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TÍTULO: Natural Cellulose as a Solution to Remediate Aldehyde Volatile Organic Compounds in Air Pollution

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DEDICATION

This final work prior to obtaining the title of Biomedical Engineer is dedicated mainly to my father Robinson Bravo, who is and has always been my strongest pillar, and who has always been my best advisor, giving me his best words in the most difficult moments. Especially because he has taught me what it is to be an exemplary father, and a good man. Also, I dedicate the present work to my wonderful mother Ivon Salazar, who has been able to support me in my worst and best moments, and who with her endless love has pushed me to the end of the road where I finally meet. Likewise, it is dedicated to her for proving me what is to be a strong woman, and an example to follow.

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RESUMEN

Los Compuestos Orgánicos Volátiles (VOCs) aldehídos son moléculas tóxicas comúnmente liberadas a la atmósfera por una variedad de fuentes antropogénicas, agravando de manera considerable la contaminación ambiental. En Ecuador, los VOCs presentes en la contaminación del aire son un inductor importante para varias enfermedades respiratorias, cardiovasculares y neurológicas. Basado en el creciente interés en el desarrollo de materiales sostenibles y amigables con el medio ambiente para la descontaminación del aire contaminado con VOCs, la celulosa se ha convertido en un posible importante candidato. Sin embargo, hoy existe una falta de entendimiento sobre las propiedades fisicoquímicas que afectan la adsorción de VOCs, y el efecto que tiene la fuente de extracción en estas características intrínsecas del material. El presente estudio se centró en la evaluación de fibras de celulosa no modificadas extraídas de fuentes naturales de Ecuador como posibles descontaminantes de VOCs. La espectroscopia infrarroja por transformada de Fourier (FTIR), el análisis termogravimétrico (TGA), la difracción de rayos X (XRD), las mediciones de adsorción de Brunauer, Emmett y Teller (BET) y los métodos de microscopía electrónica de barrido (SEM) se utilizaron para caracterizar las propiedades fisicoquímicas de las fibras aisladas. Varios trabajos de investigación sugieren que los micro- y nanomateriales modificados con aminas son agentes adecuados para la captura de VOCs. Por ello, se realizaron modificaciones superficiales de la fibra natural F28 con recubrimiento de polietilenimina (PEI) para demostrar una mayor eficacia de adsorción. Los ensayos de cromatografía de gases (GC) demostraron que las fibras de celulosa no modificadas adsorbían los VOCs aldehídos, como el hexanal, alcanzando una reducción de hasta 56.42 ± 7.30%. Además, GC demostró efectivamente que el recubrimiento electrostático de la superficie de la muestra de celulosa F28 con pequeñas cantidades de PEI mejoró sus capacidades de remediación de VOCs (es decir, 98.12 ± 1.18%). Los resultados demostraron que la fuente natural de extracción puede afectar las propiedades de las fibras aisladas para la captura del hexanal, y que estos materiales, de hecho, suponen una solución ecológica para la remediación efectiva de los VOCs aldehídos en la contaminación aérea.

Palabras Clave: Celulosa; Biodiversidad; VOCs; Descontaminación; Funcionalización Amina; Contaminación Aérea; Sostenibilidad

ABSTRACT

Aldehydes are commonly encountered in VOCs released to the atmosphere from a variety of anthropogenic sources that seriously aggravate the environmental pollution. In Ecuador, VOCs present in air pollution are an important inductor for several respiratory, cardiovascular and neurological diseases. Based on the increasing interest in developing sustainable and environmentally friendly materials for the decontamination of VOC-polluted air, cellulose has emerged as one possible candidate, but there is a lack of understanding of the physico-chemical properties affecting the adsorption of VOCs, and the effect of the extraction source on these intrinsic features. The present study focused on the evaluation of unmodified cellulose fibers extracted from natural sources of Ecuador as potential VOC decontaminants. Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), x-ray diffraction (XRD), Brunauer, Emmett, and Teller (BET) adsorption measurements, and scanning electron microscopy (SEM) methods were used to characterize the physico-chemical properties of the isolated fibers. Several research works suggest that amine-functionalized micro- and nano-materials are suitable agents for the capture of VOCs. Surface modifications of the natural fiber F28 with polyethylenimine (PEI) coating were performed to prove enhanced adsorption effectiveness. Gas chromatography (GC) assays demonstrated that unmodified cellulose fibers adsorbed aldehyde VOCs, like hexanal, reaching up to a $56.42 \pm 7.30\%$ reduction. As well, GC effectively proved that electrostatic surface coating of the cellulose sample F28 with small quantities of PEI enhanced its VOC remediation capacities (*i.e.* $98.12 \pm 1.18\%$). Results demonstrated that the biodiversity extraction source can affect the hexanal vapor capturing properties of isolated fibers, and that these materials, indeed, suppose an environmentally friendly solution for effective remediation of VOCs in polluted air.

Keywords: Natural cellulose; Biodiversity; VOCs; Decontamination; Amine-functionalization; Air Pollution; Environmental sustainability

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PROBLEM STATEMENT

Since the beginning of the industrial revolution in the XIX century, humanity has been ignoring one of the most dangerous threats to all the biological systems that make up our world, the environmental pollution. Today, environmental pollution, seriously aggravated by the massive population growth and the exhaustive technological development, is one of the significant health concerns that human kind faces. The contamination of the components of the soil and atmosphere can be divided into three principal types of pollution: land, water, and air pollution (Muralikrishna & Manickam, 2017). Soil, water, and air pollution are principally caused by anthropogenic activities, such as mining, refineries, factories, power plants, vehicles, landfills, among others. Hydrocarbons, fossil fuel derivatives, solvents and chemical wastes, organic compounds, insecticides and herbicides, and heavy metals are the most common types of contaminants released to the environment as industrial and domestic wastes (Schweitzer & Noblet, 2018).

The adverse health effects caused by the exposure to hazardous contaminants present in all types of pollution are responsible for the development of several cardiovascular, neurological, and respiratory disorders, neurodevelopmental problems in infants, infections in almost all organs, immune depression, and tumor development, among others. These chronic and acute health problems are the main reason why today's environmental pollution is an urgent health concern for international governmental organizations (Kampa & Castanas, 2008). According to the World Health Organization (WHO), in 2017, 1.7 million deaths of children under five years old are linked to the contamination of the environment, and each year 570.000 of those deaths are linked explicitly to air pollution. Base on these alarming data, air pollution can be seen as one of the most dangerous types of pollution affecting not only our health but also our social development as humans.

Currently, several biological, physical, and chemical technologies and research studies have been evaluated to address and control air pollution. In fact, nanotechnology and the manipulation of particles at the nanoscale together with the use of different organic and inorganic materials have been the most studied and developed decontamination methods in the literature (Wang et al., 2013). According to Rickerby and Morrison, in 2007, nanomaterials (NMs) exhibited an increased reactivity compared with larger particles, which are mainly caused by their specific surface area. Indeed, based on the complex chemical structures of the leading toxic gases (NO_X, SO_X, CO, NH_3 or VOCs) commonly present in air pollution, and thanks to the unique physicochemical properties that nanomaterials offer, different nanostructured materials have been specially tested as air decontamination agents (*i.e.*, TiO_2 nanoparticles (NPs), graphene-based NMs, titanate nanotubes, fullerene, carbon nanotubes, silica nanocomposites, polymeric-based NMs, among others) (Elham, 2017). Thus, these innovative methods have been gaining a lot of attention from academic and governmental organizations, since Boehm in 2006 estimated that nanotechnology applications in environmental remediation would reach in the world market a profit of approximately $6 billion by 2010.

Despite the potential and essential physicochemical properties that NMs have demonstrated throughout the literature, these particles are, usually, unstable at standard conditions, their preparation and formulation require specific and complicated procedures, and some may present high toxicity, and the possible generation of hazardous byproducts once used as remediation agents. Therefore, it is common that only a few nanotechnology applications for the remediation of polluted air come to be finally commercialized or marketed (Mueller & Nowack, 2010).

The most important objective for an effective decontamination of polluted air using engineered remediation agents is that the material utilized must not be a contaminant itself once employed. Importantly, several of the critical parameters to consider when developing a new remedial agent are cost-effectiveness, non-toxicity, biodegradability, reusability, and facile extraction and/or formulation of the particle. Consequently, biodegradable or natural materials are strongly arising in academia as sustainable and safer candidates for the efficient decontamination of polluted air (Guerra et al., 2018a). All these characteristics that a material should meet to be considered a safer and environmentally friendly solution are present in natural or biodegradable polymers, like cellulose. This polysaccharide is one of the most important structural molecules that form the skeleton of plant cell walls. Although it is an abundant polymer worldwide and is practically considered an inexhaustible source of biopolymeric raw material, the magic behind this natural material is that it has ideal physicochemical properties to carry out more effective, greener, and biocompatible decontamination processes (Klemm et al., 2005).

Interestingly, Ecuador is one of the most species-rich countries on the planet, harboring approximately twenty thousand unique species of plants from which cellulose can be obtained presenting unique native properties, like different morphologies, sizes, porosity, degradation temperatures, surface chemistry, and crystallinity index. Furthermore, Ecuador possesses seventeen different ecosystems containing abundant natural resources that still have not been undisturbed by man, as well as many endemic plant species with undiscovered properties (Valencia, 1995; Larrea, 2013). Taking advantage of the megabiodiversity that Ecuador owns makes possible to create new natural methods of solving one of the most important problems for humanity, such as air pollution. The option of using cellulose as a remediating agent holds a promise as it is cost-effective, highly marketable, and powerfully versatile, making it an ideal candidate to replace synthetic materials for the proper answer to address air pollution.

OBJECTIVES

General Objective:

Evaluate the aldehyde VOC capture capacity of unmodified and PEI-coated cellulose fibers obtained from different natural Ecuadorian resources and determine the effect of its extraction source on its VOC decontamination properties.

Specific Objectives:

- Extract and purify six natural cellulose fibers from six different biodiversity sources present in Ecuador.
- Surface modify the native cellulose isolate with poly(ethyleneimine) to enhance its capability to capture aldehyde-based VOCs.
- Characterize the physico-chemical properties of the unmodified and modified cellulose isolates along with commercial controls using TGA, FT-IR, XRD, SEM techniques, and BET adsorption measurements.
- Perform gas chromatography assays to study the VOC capturing capacities of the unmodified and amine-treated cellulose fibers and compare them with the commercially available cellulose controls.

CHAPTER 1

1. THEORETICAL FRAMEWORK

1.1 Volatile Organic Compounds (VOCs)

Air pollution is one of the biggest problems that our world is facing. The most common contaminants present in air are carbon monoxide, chlorofluorocarbons, hydrocarbons, nitrogen oxides, organic compounds (volatile organic compounds (VOCs) and dioxins), sulfur dioxide, and particulates (Taylor et al., 2012; Khin et al. 2012). Additionally, pollution can lead to the development of multiple diseases negatively influencing human wellness (Kampa & Castanas, 2008; Haseena et al., 2017). Hence, environmental pollution harms the ecosystems and the biodiversity of the world. In the same way, the appearance of different respiratory, cardiovascular, neurological diseases, adverse effects on the endocrine system, and the neurodevelopment in infants is attributable to the exposure to air pollution (Tchounwou et al., 2012). Thus, a number of toxic chemicals are commonly present in indoor air. One of the most common and hazardous pollutants present in indoor materials, such as furniture, equipment, consumer products, cleaning and maintenance agents are the VOCs. These are chemicals composed of carbon and hydrogen as regular organic particles. These compounds can be classified based on their boiling points into very volatile organic compounds (VVOCs) with boiling points from < 0 °C to 50–100 °C, volatile organic compounds (VOCs) with boiling points from 50–100 °C to 240–260 °C, semi-volatile organic compounds (SVOCs) with boiling points from 240–260 °C to 380–400 °C, and particulate organic matter (POM) with boiling points above 380 °C (Harrison, 2002).

