, it is inherently biodegradable. addressing one of the major concerns of green chemistry and nanomaterial development. On the macroscale, cellulose has already been popular for use in packaging due to its environmentally friendly properties (Gupta et al., 2019).

While more research is necessary to determine the potential human and environmental health impacts of nanocellulose, initial studies suggest that nanocellulose is relatively benign with low toxicity and limited cytotoxic potential (Endes et al., 2016). High concentrations of nanocellulose may have some impact on cells, but facing these concentrations is relatively unlikely. In addition, inhaling nanoparticles of any kind can have adverse pulmonary impacts, which could potentially be a concern in worker protection but otherwise unlikely in most final applications (Endes et al., 2016). Current research has investigated the role of nanocellulose in drug delivery, reinforcements in various composites and polymers, electronic devices such as piezoelectrics and supercapacitors, and filtration (Bacakova et al., 2019; Dias et al., 2020; Ghasemlou et al., 2021; Tayeb & H. Tayeb, 2019).

2.3 Current Investigations into Nanocellulose Recovery

Current literature has investigated various methods of extracting nanocellulose from agricultural wastes such as rice husks and specific paper wastes such as newspapers. The most common process to do so is acid hydrolysis using sulfuric acid. The recovered nanocellulose is generally characterized using analytical methods such as FT-IR, XRD, TEM, and TGA. In order to understand the methodology developed for this project's goal of extracting and characterizing nanocellulose recovered from waste papers using organic acids, the current knowledge base of nanocellulose extraction from wastes is outlined here.

2.3.1 Nanocellulose Sources

Nanocellulose can be extracted from any form of lignocellulosic biomass, including raw materials such as wood and cotton, agricultural wastes, and aquatic wastes such as algae. Each

source varies in its lignocellulose composition and relative amounts of cellulose, lignin, and hemicellulose. Typical cellulose sources can be seen in Figure 12:
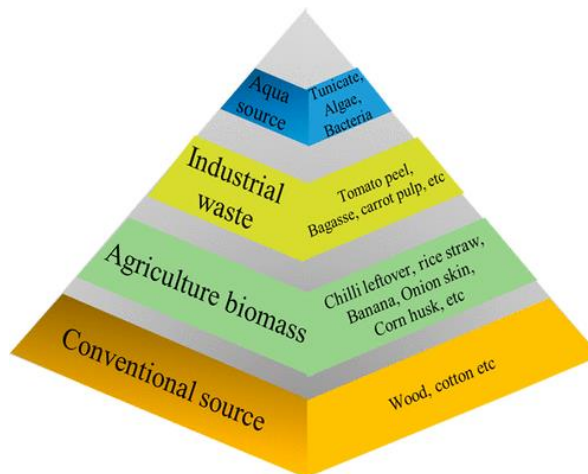

Figure 12: Pyramid of cellulose source. Currently, most nanocellulose production is focused on agricultural waste sources. Figure from Rajinipriya, Nagalakshmaiah, Robert, & Elkoun (2018).

As of now, most nanocellulose production focuses on recovery from agricultural waste due to its abundance of natural fibers, constant availability, ease of collection, and low cost (Rajinipriya et al., 2018). Two of the most prominent agricultural waste sources are sugarcane bagasse and rice husks (Gupta et al., 2019). In addition, nanocellulose extraction from "conventional" cellulose sources such as woods and bamboos are also common (Gupta et al., 2019). However, extraction from woods can be more costly, difficult, and damaging as it requires direct harvesting of a natural resource as opposed to collecting waste, and the bulk of the cellulose is within a secondary cell wall (Rajinipriya et al., 2018).

Interest has been growing in other cellulose sources, such as algae and bacterial nanocellulose. However, prohibitively high costs and low yields have proven an earlier barrier to commercialization of these sources (Gupta et al., 2019).

2.3.2 Recovery Processes

Nanocellulose extraction is a top-down process to produce nanomaterials. Whether the nanocellulose is from wood, agricultural wastes, paper, or some other source, the recovery requires some pretreatment followed by product separation. Depending on the final use of the nanocellulose, additional modifications may be made to its hydroxyl groups.

Pretreatment aims to remove any non-cellulose components from the cellulose fibrils (Kargarzadeh et al., 2017; Teo & Wahab, 2020). This usually means removing lignin and hemicellulose along with any source-specific impurities. For example, extraction from tunicates would also require removing a protein matrix, and recovering from algae would require removal of the algal cell wall matrices (Kargarzadeh et al., 2017). Pretreatment processes can be mechanical, chemical, biological, or a mix of each.

The most common pretreatment process is acid hydrolysis (Teo & Wahab, 2020). Acid hydrolysis is effective at removing hemicellulose from the structure and redistributing lignin, making it easier to further delignify the material. While sulfuric acid is the most common acid used, studies have also been done using hydrochloric acid and others (Teo & Wahab, 2020).

Acid hydrolysis is often done in conjunction with alkali treatments, with sodium hydroxide the preferred solvent (Teo & Wahab, 2020). Alkali treatments are effective in delignification, which makes cellulose fibers more accessible for hydrolysis. It is common to see alkali-acid-alkali processes, where each step makes the next more effective in removing lignin and hemicellulose (Kargarzadeh et al., 2017).

Concerns over sustainability and environmental impact, however, have pushed researchers to explore more pretreatment options. One option is the use of ionic liquids, which allows for greater recyclability. Another is the use of organic solvents, which includes alcohols and organic acids (Teo & Wahab, 2020). One previous study used a mix of formic acid, peroxyformic acid, and hydrogen peroxide from palm trunk, corn husks, and rice husk fiber, successfully extracting nanocrystals ranging from 200-50nm with high purity and high aspect ratios (Nang An et al., 2020). Citric acid has previously been explored in extraction from disposable paper cups, with the most effective concentration found to be 76wt% (Nagarajan et al., 2020). This method produced web-like nanostructures, with fibers having widths under 40nm (Nagarajan et al., 2020).

Biological processes such as the use of bacteria, fungi, and lignocellulosic enzymes have also gained traction. Bacteria, as discussed earlier, are especially popular due to their high-purity product that has no need for delignification or hemicellulose removal. Common bacteria used include those from genera such as Rhizobium, Xanthococcus, Pseudomonas, Azotobacter, Aerobacter, and Alcaligenes (Abol-Fotouh et al., 2020). However, the cost of culture medium and relatively low yields remain high barriers to commercialization (Abol-Fotouh et al., 2020).

The performance of these chemical and biological treatment processes can be improved by mechanical pretreatments. Mechanical pretreatments are usually either chipping processes, used to break up large pieces of material into smaller ones, or milling, which grinds already small pieces into particles on the millimeter scale. Unfortunately, these processes are often energy-intensive and can lower the crystallinity of the resulting nanocellulose (Teo & Wahab, 2020).

Ultrasonication, or ultrasonic homogenization, is another mechanical treatment option. This is typically performed after acid hydrolysis and caustic delignification are complete and disperses the fibrils throughout the solution (Yang et al., 2017). Ultrasonication can also be performed in conjunction with acid hydrolysis, increasing the hydrolysis efficiency and lowering the needed acid concentration (Li et al., 2011).

Once pretreatment is complete and non-cellulose components have been removed, the nanocellulose can be recovered and prepared as fibrils or crystals.

2.3.3 Characterization Processes

Common characterization techniques for nanocellulose include both scanning and transmission electron microscopy (SEM and TEM), thermo-gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), and x-ray diffraction (XRD). These allow for understanding of nanocellulose fibril and crystal size, thermal stability, presence of lignin and hemicellulose, and product crystallinity, respectively.

2.3.4 Current Challenges and Project Goals

While previous research has proposed various methods of nanocellulose extraction from biomass and provided various extraction techniques, information on extraction from paper waste is lacking. Some studies have focused on extracting nanocellulose from one specific type of paper waste or from paper waste in general, but the relationship between nanocellulose traits and

precursor paper material remains unknown. Due to the current lack of information on extracting nanocellulose from waste papers, little work has been done on potential process designs.

In addition, the majority of studies done on nanocellulose extraction use sulfuric acid for acid hydrolysis. Sulfuric acid is incredibly detrimental to the environment (*Sulfuric Acid | National Pollutant Inventory*, n.d.). Citric acid has been proven in some cases to work as a more environmentally friendly option (Nagarajan et al., 2020). However, further demonstration of its effectiveness is needed.

This project addresses these gaps by completing experimental work to characterize nanocellulose from different types of waste papers after undergoing an extraction process using sodium hydroxide, citric acid, and ultrasonic homogenization. Through the collection and analysis of qualitative data on cellulose differences in various precursor materials, potential challenges in recovering nanocellulose from a diverse paper waste stream can be identified. In addition, feasibility of recovering nanocellulose for specific applications from waste paper can be compared with that of nanocellulose from agricultural waste streams. Furthermore, the project addresses some basic design components for a waste paper nanocellulose extraction plant.

3.0 Experimental Methodology

The first goal of this project was to determine whether nanocellulose structure varied with paper waste type. In order to do so, 8 types of waste paper were collected: cardboard, printed paperboard, molded paperboard, tissue paper, napkins from recycled fibers, receipt (thermal) paper, printer paper, and kraft paper. Each paper type underwent the same extraction procedures, with various characterization methods being employed at each step.

3.1 Sample Collection

Seven different paper samples were collected for extraction from various sources, as listed in Table 2. These specific samples were chosen as they are common and differ significantly in function and use from each other.