Aldehydes are a typical toxic pollutant class of compounds with carbonyls in their chemical structure. Table 1 lists examples of aldehydes VOCs found indoor; many of them are potential sensory irritants, especially of the mucous membrane or skin sensitizers, and there is limited evidence that several may be human carcinogens. Many chemicals categorized as VOCs can be found in the indoor air. Representative compounds are benzene, ethylbenzene, limonene, p-dichlorobenzene, styrene, toluene, and xylene. Many of them are contained in paints, printing inks, adhesive agents, cleaning agents, gasoline, thinners, petrochemical oils, and kerosene (Kishi et al., 2020).

Table 1. Most common aldehyde VOCs present in indoor air pollution

Volatile Organic Compound	**Description**
Formaldehyde	Adherence
Acetaldehyde	Cigarette smoke, a metabolite of ethanol
Chloroform	Solvent
Hexanal	Flavor food additive
Benzaldehyde	Fragrance of almond
Ethyl acetate	Paint and ink additive, adhesive
Benzene	Pesticides component, paints
1-Butanol	Raw material for cosmetic
n-Octane	Solvent, fuel, detergent
Styrene	Raw material for polymeric materials
Nonanal	Fragrance

2-Methyl-1-butanol	Insect attractant
Acrolaine	Solvent, disinfectant

1.2 Biopolymers

Currently, nanotechnology approaches, different materials, and novel techniques have been explored and studied by the academic and scientific community to remediate the air contamination (Zhang, 2003; Wang et al., 2018; Bates et al., 2016; Tian et al., 2011; Carpenter et al., 2015; Ma et al., 2011; O'Connell et al., 2008; Ahmad et al., 2020). In fact, the use of different organic and inorganic materials, and the manipulation of particles at the nanoscale have been the most studied and developed decontamination methods in the literature (Wang et al., 2013). These innovative methods have been gaining a tremendous attention from academia and governmental organizations. Notwithstanding, NMs have demonstrated to be unstable at normal conditions, present synthesis complexity, and may generate adverse toxic byproducts once used (Bhandari, 2018). The process of obtaining NMs is expensive, without mentioning their lack of renewal or reuse capacity, turning them eventually into new pollutants (Mueller & Nowack, 2010). Based on the problems synthetic materials present once applied as remediation agents, several studies point out the existence of defined properties that would make a material a suitable agent for the decontamination of the environment (Guerra et al., 2018a). Features such as cost-effectiveness, non-toxicity, biodegradability, biocompatibility, reusability, and easy synthesis, preparation or extraction are vital factors that make a particle to be a suitable and sustainable decontamination material (Guerra et al., 2018a). These green-like properties are all characteristics of common natural polymers encountered in the biodiversity and listed in Table 2. Consequently, academia and government bodies are actively interested in the development and exploration of biopolymers to find new efficient and greener solutions for the remediation of the air (Klemm et al., 2005).

Table 2. Most common biopolymers and their applications in the environment pollution decontamination.

Biomaterial	Bioremediable Application	References
Cellulose	Removal of HOCs and VOCs from water and air pollution, respectively	(Tursi et al., 2018; Ion et al., 2015)
Chitosan	Water purification	(Kumar & Ioan, 2016)
Alginate	Removal of dyes and pesticides	(Wang et al., 2018)
Lignin	Heavy metal ions absorption	(Hatakeyama & Hatakeyama, 2009)
Silk	Remediation of air pollution	(Wang et al., 2016)

Chitosan: Chitosan is usually extracted from the exoskeletons of crustaceans, mainly shrimps and crabs' shells. This linear biopolymer is obtained by the incomplete alkaline deacetylation of chitin, and it is known to be the second most abundant polysaccharide on Earth after cellulose (Aider, 2010; Abdou et al., 2008). Its chemical structure is composed of β-(1,4)-2-acetamido-2-deoxy-D-glucose and b-(1,4)-2-anaino-2-deoxy-D-glucose monomers as building block repeats. This biodegradable material has a wide range of potential applications, including food preservation, packaging technologies, rice production, and tissue regeneration technologies, among others (Khan et al., 2019; Van-Toan & Hanh, 2013). According to Al-manhel et al., in 2018, chitosan has been widely used in water purification plants for the effective removal of oils, grease, and heavy metals in contaminated water. Thus, several studies have demonstrated the remediation potential properties of chitosan for the decontamination of the environment (Carvalho et al., 2019).

Alginate: Alginate is an anionic biopolymer structured as an alternative repeating of block copolymers guluronate and mannuronate. This biomaterial is commonly extracted from brown seaweed (*Phaeophyceae*), and its extraction methodology comprises the use of strong bases, salts, and acid treatments, such as NaOH, sodium chloride, and dilute HCl. Based on its promising and sustainable biological properties (*i.e.*, biocompatibility, low toxicity, relatively low cost, and mild gelation), it has been extensively used in different biomedical applications. Diverse studies exposed the wound healing and development of engineering tissue applications, as well as its use on drug delivery systems by the release of a variety of bioactive molecules (Yong & Mooney, 2012). Wang et al. (2018) extensively described the utility and application of different alginate-based composites as effective biosorbents for the environmental remediation. Thereby, they successfully demonstrate the enormous potential of these hybrid biomaterials for the removal of pollutants from contaminated air (Wang et al. 2019).

Lignin: Lignin is a racemic heteropolymer composed of aromatic subunits derived from phenylalanine. In nature, Lignin provides mechanical support to plant cell walls and is formed by the oxidative coupling of three hydroxycinnamyl alcohol monomers: p-coumaryl, coniferyl, and sinapyl alcohols (Boerjan et al., 2003). Currently, lignin is a biomaterial with prevalent importance in the industry. Many examples demonstrate how lignin can improve the efficiency of the industrial procedures in manufacturing products derived from plant biomass, and enhance the process of biofuels synthesis from the recollection of feedstock (Vanholme et al., 2008). Many studies have been conducted to assess the feasibility of lignin-based gels and green porous lignin-based spheres as potential pollutant capturing agents for the bioremediation of the environment (Parajuli et al., 2005; Li et al., 2014).

Silk: Silk is a natural fiber produced mainly by certain insects to build their cocoons or webs (Babu, 2019). Even though many insects create silk, only the filament made by the mulberry silk moth *Bombyx mori* is commercially available due to its biocompatibility, biodegradability, non-toxicity, and adsorption properties (Cao & Wang, 2009). In addition, silk produced by spiders can be used in other commercial applications, for instance, weapon and telescope cross-hairs and other optical instruments (Babu, 2019). Due to silk fibers mechanical qualities of strength, elasticity, softness, improved absorbency, affinity for dyes, and great adaptability to various form of twisting, it have been recognized as a promising biomaterials suitable for the development of surgical threads, wound dressing and other medical applications (Aigner et al., 2018). Moreover, Wang *et al.* in 2016 have reported a non-toxic, high efficient, and lightweight silk nanofibers air filter, which exhibits not only a considerable filtration efficiency for submicroninc and particulate matter particles but also antibacterial activity demonstrating that this biopolymer is appropriate for air pollution remediation.

1.2.1 Cellulose

Cellulose is the most abundant biopolymer available worldwide (Bethke et al., 2018). This water-insoluble biomaterial is a crucial component in the structural maintenance of plant cell walls. It is a highly ordered crystalline polysaccharide consisting of parallel arrays of β-1,4-linked glucose chains (Peng et al., 2019). Several studies suggest that the characteristic cellulose high order structure is the result of basic dimer repeats, known as cellobiose (Kumar & Turner, 2014; Mcnamara & Morgan, 2015; Maleki et al., 2016). Besides, these dimer repeats are described in the literature as two D-glucopyranose units linked by β-1,4-glycosidic bonds (Guerra et al., 2018b). Furthermore, cellulose characteristic chemical structure is based on the presence of strong H-bonds on their surface large number of hydroxyl groups, which confers its unique physicochemical properties, such as hydrophilicity, chirality, crystallinity or biodegradability, among others (Barakat, 2011). Moreover, the abundance of these OH-groups in its surface structure allows this natural polymer to be readily functionalized and modified by a diverse array of chemical transformation methods using a variety of functional groups enhancing its physicochemical features. Thus, making cellulose a versatile and malleable material (Thakur & Thakur, 2014). It is of particular interest due to cellulose low cost, availability, flexibility, easy processing, non-toxic and biocompatible properties, emerging as one of the most promising substitutes for synthetic and fuel-based materials (Nabili et al., 2016). Nowadays, there are several well-known sources for cellulose obtaining, such as plants, algae, bacteria, or sea animals. Because of the abundance and economic viability, plants have been the main source of cellulose extraction (Tursi et al., 2018; Moran et al., 2008). Indeed, the most common cellulose sources are wood pulp and cotton linters. Besides, agricultural wastes such as sugarcane bagasse, fruits, grasses, or rice straws are other sustainable plant sources to produce cellulose. On the other hand, this polysaccharide is the major component of the cell wall of many types of algae, in addition to certain species of bacteria. Furthermore, bacterial cellulose is unique and has several advantages over plant-derived cellulose: unique nanostructure, purity, higher-dimensional stability, greater mechanical strength, and polymerization. Additionally, the marine invertebrate tunicates are well known for assembling cellulose into their inner superficial tissues. These sea animals use cellulose as a skeletal structure in their leathery mantle tissues, which is produced by enzyme complexes found in the membrane of the tunicate epidermis (George & Sabapathi, 2015).

1.3 Currently cellulose remediation applications

Thanks to the important biological properties exhibited by cellulose fibers and the vast amount of available natural resources to extract it, numerous studies have focused on the usage of different cellulose-based materials that can effectively adsorb or capture a variety of pollutants present in all types of environmental contamination, such as the removal of heavy metals ions or hydrophobic organic compounds (HOCs) in water, and the capture of organic compounds present in polluted air (Hokkanen et al., 2016; Bismarck et al., 2002; Manjarrez et al., 2011). Also, it is important to highlight that only unmodified cellulose fibers from wood and bacteria have been mostly used for environmental remediation applications and that the mechanism and the physicochemical properties related to the efficient performance of these fibers is of significant consideration to the scientific community. Moreover, it is of maximum importance to clearly understand the role that the natural source plays in relation to the remediation features of cellulose isolate (Rinaudo, 2006; Moon et al., 2011).

For instance, Kim *et al.* in 2016 (Kim et al., 2016), developed activated carbon-impregnated cellulose filters as a material for removing several VOCs (benzene, toluene, ethylbenzene, and m-xylene) and dust from indoor pollution. Cellulose filters were engineered with four levels of activated carbon contents, and dust removal was performed with all of the filters showing 99.7% of average efficiency during the experiments, as well as it showed optimum remediation capacities (98.9 – 100% efficiency) for the absorption of VOCs. The successful decontamination performance reached was due to the high surface area of the activated carbon-impregnated cellulose filter provided. Likewise, Ion *et al.* (Ion et al., 2015), have demonstrated that bacterial cellulose might be a promising adsorbent for the vapor removal of polar and non-polar VOCs from the contaminated air stream, such as isopropanol and n-hexane. Moreover, they suggested that the incorporation of magnetite nanoparticles could enhance the adsorption efficiency of this biopolymer.