Sample Type	Description
Corrugated Cardboard	Thick, stiff packaging material made from layers of kraft paper held together with an adhesive Sourced from: Shipping box
Napkin (Recycled Fibers)	Thin, soft paper made from recycled paper fibers Sourced from: Cafeteria napkin
Paperboard	Thicker form of paper, often has some recycled fiber portion. Usually has additional inks and printings completely coating one or both sides. Sourced from: Food packaging box
Kraft Paper	Stiff paper produced from the kraft paper pulp process, often used to form cardboard, wrapping material, or other packaging Sourced from: Brown paper grocery bag
Molded Paperboard	Packaging material typically made from recycled paperboard fibers Sourced from: Egg carton

Printer paper	Paper made from chemically treated wood pulp that undergoes additional bleaching and dying steps to make it suitable for printing and writing
	Sourced from: Standard 8x11 printer paper with printing
Thermal Paper	Paper that has undergone similar processing to printer paper, but is made thinner with additional coatings to allow for inkless printing
	Sourced from: Receipt

Table 2: List of paper samples and sources

3.2 Treatment Methods

Each paper sample underwent two separate treatment methods: chemical, with caustic and citric acid, and hot water. This allowed the impact of the chemical treatment method to be determined.

3.2.1 Chemical Treatment

About 4g of sample was massed and placed in 100mL of 5wt% sodium hydroxide solution at 80C for three hours for delignification (Li et al., 2011; Nagarajan et al., 2020; Rashid & Dutta, 2020). Temperature was maintained by a hot plate and the sample was continuously stirred. Some variance in temperature was noticed.

Once complete, the samples were quenched with 200mL of DI water and filtered through 0.45µm pore paper. Some samples were also centrifuged to further remove excess moisture. Samples were rinsed with DI water while on the filter paper before being removed and dried again at 100C. Samples were scanned using FT-IR again to determine relative change.

The samples then underwent acid hydrolysis in 76wt% citric acid solution for 2 hours at 80C (Nagarajan et al., 2020). Once complete, the samples were again filtered, centrifuged, and washed, and either oven dried or left to dry on the filter paper. These dried samples were pulled apart by hand, with the fibers scanned using FT-IR.

Afterwards, 0.5g of sample was placed in 80mL DI water for ultrasonic homogenization for 40 minutes. The sample was removed and cooled in a water bath every 10 minutes to under 30C.

3.2.2 Hot Water Treatment

About 8g of sample was sampled and placed in 300mL 80C water for two hours to break down the material into smaller fibers. If the sample was not fully reduced to fibers, it was heated again and left until few clumps could be seen. 200mL of paper-water solution was set aside for ultrasonic homogenization.

The remaining 100mL were dried, with excess water removed via centrifuge and filtration before oven drying at 100C. Dried sample was broken apart by hand, and fibers scanned using FT-IR.

3.2.3 Ultrasonic Homogenization

80mL of sample was placed in a 100mL beaker and propped inside a cardboard tube on a scissor lift, which elevated so that the homogenizer tip was submerged about a centimeter into the solution. Cooling pipes ran through the chamber, but due to the small beaker size and cardboard insulation, the sample temperature could not be maintained during sonication. A

QSonica Q700 sonicator with a max power of 700 Watts a frequency of 20kHz operated with a 55 amplitude for 4 10-minute intervals, with the beaker removed for cooling between each interval. The beaker was submerged in a cold water bath until the temperature was reduced to 30C or less.

Afterwards, the samples were centrifuged and allowed to settle to decant excess water. They were then placed uncovered on a hot plate at 120C for 30 minutes to boil off additional water, and eventually placed in the 100C oven to dry overnight.

3.3 Analysis Methods

All samples under both treatment processes underwent the same analysis methods to allow for meaningful comparison of how the treatment impacted their structures.

3.3.1 Pre-Treatment Analysis

Around 20g of each paper type was separately massed, before soaking in room temperature water for at least 24 hours and being pulped in a standard kitchen blender. This was done to homogenize each paper type and reduce it down to smaller fibers, creating a larger surface area for hydrolysis and allowing for characterization once dried.

The samples were dried on an aluminum baking sheet. All samples except receipts were dried at 100C until their mass stopped decreasing. Dried samples rapidly absorbed water in the air once removed from the oven, and usually gained around 0.05g mass again before stabilizing. Receipts were dried at 70C after blackening was observed at 100C. Once dried, the samples were stored in resealable plastic bags at room temperature.

The dried samples were scanned using FT-IR, with peaks compared to existing literature to determine relative lignin, cellulose, and other impurity contents in and between each kind of paper. Afterwards, two different extraction methods were employed.

3.3.2 Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

Fourier Transform Infrared Spectroscopy (FT-IR) Analysis was completed between each step of the treatment process. Dried samples were pulled apart into fibers or flakes and analyzed via a Spectrum 3 FT-IR Spectrometer from Perkin Elmer. Samples were scanned 4 times each from 800 cm^{-1} to 4000 cm^{-1} with steps of 1 cm^{-1}. Due to the nature of the samples, thickness of material for the FT-IR to scan varied.

3.3.3 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) analysis was completed on each of the chemically treated samples after homogenization, the water treated samples after homogenization, and the original paper wastes after being bloated with water and shredded so that they could be pulled apart into fibers. Samples were loaded onto double-sided tape and coated in a 40% Au, 60% Pd sputter using an EMS150R Plus Rotary Pumped Coater. Samples were then loaded into a JEOL 7000F SEM, with images taken of each within the 100μm and 10μm ranges.

4.0 Experimental Results and Discussion

Various methods were used to extract and characterize each sample, as explained in Section 3. The results of FT-IR and SEM analysis for each sample under each process are explained and analyzed here.

4.1 FT-IR

    FT-IR results demonstrated that the chemical treatment process had minimal impact on the chemical composition of the cellulose in the paper, and that each precursor material consisted of similar components.

4.1.1 Chemical Treatment Process FT-IR

    Three representative FT-IR spectra from the caustic-citric acid process are shown with peaks labelled in Figure 13. The top blue line is the scan of the untreated samples, the middle orange line is the scan of the sample after caustic treatment, the middle gray line is the scan of the sample after citric acid treatment, and the bottom red line is the scan after 40 minutes of homogenization under acidic conditions.

    While the shapes and sizes of peaks varied from sample to sample, most samples shared the following similarities prior to treatment: a broad, low peak in the 3600-3000 cm^{-1} range (corresponding to lignin), two small, sharp peaks near 2918 cm^{-1} and 2850 cm^{-1} (corresponding to asymmetric methyl and methylene groups in both cellulose and lignin), a broad peak near 1420 cm^{-1} (crystalline cellulose), and a number of peaks conjoined in the 1100-900 cm^{-1} range with the highest typically appearing at around 1030 cm^{-1} (C-O-C bonds in cellulose), and one final additional peak at 875 cm^{-1} (glycosidic linkage in hemicellulose). The assignment of these peaks came from comparisons of spectra from previous studies on cellulose (Hospodarova et al., 2018; Kubovský et al., 2020; Poletto et al., 2014).

    After caustic treatment, the shape of these peaks shifted. Samples tended to have inverted peaks, or significantly less absorption, at 1040 cm^{-1} and 1009 cm^{-1} within the 1200-900 cm^{-1} bands. This 1040 cm^{-1} inversion could correspond to C-O, $C \equiv C$, or C-C-O bonds within hemicellulose and lignin. Most peak areas decreased, but the proportions in area of the major peaks and bands remained similar.

    After citric acid treatment, an increase in each of the peaks as well as the addition of peaks in the 1800-1200 cm^{-1}, with the most notable at 1720 cm^{-1}, became apparent. This is expected to be due to interference from the citric acid: high concentrations used in the process resulted in difficulty fully rinsing the acid from the sample. The amount of interference from the citric acid thus depended on how well-rinsed each sample was, which related in part to how absorbent it was. Either way, it is difficult to determine how much the citric acid treatment impacted the wastepaper due to this interference. That being said, the removal or reduction of the peak near 1420 cm^{-1} and 872 cm^{-1} occurred in all the samples.

    Homogenization under acidic conditions resulted in spectra extremely similar in shape to those of the citric acid treatment.

    Two samples had additional rinsing after the initial FT-IR analysis. These samples showed drastic reduction in all peaks, with inverted peaks at around 1038 cm^{-1}, 1008 cm^{-1}, and 917 cm^{-1}.
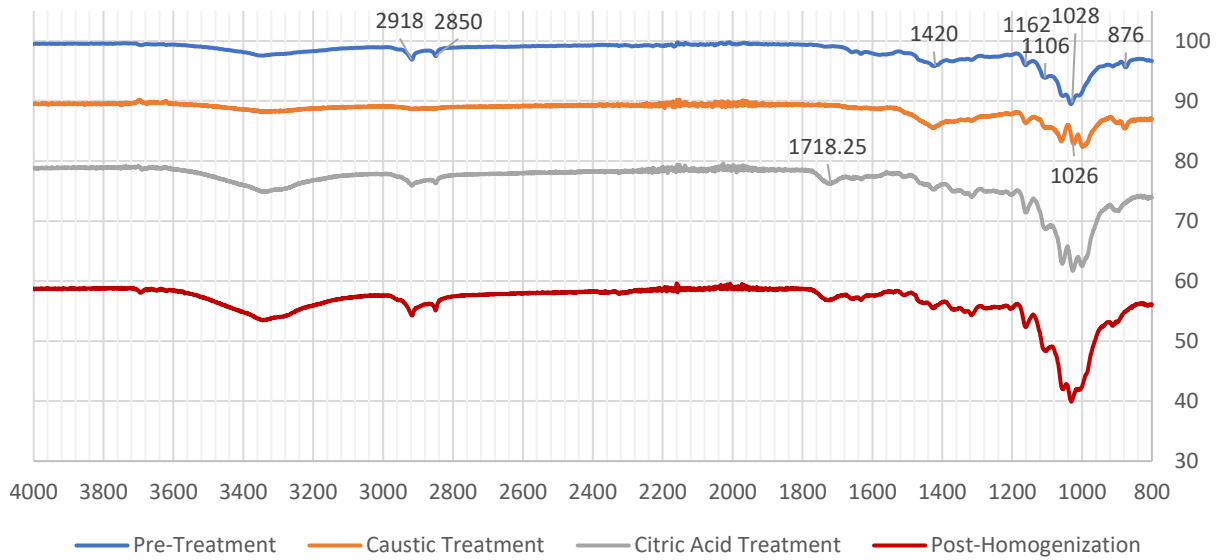
    Both the paperboard and corrugated cardboard samples did not fully break down throughout the process, so separate analyses were completed on the fine, fiber-like products, and the remaining clumped pieces of paper material. The clumped pieces had far more extreme peaks, likely due to having denser and thicker material for the FT-IR to penetrate and significantly higher absorbance of citric acid.

    The recycled-fiber napkin sample was an anomaly, with high variance across the entire spectra. Transmittance higher than 100% occurred at various wavelengths. However, some common characteristics, such as the broad peak from 3600-3000 and peaks at 1420 and from 1100-900 can still be seen.
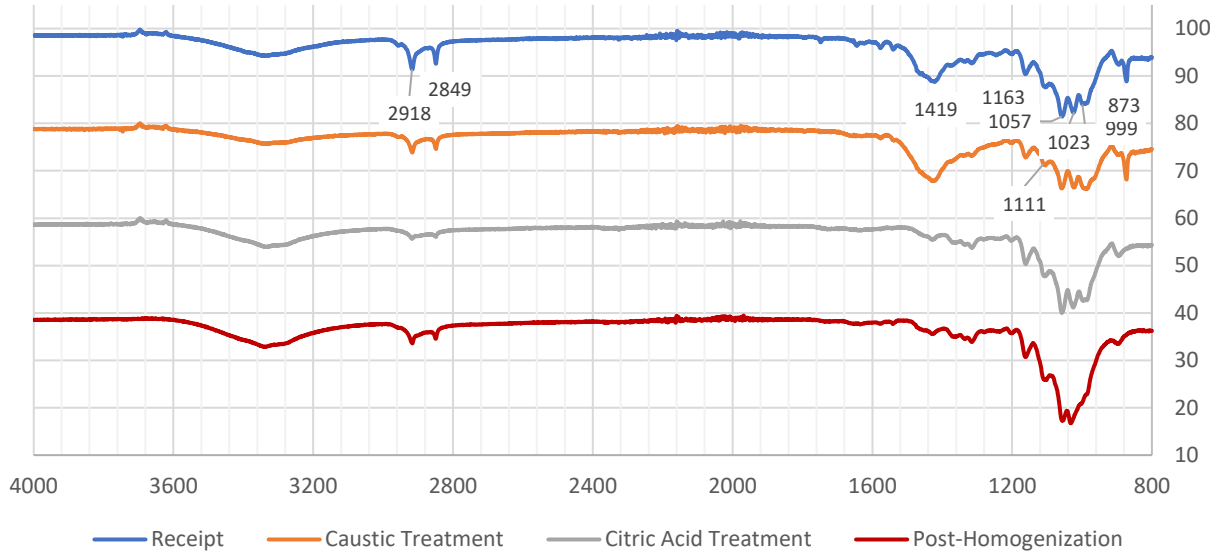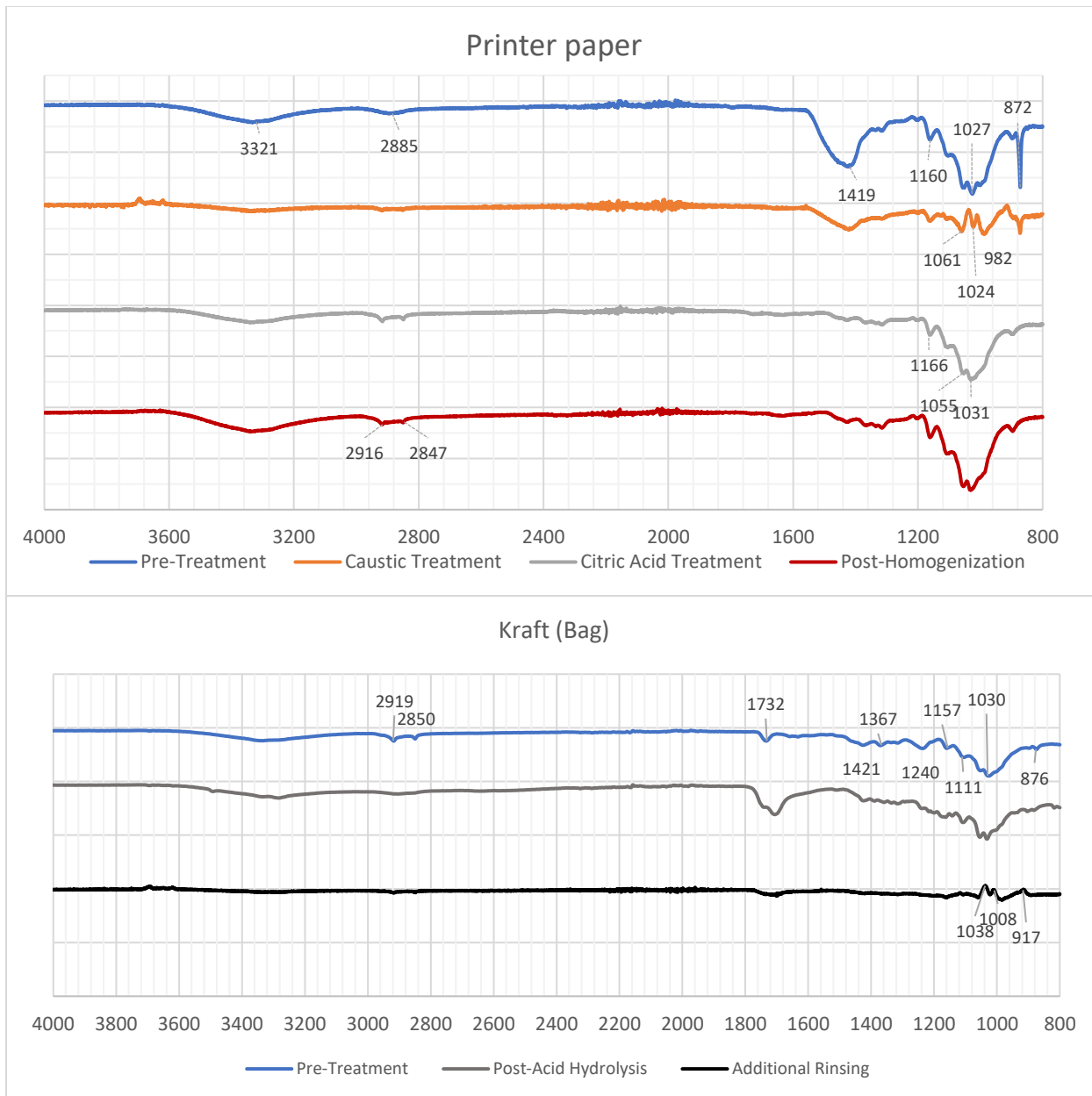
Figure 13: FT-IR spectra for samples throughout the caustic and citric acid treatment process. Receipt paper, paperboard, and printer paper all had similar spectra throughout the treatment process, with the spectra pre- and post-homogenization both incredibly similar. Kraft paper spectra (bottom) demonstrates that washing the sample to remove citric acid influence (bands in 1800-1200 range) reduced all peaks dramatically.

4.1.2 Hot Water vs Chemical Treatment

The FT-IR spectra of both hot water treated and chemically treated kraft paper and paperboard is shown in Figure 14. The top two lines correspond to the paperboard, while the bottom two correspond to the kraft paper, with green lines representing chemical treatment and blue hot water treatment. The amount of citric acid in the sample likely impacted the FT-IR readings, but the spectra remained fairly similar in peak location regardless of treatment. Chemically treated samples had additional peaks at around 1720 cm^{-1}, though the peak size varied from sample to sample.
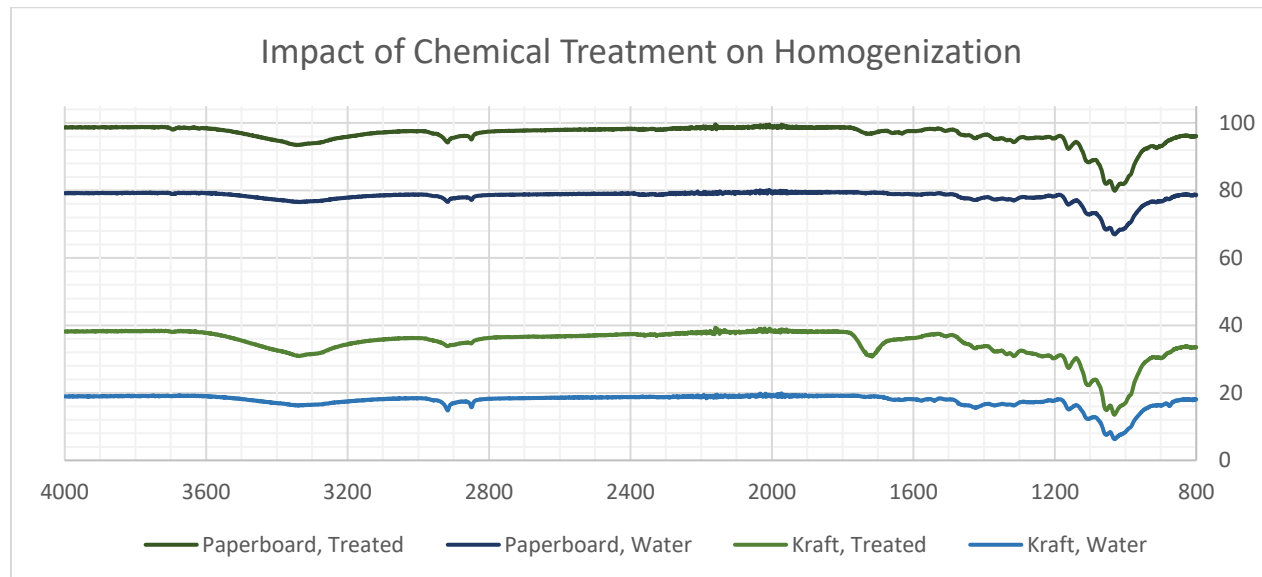

Figure 14: FT-IR spectra comparing chemical and water treatment of both paperboard and kraft samples. The paperboard spectra are the top two lines and the kraft are the bottom two, with chemical treated in green and water treated in blue.