Further, Guerra *et al.* (Guerra et al., 2018b), have studied the amine-functionalization of commercially available micro and nano-scale cellulose with poly(ethylenimine), resulting in materials that present the ability to capture aldehydes and carboxylic acid VOCs involved to indoor air pollution. The amine-modified cellulose materials were physicochemically characterized using TGA, FTIR, EDS, and elemental analysis. Gas chromatography experiments were conducted to identify the capacity of the amine-modified cellulose materials to capture hexanal and octanal gases. The so-obtained results pointed out that the size of the cellulose substrate and the surface are critical parameters for the efficient remediation of air pollution.

In consequence of the easy modification of cellulose by a vast number of functional groups via chemical or physical methods, other fundamental applications for functionalized cellulose is the remediation of contaminated water with different toxic residues. For instance, Tursi *et al.* (Tursi et al., 2018) demonstrated that hydrophobic cellulose fibers extracted from Spanish Broom (SB) are a suitable material for the fast and large adsorption of HOCs present in polluted water. Specifically, they modified the surface of the SB cellulose fibers by chemical nebulization protocols using 4,4'–diphenylmethane diisocyanate to switch the hydrophilic surface properties of cellulose fibers into hydrophobic ones. Once the functionalization of the cellulose is confirmed by XPS and ATR-FTIR, the group performed batch experiments to monitor the absorption kinetics and capacity of the fibers to remediate polluted water with gasoline petrol. The results successfully proved that hydrophobically functionalized SB cellulose fibers can adsorb petroleum hydrocarbons with an efficiency bigger than 90% within a few minutes, which makes this biomaterial a novel green technology for the remediation of polluted water.

Despite the usage of cellulosic materials for the efficient removal of pollutants in air and water, cellulose micro- and nano-materials can be engineered for the fabrication of filtration membranes for water or air treatment (Carpenter et al., 2015). According to Wang *et al*., (Wang et al., 2013) the development of efficient microfiltration membranes is conducted by the integration of ultrafine cellulose nanofibers onto a platform based on a nanoscale layer polyacrylonitrile deposited on a microscale polyethylene terephthalate film. They proved that the high surface area and large pore density are critical parameters that can enhance the retention of bacteria (*Escherichia coli*), heavy metals (*e.g*., Cr(VI) and Pb(II)), and viruses (MS2 bacteriophage), common pollutants encountered in contaminated water samples. These membranes are unique as they can simultaneously remove toxic contaminants, becoming a promising tool for use in drinking water purification (Ma et al., 2011).

At present, these research works have demonstrated that materials presenting higher surface-to-volume ratio exhibit better VOC adsorption performances (Guerra et al., 2017; Kim et al., 2016; Ion et al., 2015). In fact, chemically modified cellulose fibers can capture VOCs due to a chemical interaction between the pollutant and the natural fiber itself, but any intrinsic capture or adsorption employing covalent or electrostatic interactions has not been studied yet. More importantly, these works are limited to commercial sources of micro- or nano-scale cellulose with or without further chemical functionalization. There are no scientific studies that evaluate the potential effects of the natural cellulose extraction source on the resulting physicochemical properties of the biomaterial. Besides, the significant challenges for remediation of air pollution are the development of new materials presenting high durability, low cost, and small to no environmental concerns (Ma et al., 2011). Thus, the present study aims at extracting natural encountered cellulose fibers from different biological sources and effectively screening their aldehyde VOCs remediation capacity to, finally, use cellulose as a novel decontamination agent to finally replace synthetic materials for the remediation of the environment, as shown in Fig. 1.

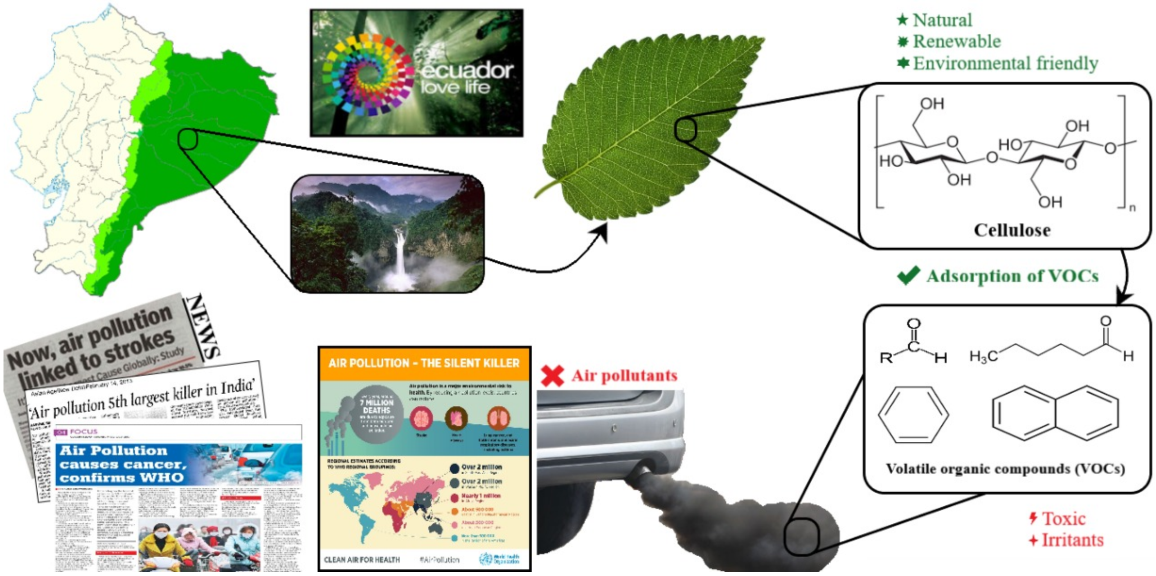


Figure 1. The use of Ecuadorian biodiversity to extract unique cellulose fibers for the effective capture of aldehyde VOCs in air pollution

1.4 Ecuadorian biodiversity

In accordance with the excellent and promising biological properties that biopolymers possess, and in particularly cellulose fiber, Ecuador and Latin America (LATAM) biodiversity plays an essential role as the ideal scenario for the extraction of an abundant unique variety of cellulose isolate (Almeida, 2007). LATAM houses a broad fraction of the world's biodiversity, including the most abundant biomass on Earth. As well, LATAM is formed by megabiodiverse countries, few of them included in the Amazon region (Luque et al., 2010). The richness in flora and fauna of the Amazonian biodiversity plays an important role in the obtaining of unique, diverse, and eco-friendly native biomaterials mentioned above (Almeida, 2007). In particular, Ecuador, in spite of its small size (250.000 km^2 or 1.5% of South America extension), hosts 18.000-22.000 species of plants becoming one of the most biodiverse countries in the world and an ideal platform for obtaining unique cellulose fibers (Valencia, 1995; Larrea, 2013). In the present work, I explored the potential use of six natural cellulose fibers extracted from six different natural sources to use them as potential air remediation agents, more specific to use them as aldehyde VOC capture materials and compare their capture performance to the commercially available cellulose materials used as controls. Furthermore, I detail and discuss, in the result section, the methodology used for the physicochemical characterization of the fibers, as well as the evaluation of their remediation capacities by gas chromatography assays. Moreover, amine-functionalized cellulose fibers are also described and characterized, and their capturing efficiencies are compared to all the native fibers and the commercial controls used.

CHAPTER 2

2. METHODOLOGY AND MATERIALS

The present research study was realized principally in the lab facilities of the Universidad Yachay Tech (YT) at San Miguel de Urcuquí, Universidad de las Fuerzas Armadas – ESPE located in the Sangolqui Valley (Pichincha), and Clemson University (CU) located in South Carolina, USA. Specifically, the chemical extraction of natural, unmodified cellulose fibers from different various bioresources was performed in YT laboratories, the consequent fully physicochemical characterization of the commercially available controls, natural and modified cellulose fibers were carried out in the laboratory equipment/facilities of YT, ESPE, and CU. Finally, all the gas chromatography experiments and assays on the fibers were performed in the Organic Chemistry labs of the Chemistry Department at CU during a research internship hold in the summer of 2018. The whole project was principally funded and supported by YT, ESPE, and CU.

2.1 Extraction of cellulose fibers

Six different natural sources were selected based on their inherent properties from the Americas and Andes region, to perform cellulose extraction. Cellulose extraction was carried out using established protocols of chemical extraction. The same process was used for each cellulose sample to prevent any effect of the protocol on the cellulose property. Commercially available cellulose microcrystals (CMC) and cellulose nanocrystals (CNC) used as controls during this work were supplied by Sigma-Aldrich.

2.2 Surface amine coating on cellulose fiber F28

The poly(ethyleneimine) solution (PEI) (1200 - 1300 Mwt, 50wt% in H_2O), used for the electrostatic coating of the natural fiber F28, was supplied by Sigma-Aldrich. For the preparation of the PEI-modified F28 cellulose, a 30-mg sample of unmodified cellulose fibers was suspended in a 0.01% v/v PEI solution (*i.e.*, 1 µL of PEI, 10 mL of H_2O). The suspension was then placed in an ultrasonicator bath at 80 °C for 25 min. The coated cellulose materials were then collected by centrifugation (3000 rpm, 3 min) and dried at room temperature (RT) for two days in an oven. The PEI-modified cellulose fibers were thoroughly washed with water employing vacuum filtration. Finally, the successfully electrostatic coating of the fibers was confirmed by the characterization techniques explained below

2.3 Physico-chemical characterization

The surface structure and morphology of the different unmodified cellulose fibers and the cellulose controls were examined by using a MIRA 3 (TESCAN, CZ) field emission scanning electron microscope (FEG - SEM). X-ray diffraction (XRD) patterns were collected on an EMPYREAN diffractometer (PANalytical, NL) in a Bragg-Brentano configuration at 40 kV and 45 A and monochromatic X Rays of Cu K-α wavelength (λ = 1.541 Å) using a Ni filter. The crystallinity index (CrI) was determined for each cellulose sample and controls following the method described by Segal *et al*. using Equation (1):

$$\text{Equation (1): } CrI(\%) = \frac{I_{002} - I_{am}}{I_{002}} x 100\%$$

where I_{002} is the maximum intensity of the (002) lattice diffraction peak, and I_{am} is the intensity shown by the amorphous part of the cellulose samples. Lyophilized cellulose samples were mounted on a zero-background substrate. Scans were obtained from 5 to 90 ° in 0,01 ° steps, 10 seconds per step, 16 spinner revolution time by minute, repeated eight times. CrI was calculated from the height ratio of the (200) peak and the height of the minimum between the (200) and (110) peaks (Segal et al., 1959; De Souza and Borsali, 2004). Fourier Transform Infrared Spectroscopy (FT-IR) was performed to identify the purity and the successful removal of several components of the cellular wall of the sources used in all the cellulose samples and the control crystals (*i.e.*, lignin and hemicellulose). FT-IR data were recorded using a Spectrum Spotlight 200 FT-IR instrument supplied by Perkin Elmer, at the USA. First, a spectrum of the gold-plated sample holder was acquired as background, and then the spectra of the samples were recorded. The wavenumber range of the analysis was between 4000 to 500 cm^{-1} with a total number of scans of 36 and a 4 cm^{-1} resolution. Thermogravimetric analysis (TGA) was used to determine the thermostability of the unmodified, PEI-treated, and cellulose controls using a Q500 instrument (provided from TA Instruments, USA) under nitrogen over the temperature range of 27 °C to 600 °C with a heating rate of 10 $°Cmin^{-1}$. Nitrogen gas adsorption was performed at 77 K with an ASAP 2020 analyzer (Micromeritics Instrument Corp. U.S.); pore size distribution of the cellulose samples and controls was determined using density functional theory (DFT), and the sample's surface areas were calculated using the Brunauer–Emmett–Teller (BET) equation.