4.2 Scanning Electron Microscopy

Scanning electron microscopy photos were taken of each sample with magnification levels ranging from 65 to 800, showing images on the scale of hundreds of micrometers, to see both overall cellulose fibril shapes and the surface morphology. Each sample has photos taken before treatment (BT), after chemical treatment with homogenization (CH), and after hot water treatment with homogenization (WH).

All of the samples were clearly not broken down to the nanoscale, with fibers varying widely in dimensions. Lengths could not be accurately estimated as most fibers were at least hundreds of micrometers long, stretched beyond the photo frames, or were obscured by other fibers. Widths varied from being under 10µm, such as in the printer paper and receipt samples, to over 40µm in some of the paperboard and cardboard samples. A small portion of fibers, seen in the CH carton in Figure 15, had widths in the nanoscale. Fiber size did not vary much throughout the treatment process, with the possible exception of the CH carton.
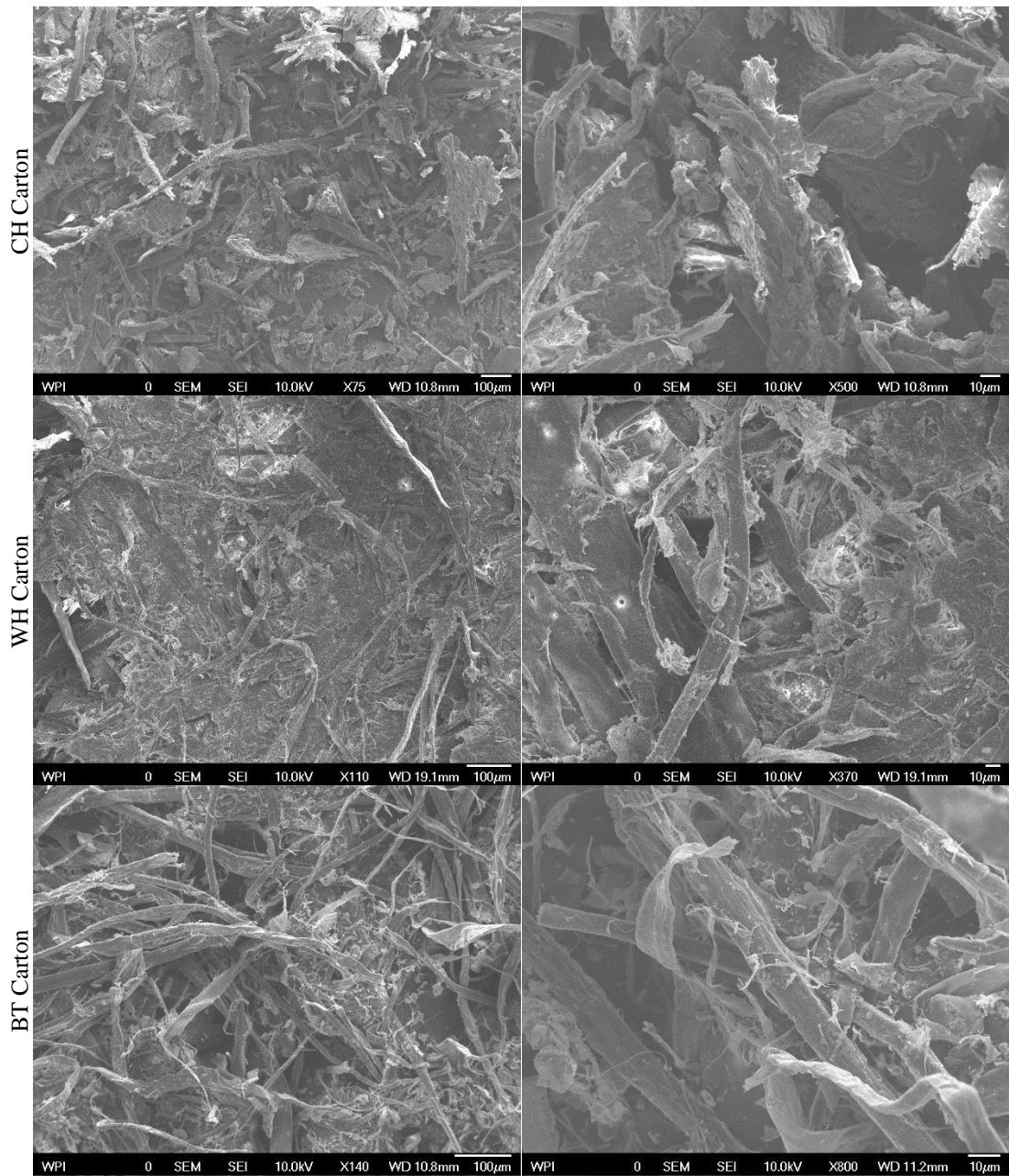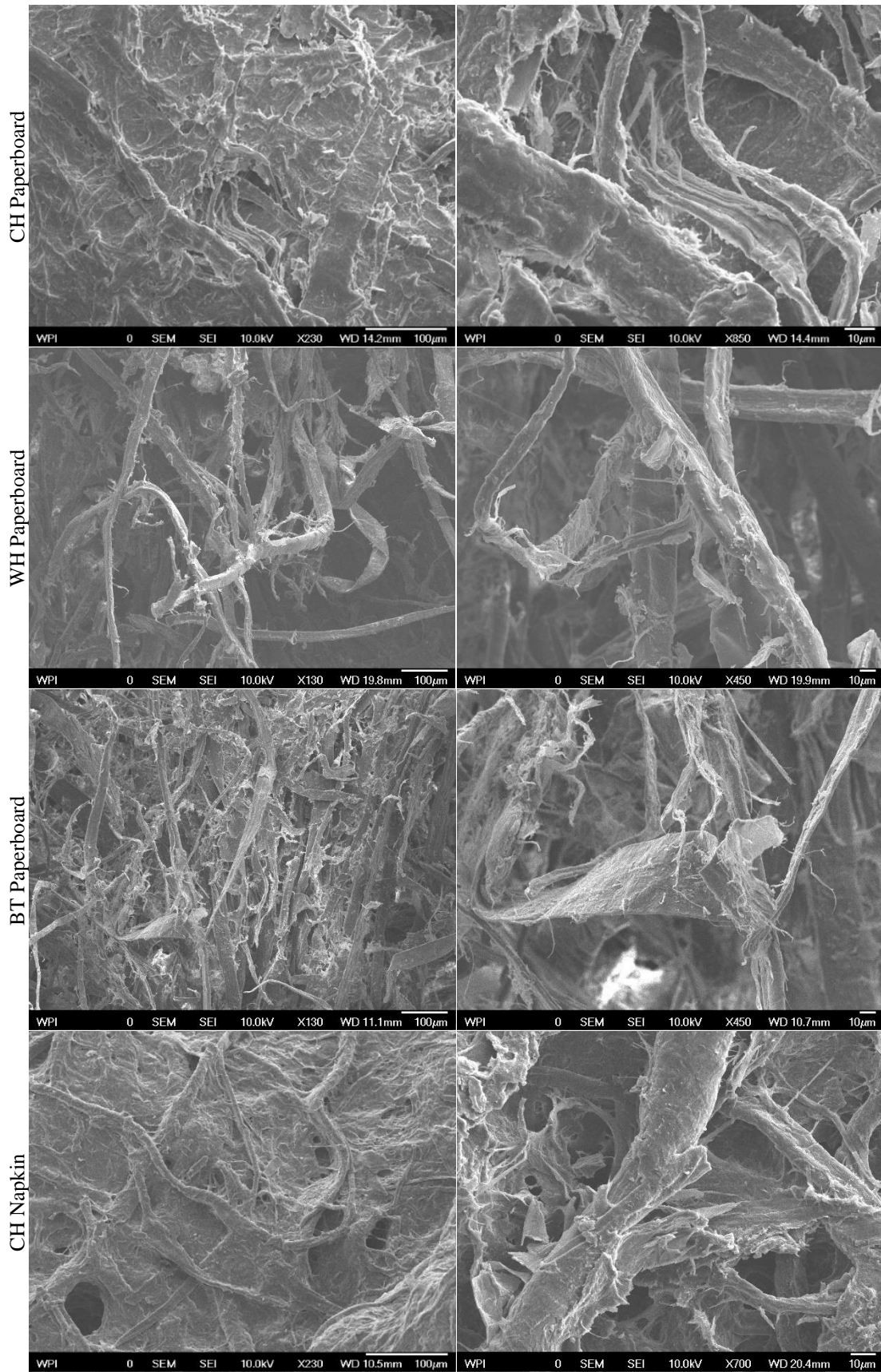
21

Figure 15: Before Treatment (BT), Water Treated and Homogenized (WH) and Chemical Treated and Homogenized (CH) carton samples.

Many fibers were flat, which can be most clearly seen in the paperboard (Figure 16) and receipt samples. Fewer were cylindrical, like that in the homogenized napkin sample (Figure 16). Overall fiber shape did not appear to change throughout treatment. Both fiber shape and size varied even within samples, with the most obvious example being the napkin samples. This is likely due to the fact that the napkins comprised recycled papers. As a conglomeration of cellulose fibers from different paper sources, it makes sense that these fibers would vary.

CH Paperboard

WH Paperboard

BT Paperboard

CH Napkin

WH Napkin

WPI   0   SEM   SEI   10.0kV   X140   WD 20.1mm   100μm

WPI   0   SEM   SEI   10.0kV   X650   WD 20.1mm   10μm

BT Napkin

WPI   0   SEM   SEI   10.0kV   X75   WD 11.3mm   100μm

WPI   0   SEM   SEI   10.0kV   X600   WD 11.3mm   10μm

CH Kraft

WPI   0   SEM   SEI   10.0kV   X95   WD 14.3mm   100μm

WPI   0   SEM   SEI   10.0kV   X500   WD 14.3mm   10μm

WH Kraft

WPI   0   SEM   SEI   10.0kV   X170   WD 20.4mm   100μm

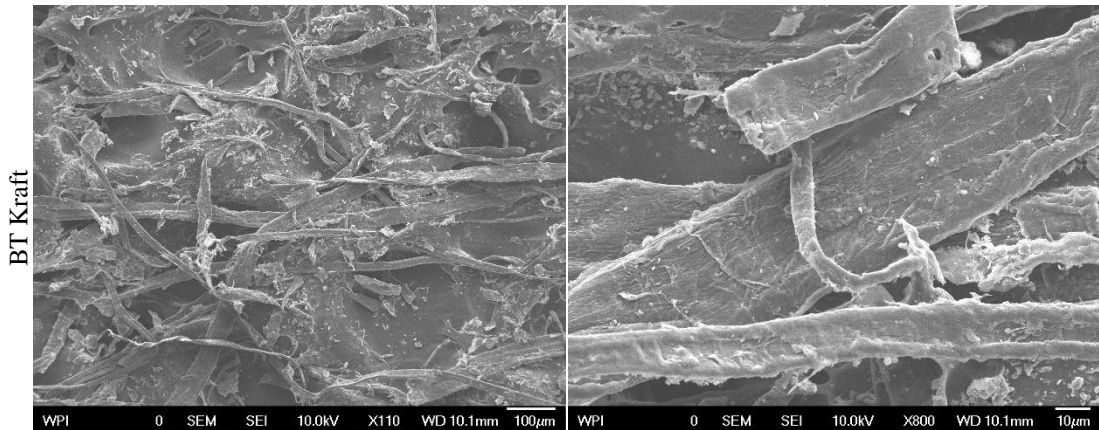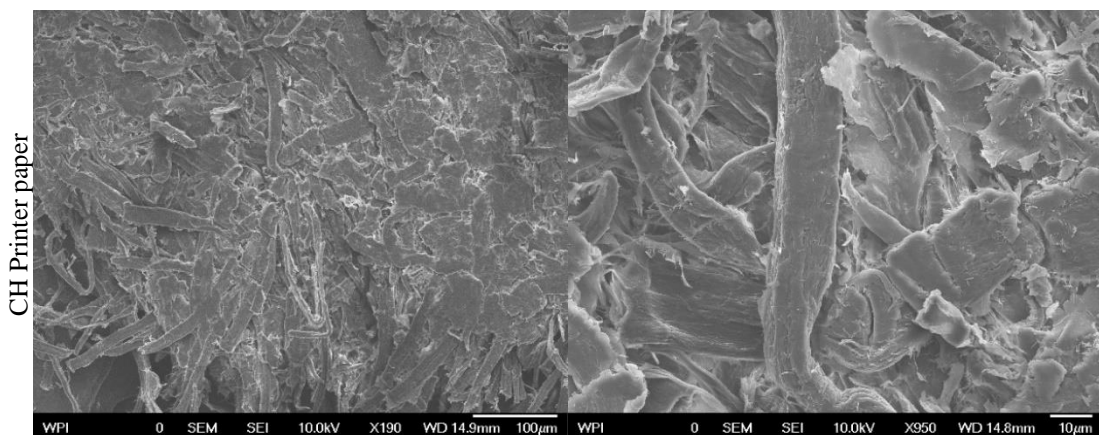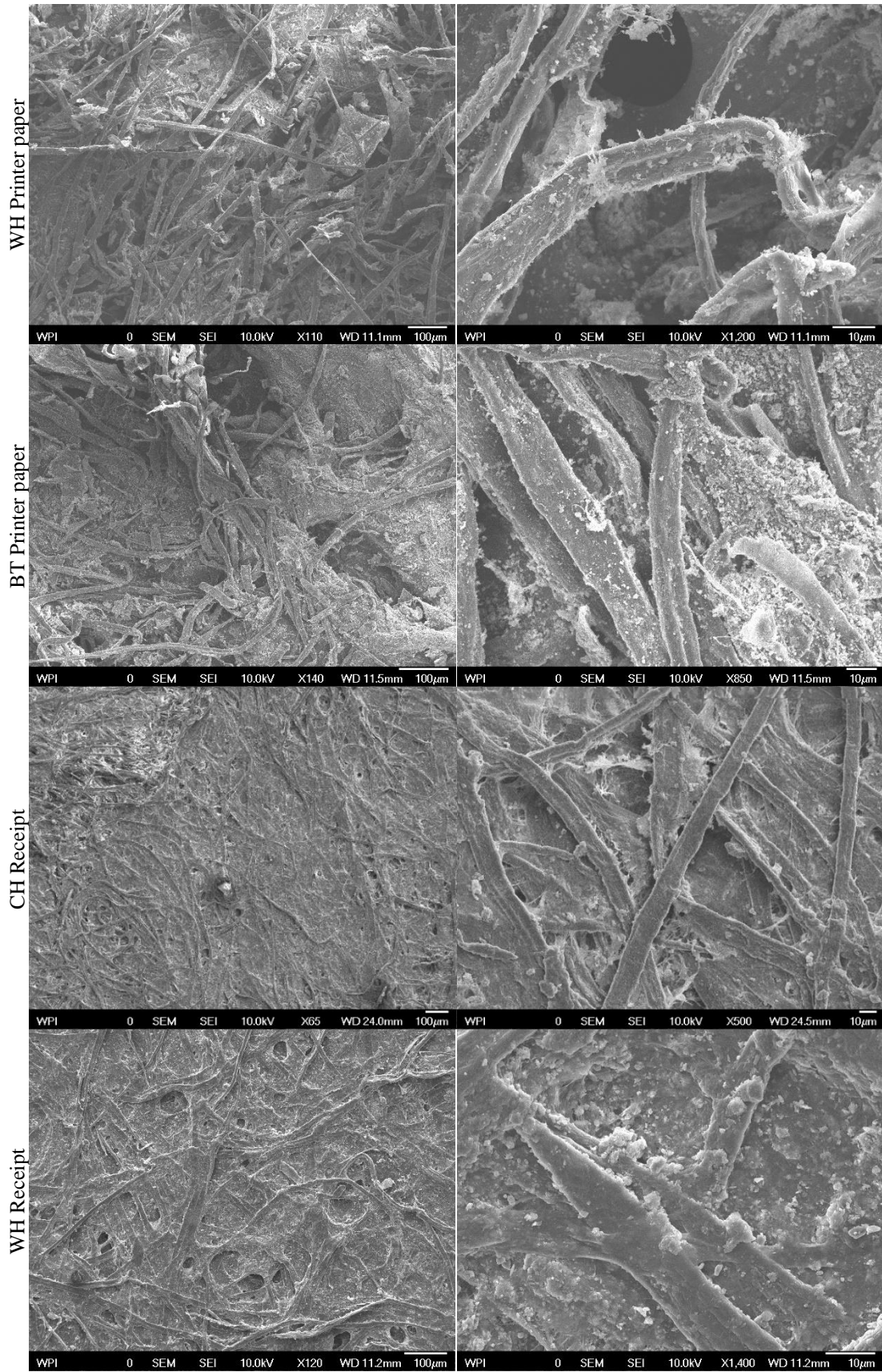WPI   0   SEM   SEI   10.0kV   X750   WD 20.4mm   10μm

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Figure 16: SEM images of Before Treatment (BT), Water Treated and Homogenized (WH) and Chemical Treated and Homogenized (CH) paperboard, napkin, and kraft samples.

The most obvious changes throughout the treatment process were in the surface morphology and pieces attached to the fibers. The BT corrugated cardboard, napkin, paperboard, kraft (Figure 16), and carton samples all clearly have thin frills and strands attached to the main fibers. These frills remained attached in the WH samples, though there were fewer in the WH paperboard and kraft samples. Chemical treatment with homogenization was most effective at removing the frills, with the CH cardboard, paperboard, kraft, and carton samples having noticeably less frills attached. The CH napkin samples did not appear to change much. The CH carton sample frills appeared to change shape and diminish, but the fibers still are not isolated.

Meanwhile, the BT printer paper and receipt samples, seen in Figure 17, were covered in small, bright particles. The WH samples had a much lower density of these particles, while the CH samples had almost none. Similar particles can also be seen in the BT kraft sample, though in significantly lower quantity.

Figure 17: SEM images of Before Treatment (BT), Water Treated and Homogenized (WH) and Chemical Treated and Homogenized (CH) printer paper and receipt samples.