2.4 Gas chromatography experiments

According to the literature, assays based on Gas Chromatography analysis have proven to be an efficient tool to identify the capacity of several materials to capture a wide variety of VOCs. Thus, several works have also used the hexanal, an aldehyde, as a VOC standard model, which efficiently reduces tedious experimental steps (Guerra et al., 2018b; Guerra et al., 2017; Campbell et al., 2015; Swasy et al., 2018). Hexanal commercially available was purchased and used as received. Agilent Technologies Gas Chromatography vials with septum crimp-caps were used along with a Shimadzu GC-2014 gas chromatograph equipped with a Shimadzu AOC-20i autoinjector, a flame ionization detector (FID) and a 30 m x 0.25 mm x 0.25 µm Zebron ZB-WAX Plus capillary GC column. For the preparation of the GC experiments (Fig. 2), 10 mg of a cellulose fiber sample were placed carefully inside the paper chamber previously created on the GC vial. 1 µL of hexanal is injected on the bottom of the vial without damaging the paper chamber. The vial was then placed in a water bath at RT for 30 min, to evaporate the hexanal. The vial then was inserted in the gas chromatograph to record the percentage of hexanal remaining in the vial after the vapor has been exposed to the cellulose sample. The GC analyses were carried out on all the cellulose samples and controls in triplicate.

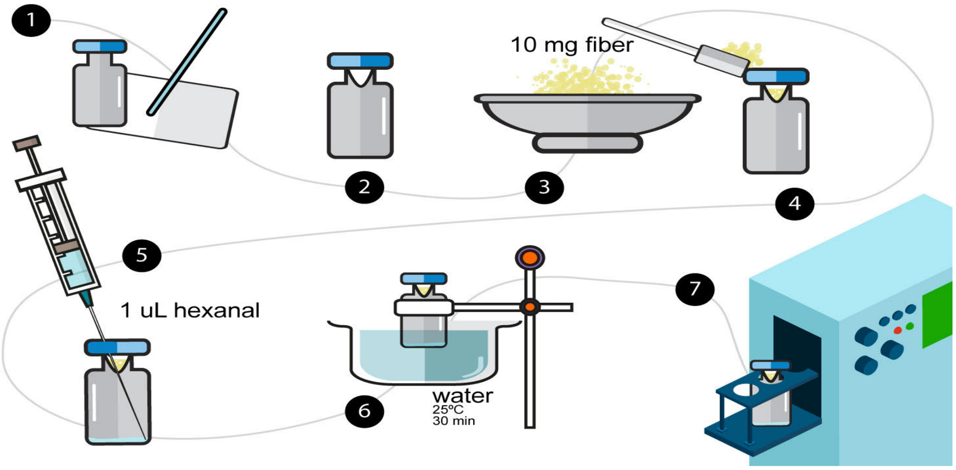


Figure 2. The hexanal vapor GC studies protocol followed using all modified, unmodified cellulose samples and controls

CHAPTER 3

3.1 RESULTS

After the chemical extraction, six different unique unmodified cellulose fibers were successfully obtained (*i.e.*, F17, F19, F20, F25, F27, and F28). All the natural fibers were physicochemically characterized and compared with commercially available cellulose microcrystals (CMCs), and cellulose nanocrystals (CNCs) purified from cotton linters, to highlight unique natural properties present in native cellulose and to enable VOC adsorption capacity comparisons. Furthermore, PEI-modified cellulose F28 was as well, fully characterized, and compared with the natural and commercially available cellulose fibers.

3.1.1 Characterization of commercially available cellulose controls

Thermogravimetric analyses (TGA) were performed on cellulose controls to identify their thermostability and degradation rates as a function of time and temperature. The TGA results revealed that CNC maintains higher weight percentage at temperatures higher than 300 °C when compared with CMC, as shown in Fig. 3. Initial degradation values for the cellulose crystal controls can be observed in the following post Table 2.

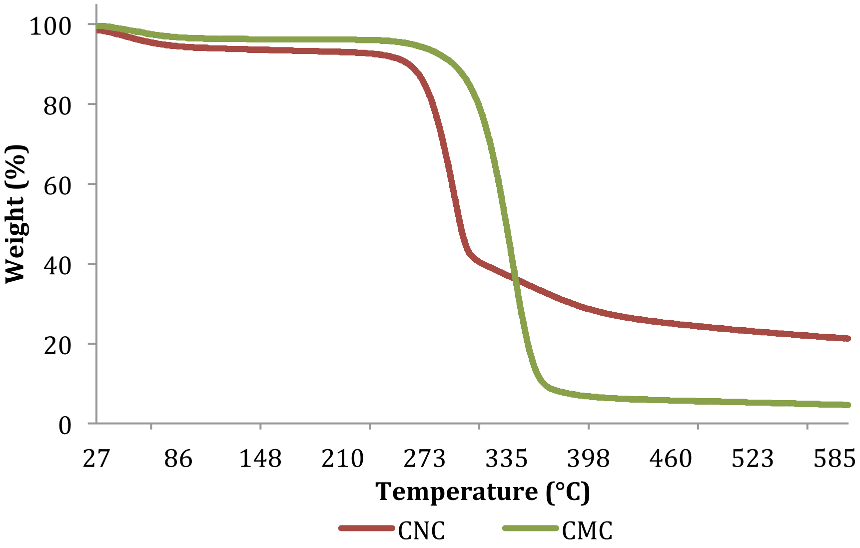


Figure 3. Thermal stability analysis comparison of cellulose crystals controls (*i.e.* CMC vs. CNC)

The Fourier transform-infrared (FTIR) spectrum of commercial CMC and CNC samples, illustrated in Fig. 4, show that both samples have cellulose characteristic peaks. For instance, CMC spectrum displays C-C, C-OH, C-H ring and side group vibrations bands which arise at ~1000 cm^{-1}, and also C-O-C glycosidic ether band notably appears at ~1105 cm^{-1}. Additionally, important cellulose peaks are also evident in CMCs spectrum at ~1304 cm^{-1}, ~1625 cm^{-1}, ~2900 cm^{-1}, and ~ 3300 cm$^{-1,}$ which correspond to CH_2 rocking vibrations at C6 band, OH bending of adsorbed water, sp3 C-H stretching and OH stretching frequencies, respectively. On the other hand, analyzing CNC spectrum, the C-C ring breathing, OH bending, and CH_2 rocking vibrations at C6 bands are marginally displaced to the left at ~1050 cm^{-1}, ~1314 cm^{-1}, and ~1630 cm^{-1}, respectively, and the peak corresponding to C-O-C group is at the same wavenumber when compared with CMC spectrum. Based on details exposed above, FTIR results confirm that control materials used are mainly composed of cellulose, and as expected, they do not contain residual contaminants.

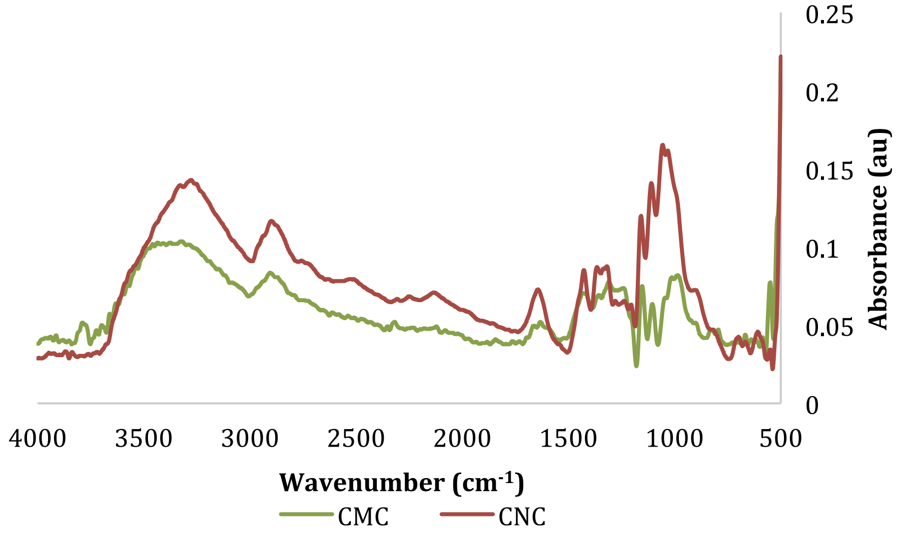


Figure 4. FT-IR of CMC and CNC

The crystallinity index of the crystal controls (illustrated later in Table 3) were analyzed by X-ray powder diffraction (XRD). The intensity of peaks observed for CMCs and CNCs XRD patterns, displayed in Fig. 5, is quite similar and allows to estimate the index of crystallinity to 78.1% and 81.5%, respectively.

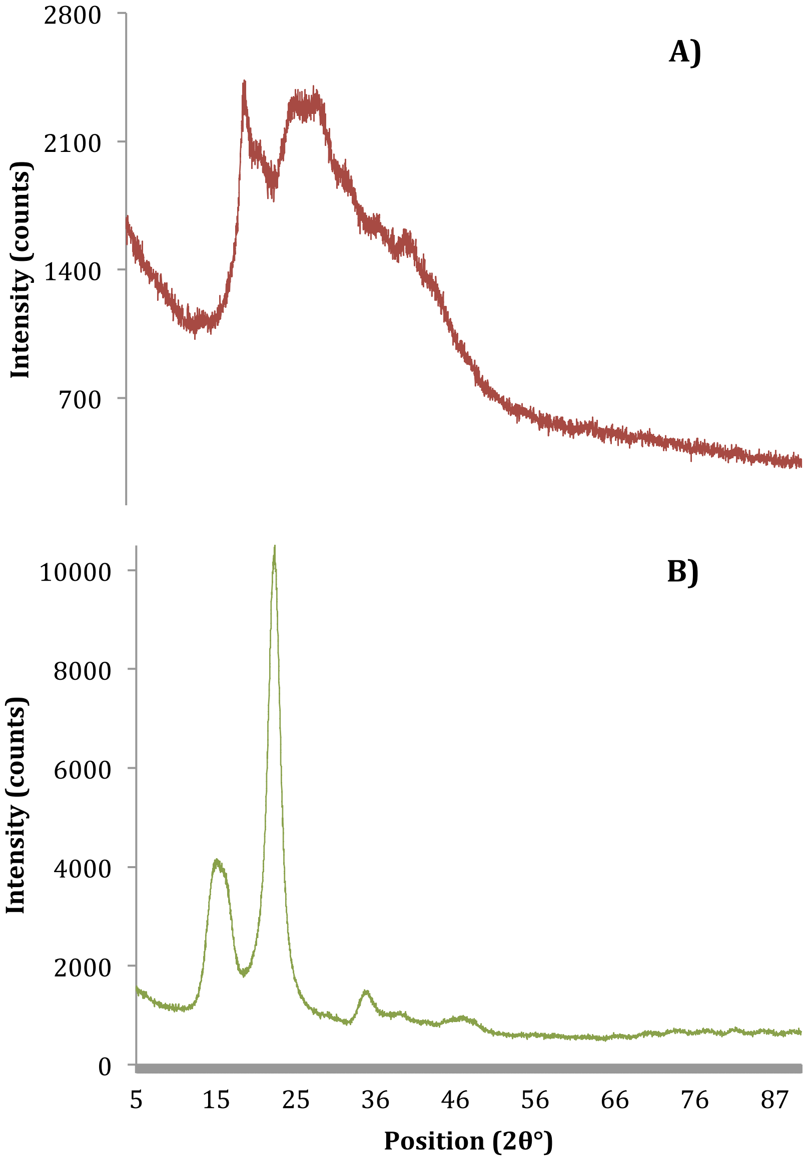


Figure 5. X-ray diffractograms of A) CMC; and B) CNC

Scanning electron microscopy (SEM) micrographs provided evidence for the identification of important cellulose controls morphology differences at their surfaces. CMCs present a tube-like microstructure while the CNCs possess a flake-like nanostructure due to partial aggregation when loading the sample into the microscope (Fig. 6).