Other differences in microstructure were apparent; some of the corrugated cardboard (Figure 18) and carton fibers contained regularly spaced nanoscopic perforations, most clearly visible in the 10µm BT cardboard image. The cause of these perforations is unknown. In addition, the CH carton samples contains many small, non-fibril shaped pieces, which may have been produced by breaking down the fibers. This was not observed in any other sample.
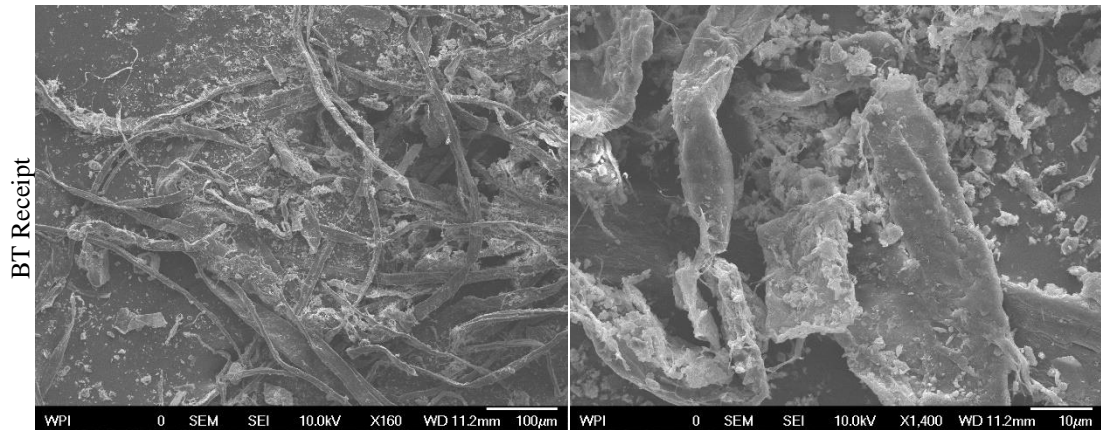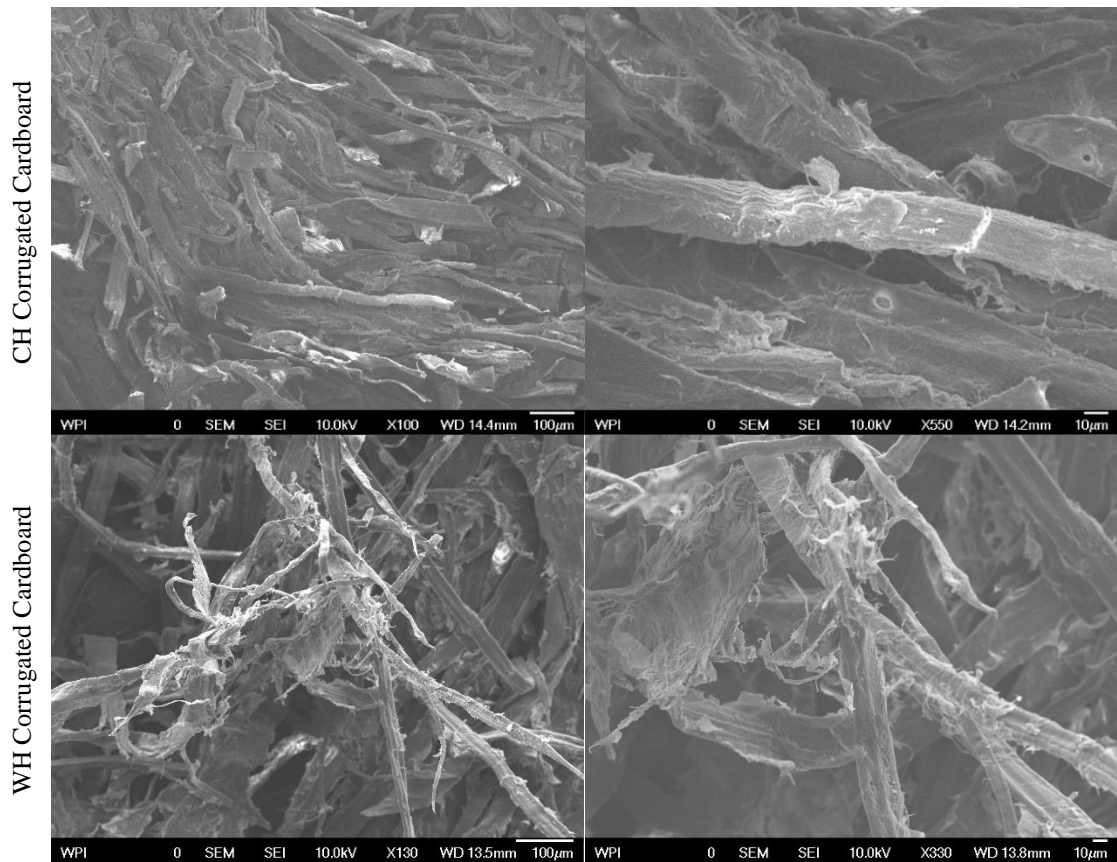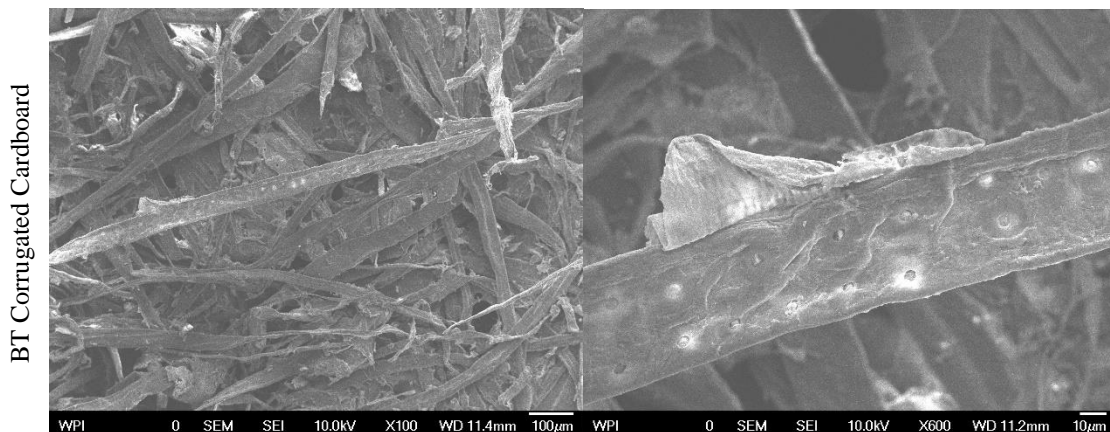
BT Corrugated Cardboard

Figure 18: SEM images of Before Treatment (BT), Water Treated and Homogenized (WH) and Chemical Treated and Homogenized (CH) corrugated cardboard samples.

Many of these images align with what was observed in Li et al., which used similar methods for nanocellulose extraction from softwood kraft pulp. These SEM images can be seen in Figure 19. Long, flat fibers with microscale dimensions can be seen. However, they have significantly less "frills" and other impurities pre-treatment compared to the pre-treatment papers, as seen in the first image of Figure 19. This is likely due to the lack of additives in kraft pulp, whereas paper products have undergone additional processes with dyes an adhesives to form the product.

After the softwood kraft pulp underwent ultrasonication, peeling, surface erosion and fibrillation can be seen on the fibers. These could be the cause of many of the "frills" on many of the paper product samples, and surface erosion is apparent on many of the CT samples, especially the printer paper, corrugated cardboard, kraft, and napkin samples.
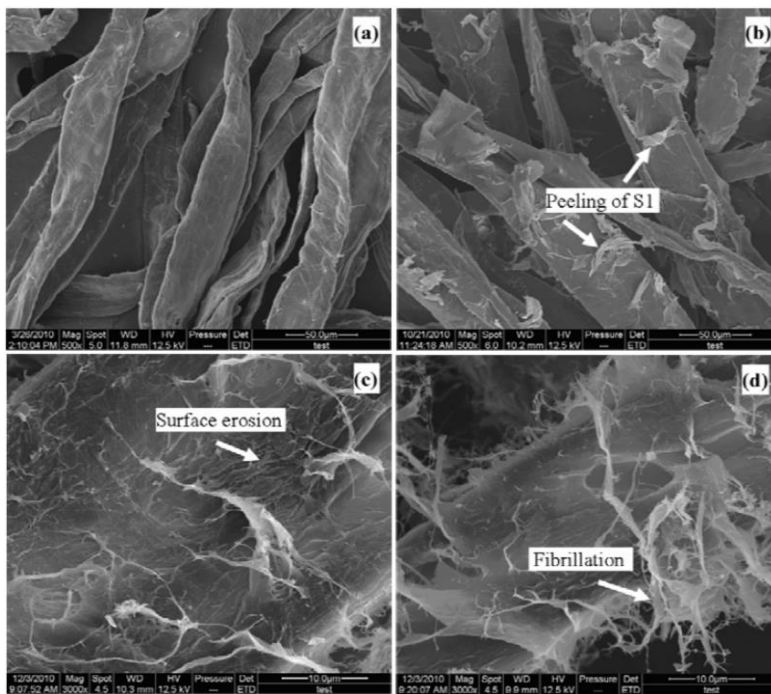

Figure 19: Microfibrils of softwood kraft pulp, before (a) and after (b,c,d) homogenization. Figure from Li, 2011.

However, the Li samples underwent additional ultrasonication with sulfuric acid, effectively breaking them down entirely into the nano scale, and those nanofibrils were successfully extracted and analyzed again under TEM. These results can be seen in Figure 20.
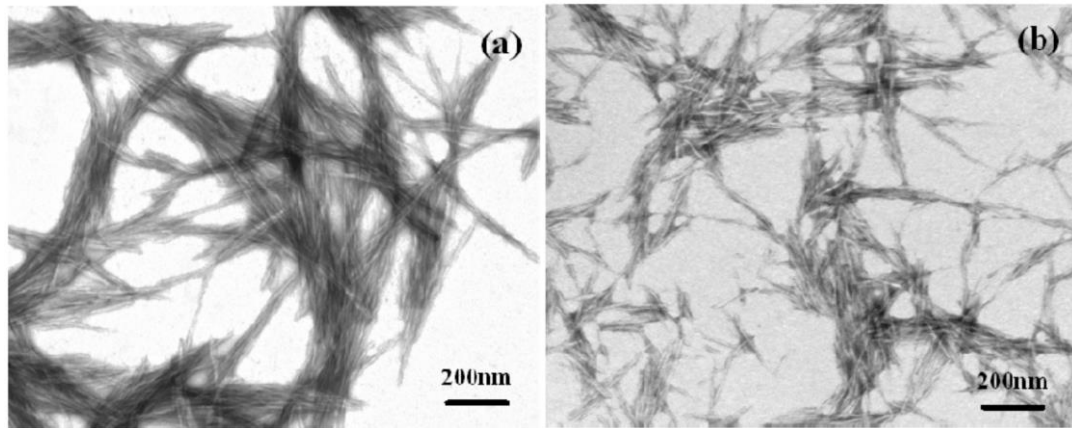

Figure 20: Cellulose nanofibrils after chemical treatment and sonication. Figure from Li, 2011.

While it is likely that some fibrils were broken down into the nanoscale from this project, not all microfibrils were, and no separation was done to remove nanofibrils from the mixture. In addition, TEM would be necessary to study nanoscale cellulose material, as magnifying on that scale with SEM would burn the sample. As a result, it cannot be determined whether this process managed to produce nanofibrils, and, if it did, what the characteristics of those nanofibrils were.