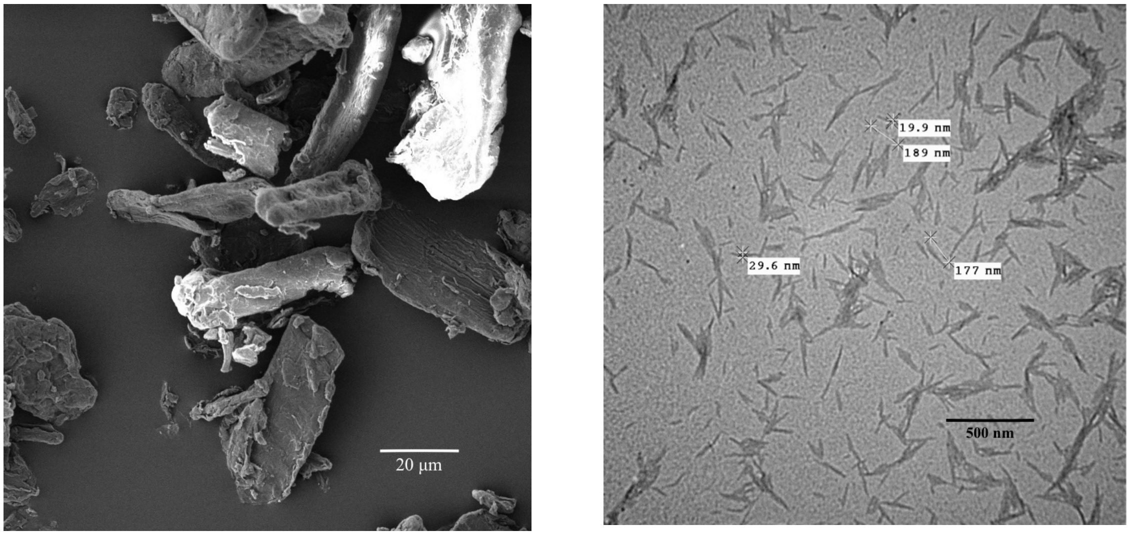
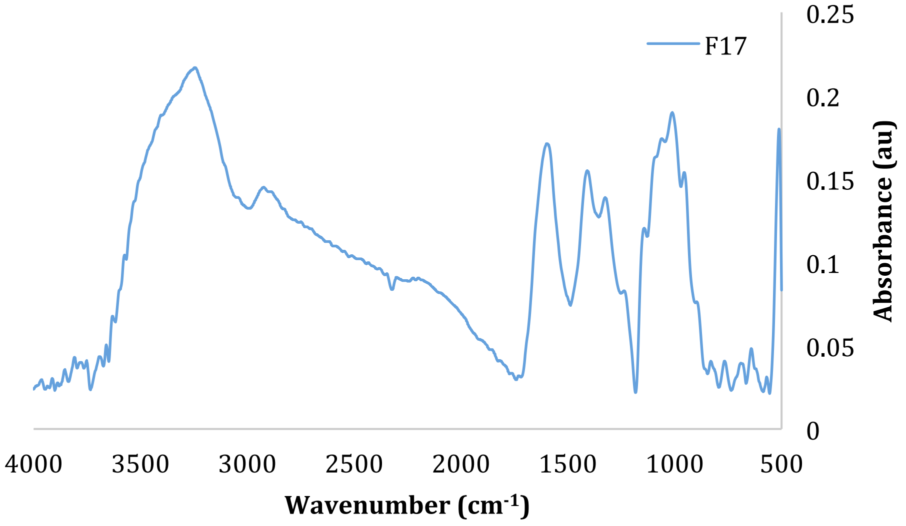
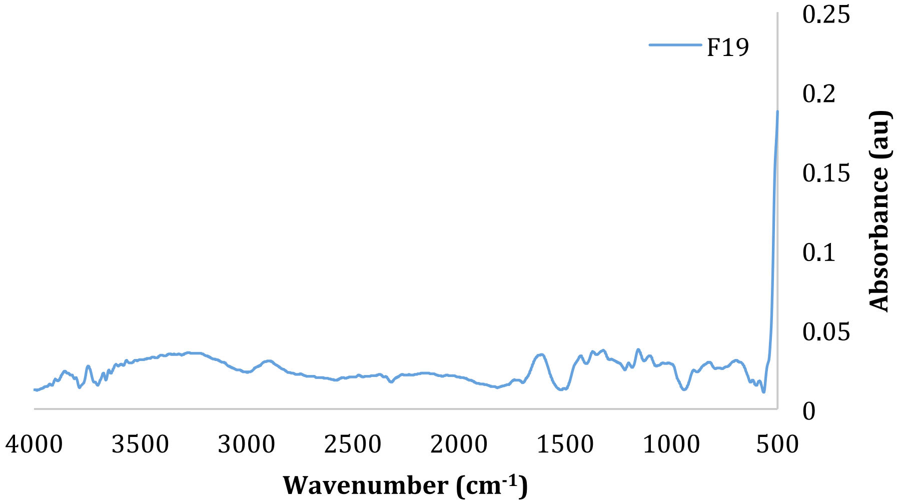


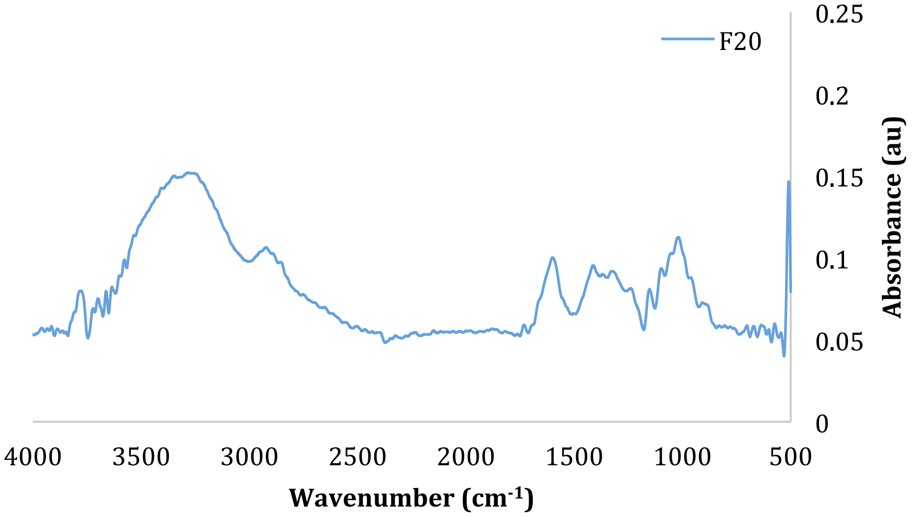
Figure 6. SEM micrographs of commercially available controls: A) CMC, and B) CNC.

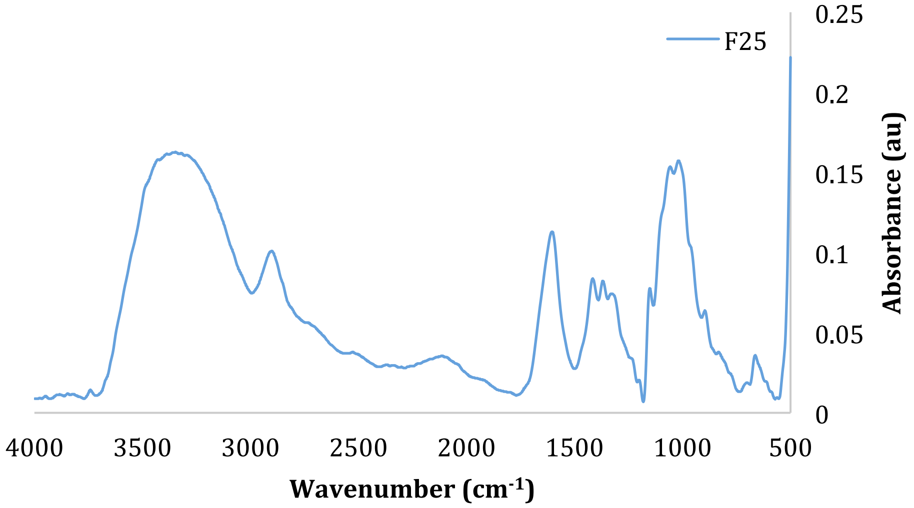
3.1.2 Characterization of unmodified cellulose fibers

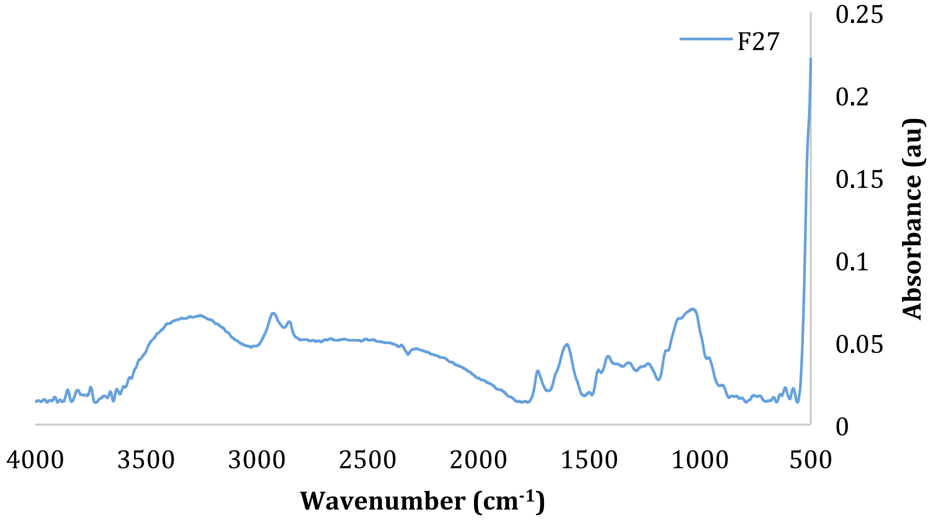
Individual analysis based on FTIR spectra and TGA graphs identified the content, purity, and thermostability of the cellulose fibers. It confirmed the absence of the residual plant cell wall components, such as hemicellulose or lignin, after the chemical extraction. In addition, Fig. 7 indicates that each fiber sample (i.e., F17, F19, F20, F25, F27, F28) present all cellulose characteristic peaks, and similar FTIR spectra to the commercial controls, CNC and CMC.


F17
0.25
0.2
0.15
0.1
0.05
0
Absorbance (au)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)


F19
0.25
0.2
0.15
0.1
0.05
0
Absorbance (au)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)


F20
0.25
0.2
0.15
0.1
0.05
0
Absorbance (au)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)


F25
0.25
0.2
0.15
0.1
0.05
0
Absorbance (au)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)


F27
0.25
0.2
0.15
0.1
0.05
0
Absorbance (au)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

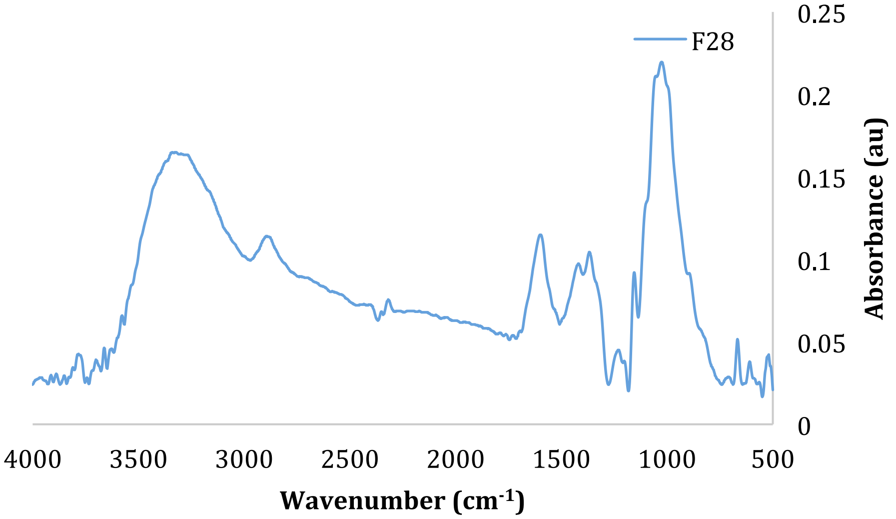
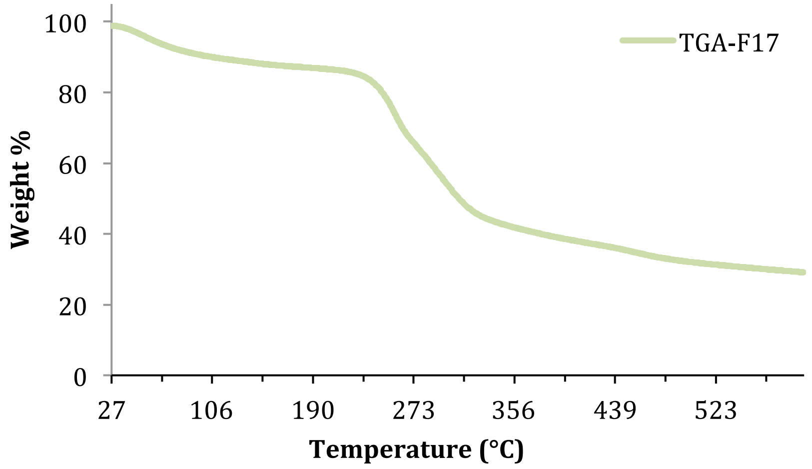
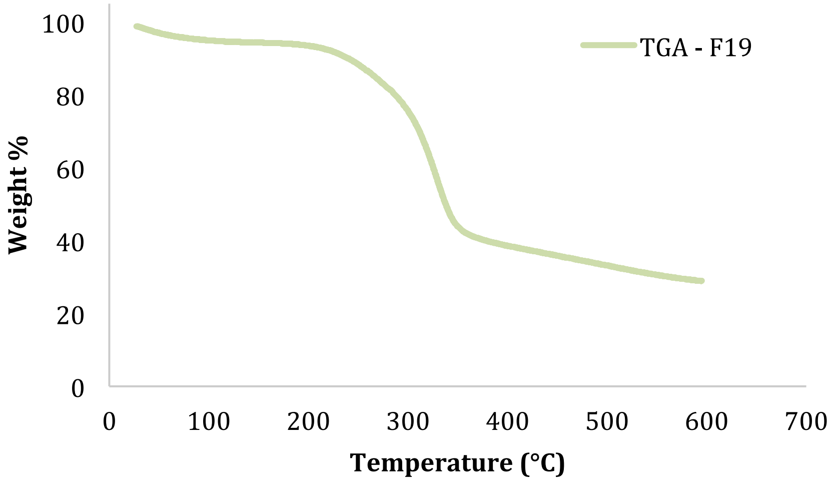
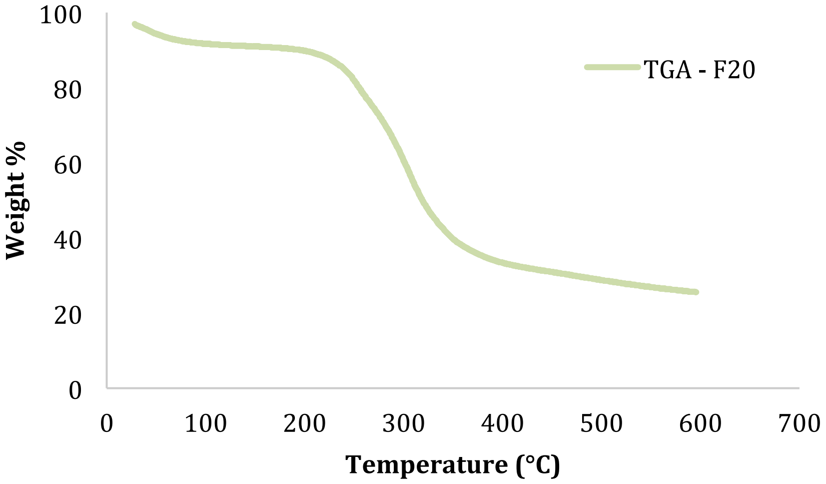

F28
0.25
0.2
0.15
0.1
0.05
0
Absorbance (au)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

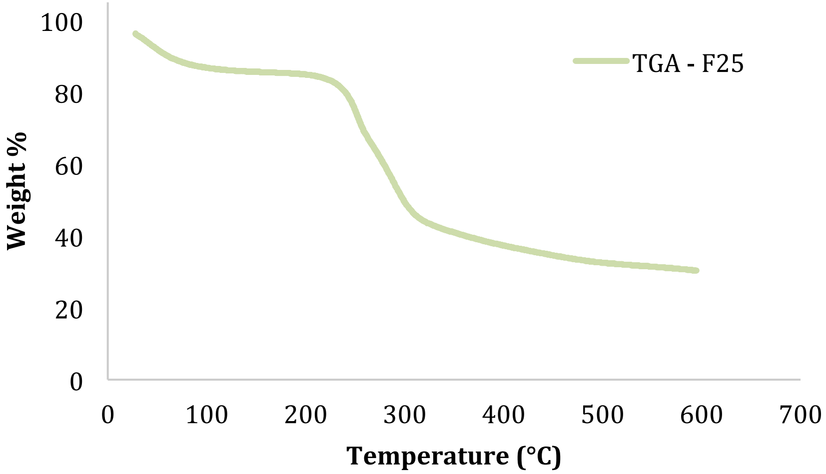
Figure 7. Individual FT-IR spectra of each unmodified cellulose fiber

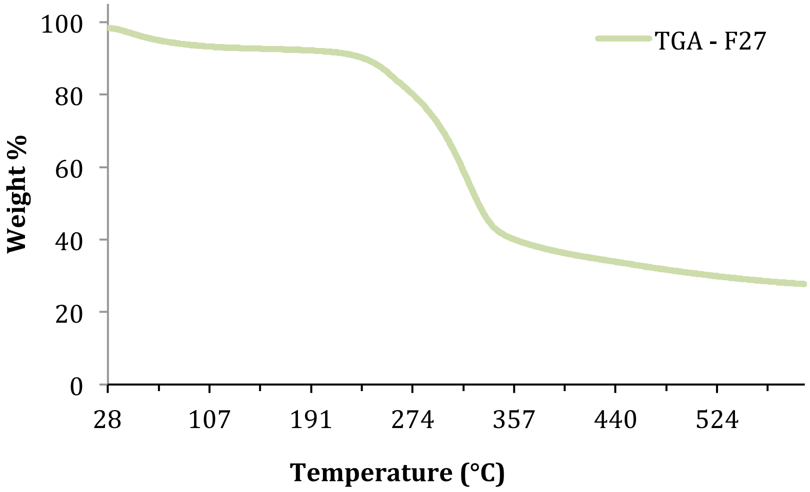
The thermogravimetric analysis of each fiber, displayed in Fig. 8, showed minor changes in the degradation profiles of the materials.






100
80
60
40
20
0
Weight %
0
100
200
300
400
500
600
700
Temperature (°C)
TGA - F20


100
80
60
40
20
0
Weight %
0
100
200
300
400
500
600
700
Temperature (°C)
TGA - F25


100
80
60
40
20
0
Weight %
28
107
191
274
357
440
524
Temperature (°C)
TGA - F27

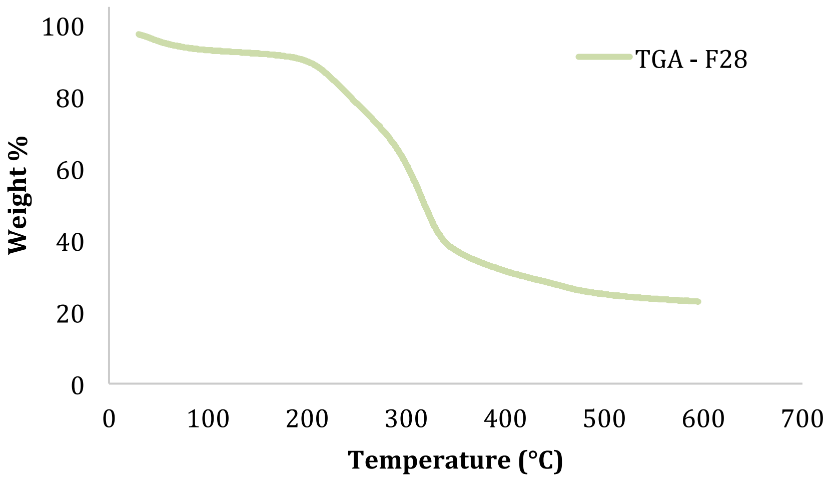


Figure 8. Individual TGA graphs of each unmodified cellulose fiber

It is important to note that even though cellulose fibers were extracted following strictly the same chemical extraction protocol to avoid sample contamination, and that FTIR and TGA results show similar thermostabilities and pure cellulose contents, all the fibers present different natural physicochemical features, as shown in Figure 9.

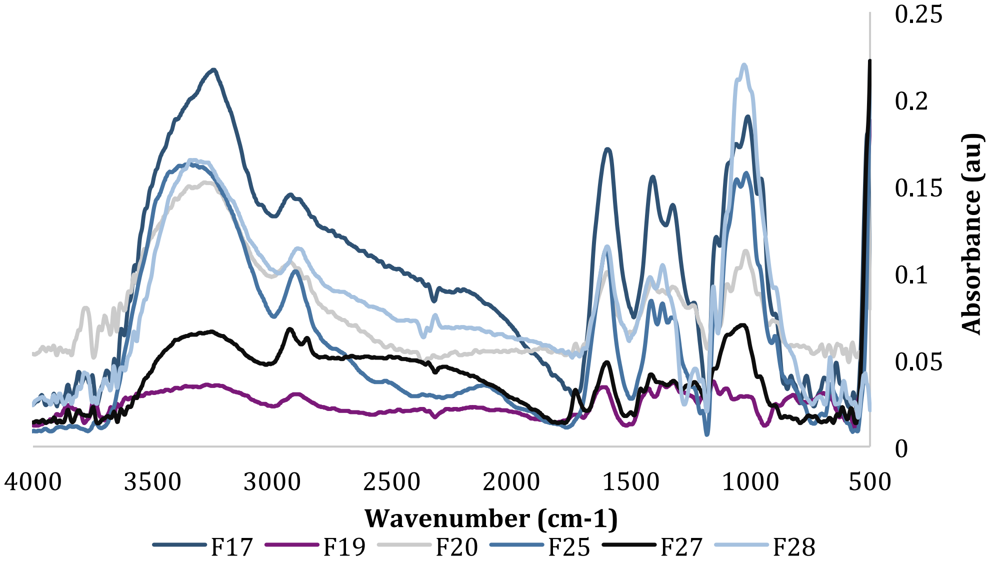


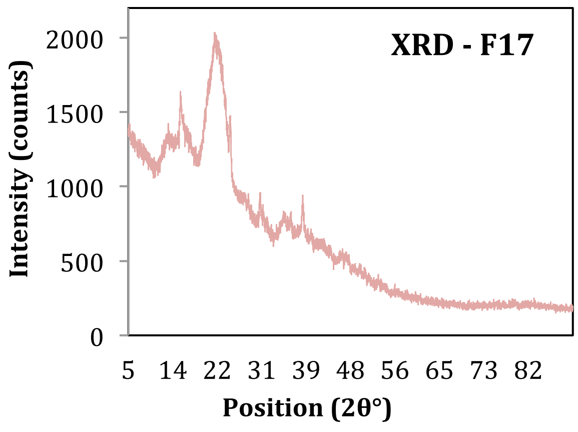
Figure 9. Comparison of FT-IR spectra of the unmodified cellulose fibers, characteristic cellulose peaks are highlighted