However, the microfibrils can still be compared with those from other sources. As expected, the paper product cellulose fibrils overall bore similar structures to that of softwood kraft pulp, as paper is made from kraft pulp. This morphology is different from that of cellulose found in agricultural products, such as those seen in Figure 21. These SEM images are of cellulose extracted from groundnut shells. On the microscale, the fibers bundle together and have clear ridges and waves not present in the paper samples. The nanocellulose extracted also has a different morphology from that of the softwood kraft pulp, where the crystals are longer, straight, and do not have "branches" across the structure.
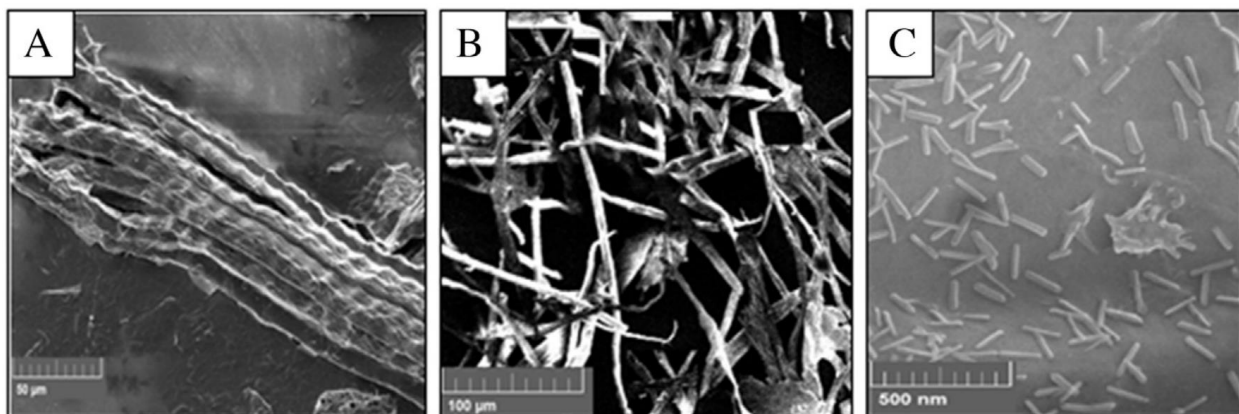

Figure 21: Cellulose microfibrils recovered from groundnut shells (a) and the produced cellulose nanocrystals (b,c). Figure from Bano & Negi, 2017.

Whether the microfibril structure impacted the nanocrystal structure, or whether it is purely a product of the processing the microfibrils underwent to produce the nanofibrils, is unclear. Either way, it is expected that further processing and nanofibril separation from paper products would result in fibrils more similar to those from Li et al.

Ultimately, the main takeaways from SEM analysis are that:

- Microfibrils vary significantly in morphology across paper sources but are still distinct from those derived from other sources
- Treatment reduced the amount of other impurities in the samples and generally increased peeling and fibrillation
- Chemical treatment was more effective than water treatment in removing impurities and increasing microfibril treatment
- It is unsure whether any nanofibrils were produced, and, if so, what their characteristics were

4.3 Energy Dispersive X-Ray (EDX)

Energy Dispersive X-Ray analysis (EDX) was attempted to determine the identity of substances stuck to the cellulose fibers. However, due to the nature of EDX and flammability of cellulose, EDX analysis could not be completed. Magnifying enough for EDX resulted in the sample burning before EDX could be completed, and at a lower magnification, EDX itself also burned the sample. Only the presence of carbon could be determined, as seen in Figures 22 and 23.
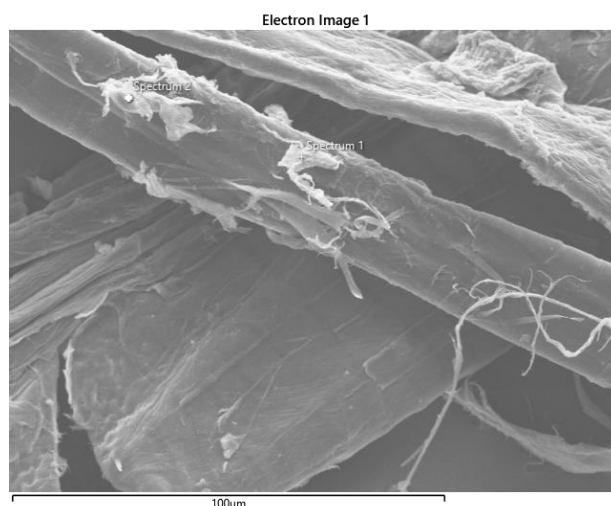

Figure 22: SEM image of EDX site, marked near the middle as "Spectrum 1". The fibrils warped during analysis, indicating burning.
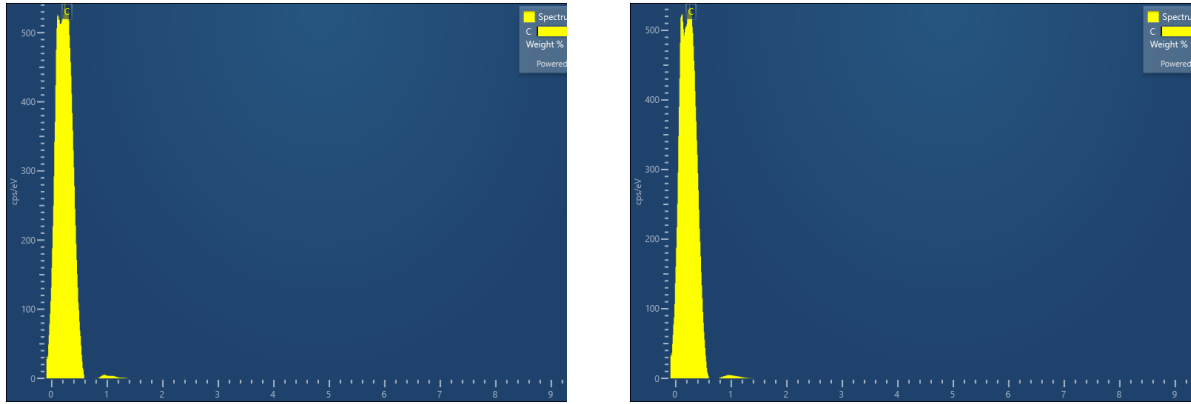
Figure 23: EDX Spectra from the sample. Due to the low magnification, the only element able to be identified was carbon.

5.0 Process Design and Feasibility

In order to understand and visualize the requirements for creating this process on an industrial scale, various aspects of plant design including plant size, worker safety, and reactor types were considered. As far more research needs to be complete to develop accurate assumptions for a scaled-up process, a simple adjustable model was developed using Microsoft Excel was developed to determine plant size, chemical storage requirements, and material costs.

5.1 Process Design and Requirements

The process flow diagram (PFD) for the proposed process is shown in Figure 24. All incoming paper undergoes shredding and drying. Afterwards, the stream enters a continuous stirred-tank reactor (CSTR) with 5wt% caustic solution for delignification. The resulting fibers then enter a settling tank, with a portion of the caustic bath recycled back into the CSTR. The fibers are then washed with water until the pH is neutral, dried again, and fed into a citric acid CSTR. This solution is then fed into ultrasonic homogenization, still including the acid. Once homogenization is complete, the fibers are settled and dried into product.
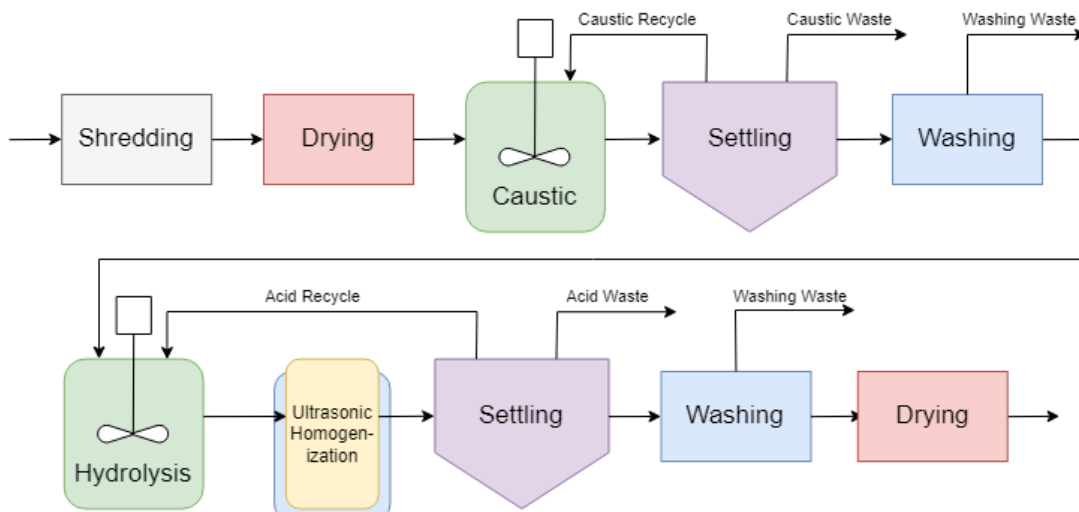

Figure 24: PFD for industrial scale nanocellulose extraction from paper.

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All incoming paper is shredded into small flakes to maximize the surface area that the caustic and acid can react with. Given the experimental results, additional mechanical breakdown steps such as ball milling may be useful and lessen the time and concentrations required for chemical treatment. Drying is done to eliminate any moisture that could interfere with the delignification and hydrolysis steps and drive off any volatile impurities.

The reaction is assumed to have zero-order kinetics with respect to paper concentration. Assuming that the paper input is shredded enough to have adequate reaction surface area and that the concentration is low enough to prevent large amounts of flocculation, the rate at which the paper is broken down is assumed not to change with time and varying concentration.

Each chemical treatment step, caustic and acid, is suggested to be done in a CSTR. This is preferable to a Plug Flow Reactor due to large amounts of paper fiber solids that would settle without constant stirring, and Batch Reactors or Sequenced Batch Reactors that do not allow for a continuous process. Due to the zero-order kinetics, the volume required would not be impacted by reactor type.