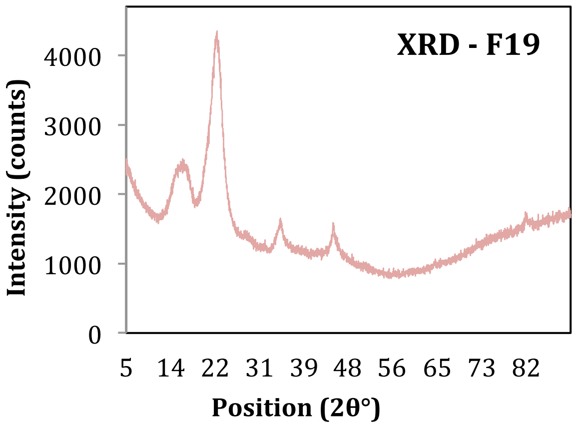
Furthermore, the initial degradation temperatures (IDT, Table 3) obtained from TGA thermograms indicated that all natural fibers are thermostable at near or above 200 ºC, suggesting that all six cellulose samples are amenable for industrial applications involving high temperatures.

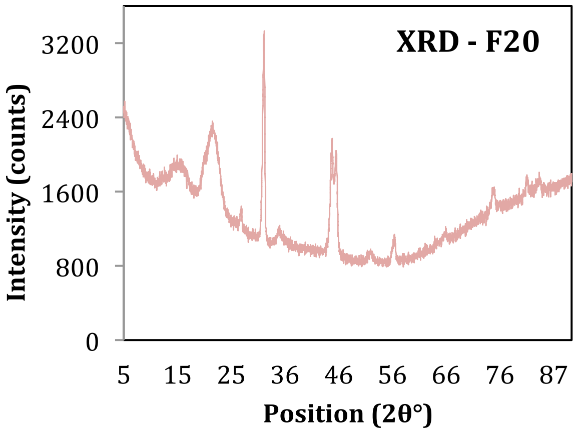
Fiber	IDT (°C)
CMC	294.4
CNC	260.43
F17	228.12
F19	239.86
F20	195.88
F25	196.59
F27	233.62
F28	198.34
F28-PEI	239.79

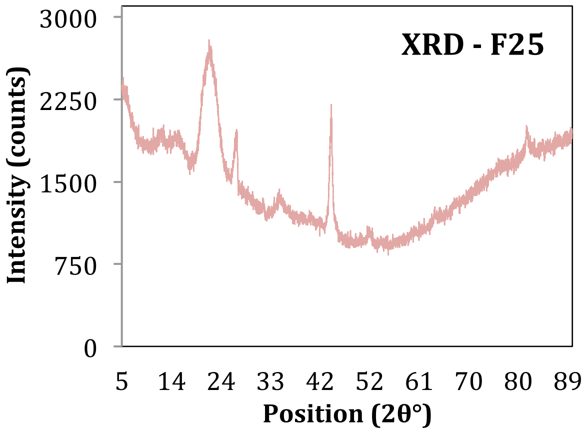
Table 3. Initial degradation temperature (IDT) calculated when cellulose weight is at 90% of its total composition

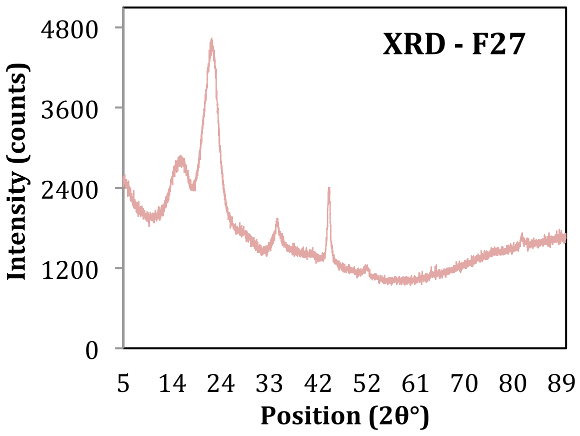
X-ray diffraction (XRD) analysis of the six cellulose samples depicted distinct patterns for each, as shown in Fig. 10. The major intensity peaks around $2\theta = 20$ - 25º are attributed to cellulose crystalline structure, while the peaks around $2\theta = 15$ - 18º represent the samples' amorphous region (Segal et al., 1959; De Souza and Borsali, 2004).


XRD - F17
Intensity (counts)
2000
1500
1000
500
0
5
14
22
31
39
48
56
65
73
82
Position (2θ°)


XRD - F19
Intensity (counts)
4000
3000
2000
1000
0
5
14
22
31
39
48
56
65
73
82
Position (2θ°)


XRD - F20
Intensity (counts)
3200
2400
1600
800
0
5
15
25
36
46
56
66
76
87
Position (2θ°)


XRD - F25
Intensity (counts)
3000
2250
1500
750
0
5
14
24
33
42
52
61
70
80
89
Position (2θ°)


XRD - F27
Intensity (counts)
4800
3600
2400
1200
0
5
14
24
33
42
52
61
70
80
89
Position (2θ°)

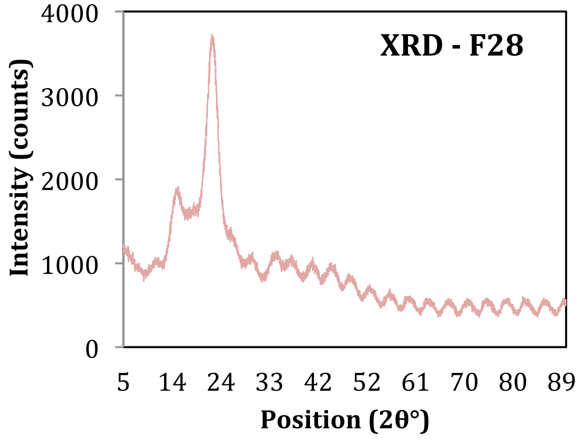

XRD - F28
Intensity (counts)
4000
3000
2000
1000
0
5
14
24
33
42
52
61
70
80
89
Position (2θ°)

Figure 10. XRD analysis of each unmodified cellulose fiber

Using XRD analysis, crystalline degrees were calculated for each cellulose sample and controls, which are listed in Table 4. The notable differences in the crystallinity indexes that the samples present, again demonstrates that the physicochemical properties of each fiber vary according to the natural source used for its extraction. For instance, commercially available controls obtained from cotton linters present higher crystalline degrees when compared to native fibers.

Fiber	Crystallinity Index
CMC	78.10%
CNC	81.50%
F17	39.70%
F19	55.80%
F20	28.20%
F25	36.80%
F27	45.90%
F28	56.20%

Table 4. Crystallinity Index (CrI) obtained based on XRD diffractograms of each cellulose fiber

Scanning electron microscopy (SEM) observations on the natural cellulose samples revealed that each fiber, regardless of following the same extraction procedure, presents a unique morphology, porosity, and size (Fig. 11).

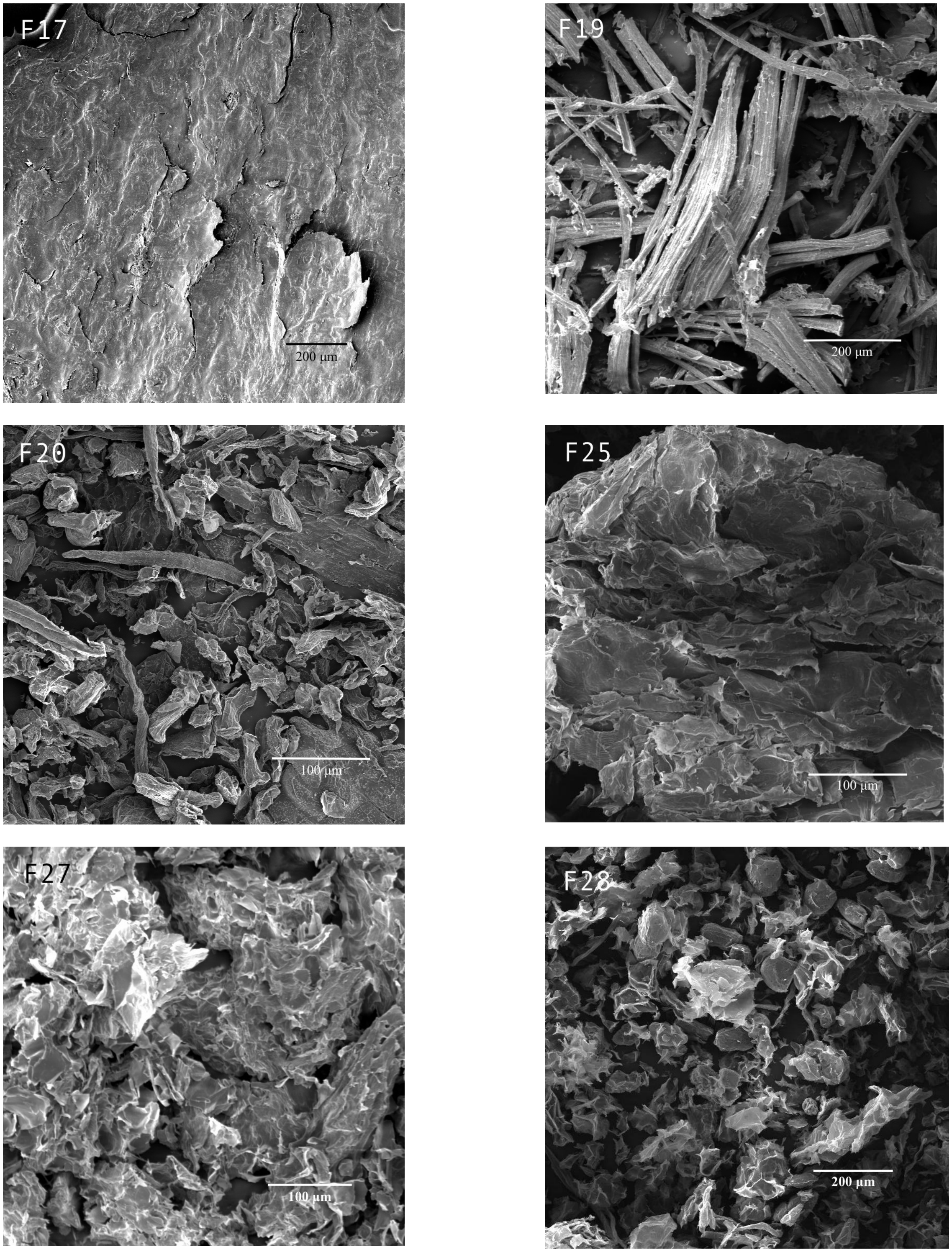


Figure 11. SEM micrographs of each unmodified cellulose sample

Additionally, samples surface areas (SSA) and pore volumes (PV) obtained from the BET measurements are both listed in Fig. 12. The correlation graph between the surface area and pore volume of samples is also illustrated in Fig. 12. SSA and PV of the natural fibers are compared with cellulose controls to highlight important unmodified cellulose physicochemical properties that might explain their capacity to capture aldehyde VOCs effectively.