Assuming a solvent:paper ratio of 20:1, residence times of 3 hours, a dry paper density of $200g/cm^3$, and that the paper swells to three times its initial size in solution, both the caustic and acid CSTRs would have required volumes of at least 25,000L for a plant processing 10,000kg of paper waste per day.

Without recycle streams, 66,500kg caustic and 1,010,800kg citric acid would be required per week. Due to the high cost of caustic and high quantity of citric acid, recycle streams could drastically cut down on potential cost. However, due to accumulation of other impurities, occasional purging would be necessary. Some solution will inevitably be lost as the saturated fibers are washed.

Settling steps are necessary to allow for recycling of solvent off the top and collection of the settled, saturated paper fibers. Allowing for residence times of 8 hours, each settling tank would need to be at least 67,000L. Washing is necessary after the caustic step to prevent caustic from entering the acid hydrolysis step and increasing the pH. Completing homogenization under acidic conditions will give additional time for hydrolysis. A cooling jacket around the homogenization chamber is necessary to prevent overheating of the reactor. This cooling jacket, depending on material, could use the waste from the wash steps to reduce additional need for outside waters. Depending on how much the homogenization heats the cooling jacket, it could be possible to recapture some of this energy for use in the CSTR heating. The homogenization is expected to be the most energy-intensive step.

The first washing step is performed by pumping neutral pH water through the settled paper fibers against a filter. Determination of fiber size after each step will be necessary to pick appropriate sized filters that prevent loss of nanomaterial.

The final product is then dried and sold. Traditional oven drying is less energy intensive than freeze-drying, but depending on the thermal stability of the final product, freeze-drying may be necessary.

All calculations were completed using the Excel model, screenshotted in formula view below in Figure 25. Recommended values can be more accurately determined when optimization is complete; for now, placeholders similar to those used in the experimental setup are used, with increased acid residence time. Sample outputs are shown in Figure 26.

Figure 25: Excel model for preliminary plant information shown in formula view.

Figure 26: Sample model output.

	A	B	C	D	E	F	G	H	I
1	User Inputs					Process Requirements			
2									
3	Operating Parameters					Consummables	Per Week	Per Month	Per Year
4	Hours per week	134				Caustic (kg)	2,219	9,508	115,680
5						Citric Acid (kg)	33,721	144,520	1,758,331
6	Feed and Sorting	User Input	Recommended			Caustic Water (L)	42,152	180,650	2,197,913
7	Mass per day (kg)	10000				Acid Water (L)	10,649	45,638	555,262
8	Feed Composition (mass%)	100%				Energy (kWh)			
9	Paper Product	80%							
10	Non-Paper Product	20%				On-Site Storage	Per 2 Weeks		
11	Paper Yield	95%				Caustic (kg)	4,437.03		
12	Paper Density (kg/L)	300.00				Citric Acid (kg)	67,442.82		
13	Paper Vol Increase in Solution	200%							
14	Paper Entering Process	7600.00				Reactor Sizes			
15						Caustic CSTR (L)	305.07		
16	Caustic Process					Citric Acid CSTR (L)	305.07		
17	Caustic Concentration (mass%)	5.0%	5%						
18	Caustic Temperature ©	80	80						
19	Caustic Residence Time (hr)	3	3						
20	Solution:Paper (Liters:Kg)	20:01	20:01						
21									
22	Washing Process								
23	Yield	100%							
24									
25	Citric Acid Process								
26	Citric Acid Concentration (mass%)	76.0%	76%						
27	Acid Temperature ©	80	80						
28	Acid Residence Time (hr)	3	3						
29	Solution:Paper (Liters:Kg)	20:01	20:01						
30									
31	Storage								
32	Caustic (weeks)	2	2						
33	Citric Acid (weeks)	2	2						

5.2 Worker Safety

Neither caustic nor citric acid are hazardous substances regulated by OSHA (*1910 / Occupational Safety and Health Administration*, n.d.). However, caustic has a number of associated health risks. It is highly corrosive to metals, can cause severe chemical burns and eye damages, and fumes can cause respiratory irritation (ThermoFisher Scientific, 2021). Citric acid is relatively benign, but can cause eye irritation (ThermoFisher Scientific, 2014). As a result, workers should wear personal protective equipment including eye protection and protective coverings when working with the stored anhydrous chemicals. Should any work be done on the caustic CSTR, a breathing apparatus is highly recommended to prevent inhalation of caustic fumes. In addition, the inside of the caustic CSTR and any pipes delivering caustic material should be treated or coated to prevent corrosion.

The CSTRs operate each operate at 80C. Third degree burns can occur in less than a second at any temperatures above 68C; as a result, ensuring that the reactors are properly insulated is important for worker safety in addition to maintaining high energy efficiency. Heat protective gear needs to be accessible for any work dealing with hot effluent or the CSTRs.

In order to prevent hearing damage from the ultrasonic homogenizer, hearing protection such as sound mufflers are recommended, and the sonicator room should be sound-proofed with doors shut during operation (*UofR: EHS: Occupational Safety: Sonicator Safety*, n.d.).

5.3 Environmental Safety and Regulations

Regulations are assumed to be similar to those the EPA requires of polymer and synthetic polymer manufacturers.

Neither citric acid nor caustic are priority pollutants, leaving the main concern as high and low pH discharges. The EPA requires that any wastewater be above a pH of 6.5 and under 11. One of the simplest ways to address this is by combining the two streams, testing the pH, and adding additional caustic or lime to ensure that the pH is higher than 6.5. This may or may not be necessary depending on the ratio of spent caustic to spent citric acid. Other pollutants from papers entering the process may need to be addressed. For example, depending on the amount of thermal papers entering the process, BPA may be present in damaging concentrations for marine life.

Wastewater should be directed to a nearby wastewater treatment plant, and as a result, it will be necessary to ensure any wastewater meets their standards and any specific, difficult to treat pollutants, are taken care of beforehand.

6.0 Conclusions and Recommendations

The experimental work has demonstrated that the microfibrils from different paper sources vary significantly in shape, size, and overall structure. Lots of impurities – especially in colored paper products, such as printer paper and receipts – cling to the fibrils but can be removed through chemical treatment, as seen in the SEM photos. Chemical treatment appeared to have a greater impact on the fibril impurities than water treatment. In addition, in comparison to fibrils from fresh kraft pulp photographed from other studies, SEM photos showed that fibrils in processed paper waste have undergone significant amounts of peeling and tearing.

Further analysis on the peeling and impurities will need to rely on characterization methods other than SEM and EDX due to sample burning. Potential alternatives could be using an optical microscope or transmission electron microscopy (TEM) to better visualize the peeling and size of fibrils, while methods such as ICP-OES can determine the composition of impurities.

Determining what impurities are present will be especially important for process commercialization, as the presence of certain toxic compounds such as BPA in receipts may impact where a plant can discharge spent solvents and how the process waste can be handled. In addition, impurity removal from potential nanocellulose will be important for creating a commercially viable product.

A plant could potentially produce nanofibrils from recovered waste paper using a caustic-citric acid-ultrasonication treatment method, but more changes would need to be made to this method to make it viable. In addition, ultrasonication could prove to be too energy intensive to be sustainable. Future work should stay in the preliminary process development on adjusting the method until nanofibrils are produced from paper, determining whether the waste paper

nanofibrils will vary as much as the microfibrils do, and eventually optimizing the process in terms of cost, energy, and overall environmental impact.

In order to develop a process successful in producing nanofibrils, we recommend using ball milling, a different ultrasonication method, cryogenic freeze drying, and increasing residence times in the caustic and acid baths.

Ball milling has been cited in some studies as significantly reducing the acid concentration required to break down lignin and hemicelluloses by further mechanically breaking down fibrils before the chemical process begins (Phanthong et al., 2016). Given that the current high citric acid concentration interfered with FT-IR analysis and may be difficult to remove from a final product, its additional requirements may be worth it. In addition, breaking down microfibrils before treatment will increase overall reaction surface area and make it easier to further reduce them to nanofibrils chemically.

Furthermore, a different ultrasonication method is necessary to break down microfibrils into nanofibrils. The ultrasonic homogenizer used in this project had a power of 700W operating at a 55 amplitude. Some successful studies have reported similar power levels, such as 500W and 800W, with times varying from 30 minutes to 180 minutes (Lee et al., 2014; Takagi et al., 2013; Yang et al., 2017). This project was on the lower end, with 40 minutes broken up into 4 10-minute intervals.

Most other studies did not report solid:liquid ratio for ultrasonication, though Yang et al. reports a 1:300 ratio. This project used a 1:160 ratio. Further dilution may yield better results, in addition to increasing amplitude or using a higher powered ultrasonic homogenization. The use of catalysts in ultrasonication may also be explored, such as the use of $FeCl_3$.

In addition, longer residence times in each bath could allow for the samples to break down further before ultrasonication. Ultrasonication can also occur in an acid bath and be maintained at higher temperatures so that samples break down both chemically and mechanically. The pH of the bath varied in this project due to the inability to completely rinse samples of citric acid. FT-IR data demonstrated that citric acid remained in the samples even after washing, which could impact final product uses and the ability to modify nanocellulose surface groups. Measuring and maintaining a constant pH across samples could yield different results.

Once nanocellulose extraction has been accomplished, and assuming that products are of reasonable purity from the majority of paper feeds without need for excessive additional sorting, more work will be necessary to design a pilot plant. Variables such as residence time, solvent concentrations, and solvent recycle rates will need to be established before economic analysis can be accurate and complete. The washing step will also need further testing and design. Depending on what kind of filter is used, membrane fouling could pose a major issue. Monitoring equipment will also depend on what kinds of additional chemicals are found in the paper waste throughout processing.

Large-scale yield experiments and methods of final separation and packaging will also be necessary. Once the nanocellulose has been characterized, a market for nanocellulose with that particular structure will need to be determined.

All in all, significantly more work is necessary to determine the feasibility of nanocellulose extraction from waste papers. This work presents some crucial first steps and has determined that as is, the chemical treatment method needs to be, at minimum, coupled with additional mechanical treatment for successful nanocellulose extraction.

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