Sample	SSA (m^2/g)	PV (m^3/g)
CNC	22	0.055
CMC	3	0.018
F17	4	0.022
F19	29	0.093
F20	12	0.072
F25	9	0.061
F27	8	0.034
F28	48	0.072

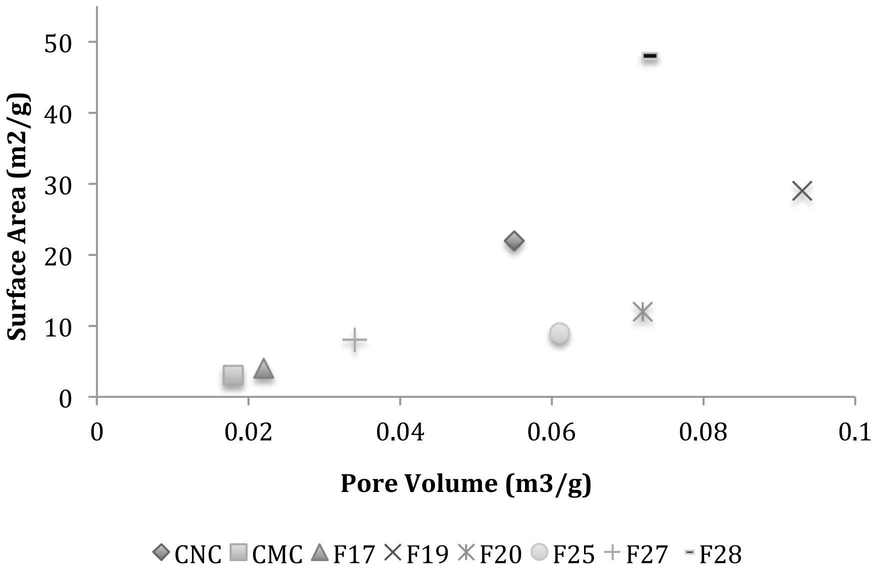


Figure 12. Pore Volume (PV) and Sample Surface Area (SSA) table of the cellulose samples, and the distribution of the pore volume correlated with the surface area of the particles and the controls

3.1.3 Characterization of PEI-modified cellulose F28

In the literature, several research works have demonstrated that the presence of amine functional groups on the surface of a material facilitates the covalent adsorption of aldehyde VOCs, and thus enhancing the material intrinsic decontamination properties. It is essential to highlight that our research focused on using small PEI quantities without following any tedious chemical modification protocol, so avoiding several reagents or solvent usage and being more time-efficient (Guerra et al., 2018b; Guerra et al., 2017; Campbell et al., 2015; Swasy et al., 2018). Based on this, the cellulose fiber F28 was surface-modify with numerous amine groups in order to enhance its aldehyde VOC capturing properties. Therefore, this native isolate was electrostatically coated with PEI upon ultrasonication with a 0.01% v/v PEI solution. The presence of PEI on the surface of the fiber was firstly identified by FTIR analysis. The emergence of new band around ~1550 cm^{-1} and attributed to N-H bending quickly confirmed the success of PEI coating (Fig. 13).

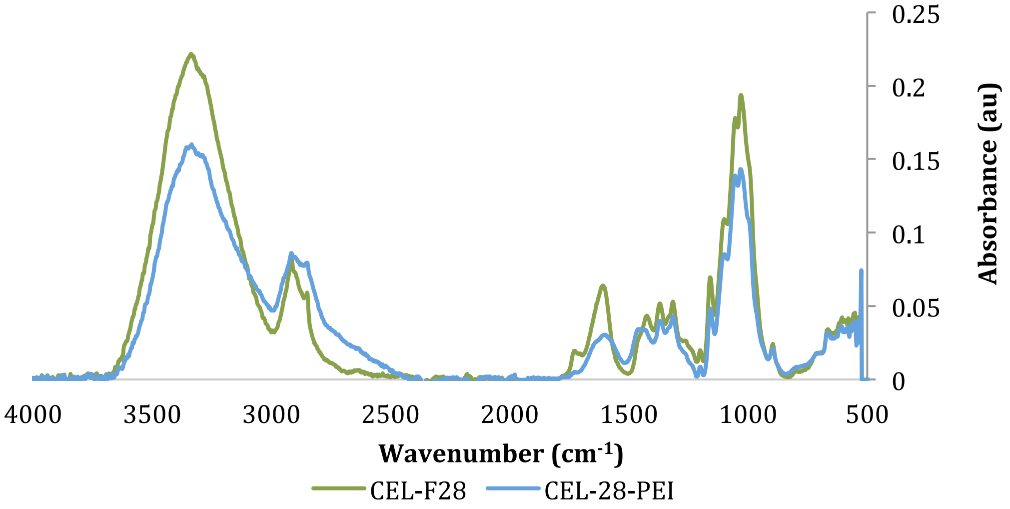


Figure 13. FT-IR spectrum comparison of unmodified F28 and PEI-modified F28 fibers

Additionally, according to the thermogravimetric analyses of unmodified F28 and PEI-F28, illustrated in Fig. 14, the thermal degradation of the natural F28 showed important differences. The degradation profile of natural F28 initiates at 229 °C, while PEI coating on the surface of cellulose isolate F28 causes the thermal degradation of the material to begin at a slightly higher temperature (*i.e.*, 240 °C).

Moreover, the weight loss curves for F28 and PEI-F28 present considerable differences in the final values of the thermograms providing additional evidence for the successful electrostatic coating of the fiber using small amounts of PEI.

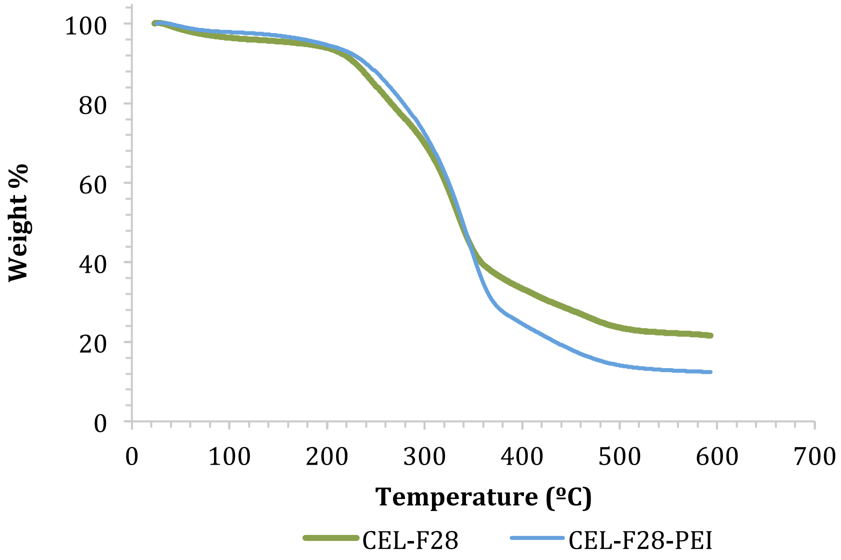


Figure 14. TGA analysis of natural F28 and surface coated with PEI F28 cellulose fibers

Structural and morphological features were observable through SEM images (Fig. 15). These micrographs indicate that even though the unmodified F28 fiber and its PEI-modified congener present similar, “shriveled” structures, there are few differences in their overall morphologies. Fiber PEI-F28 presents flat and folded rugged surfaces that are evident based on its tube-like structures due to the presence of the amine coating. On the other hand, the unmodified F28 fiber shows many uneven and pleated surfaces.

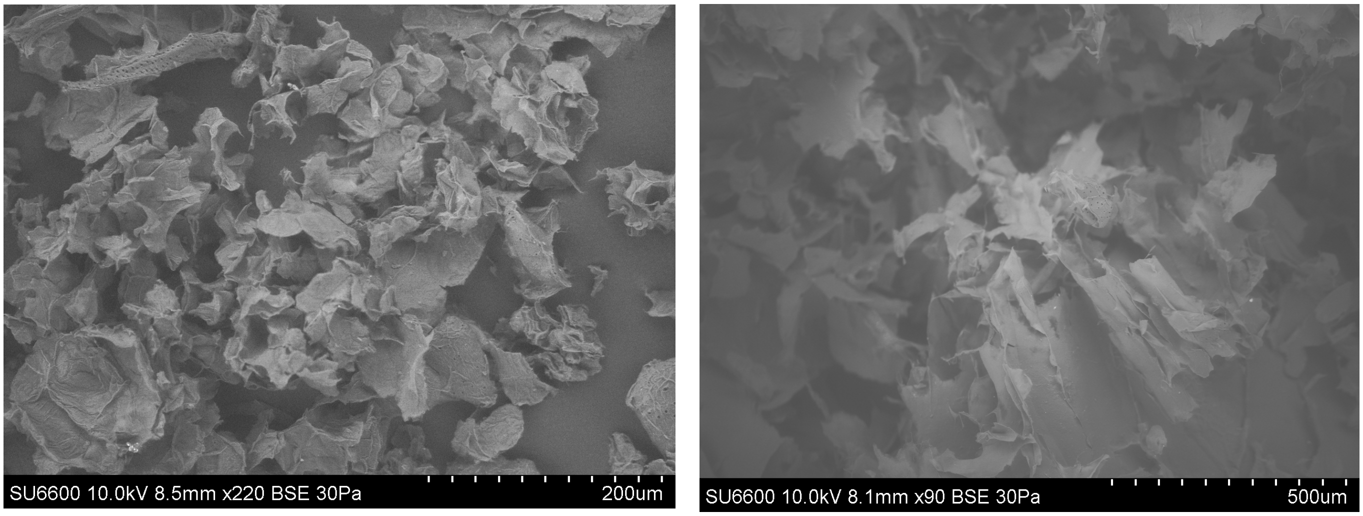


Figure 15. SEM images of unmodified (left) and PEI-treated F28 (right) cellulose

3.1.4 Gas chromatography assays

After the successful isolation and characterization of cellulose samples made of natural, PEI-modified, and controls (included as controls), gas chromatography experiments were conducted to assess the VOC adsorption capacity of the materials using a standard aldehyde VOC, hexanal. Based on the protocol followed (detailed in Chapter 2), GC results, after exposure of the cellulosic materials to hexanal vapors, are shown in Fig. 16. The results showed that unmodified F19 and F28 cellulose fibers present significantly higher capturing capacities than the commercially available cellulose controls. F19 and F28 cellulose samples were capable of a $25.49 \pm 0.36\%$ and a $56.42 \pm 7.30\%$ reduction of hexanal vapors after a 30 min exposure, respectively. Instead, the commercial CMC and CNC samples performed a poorly VOC reduction of $3.87 \pm 1.64\%$ and $4.60 \pm 2.68\%$, respectively. Figure 16 also indicates that the VOC capturing efficiencies of the controls obtained are similar (*i.e.*, no statistical differences) to the performance of isolates F17, F20, F25, and F27, which show absorption capacities of $1.15 \pm 3.47\%$, $13.90 \pm 2.26\%$, $9.98 \pm 8.97\%$, and $5.33 \pm 4.62\%$, respectively. As explained above, several studies carried out with different cellulosic, polymeric-NPs, and clay-based materials have demonstrated that the presence of reactive amine functional groups on their surface can significantly increase their VOC remediation properties (Guerra et al., 2018; Guerra et al., 2017; Campbell et al., 2015; Swasy et al., 2018). Indeed, PEI-coated F28 sample GC chromatogram (also displayed in Fig. 16) demonstrated almost full adsorption of hexanal vapors, yielding in a 98.12 ± 1.17% reduction.

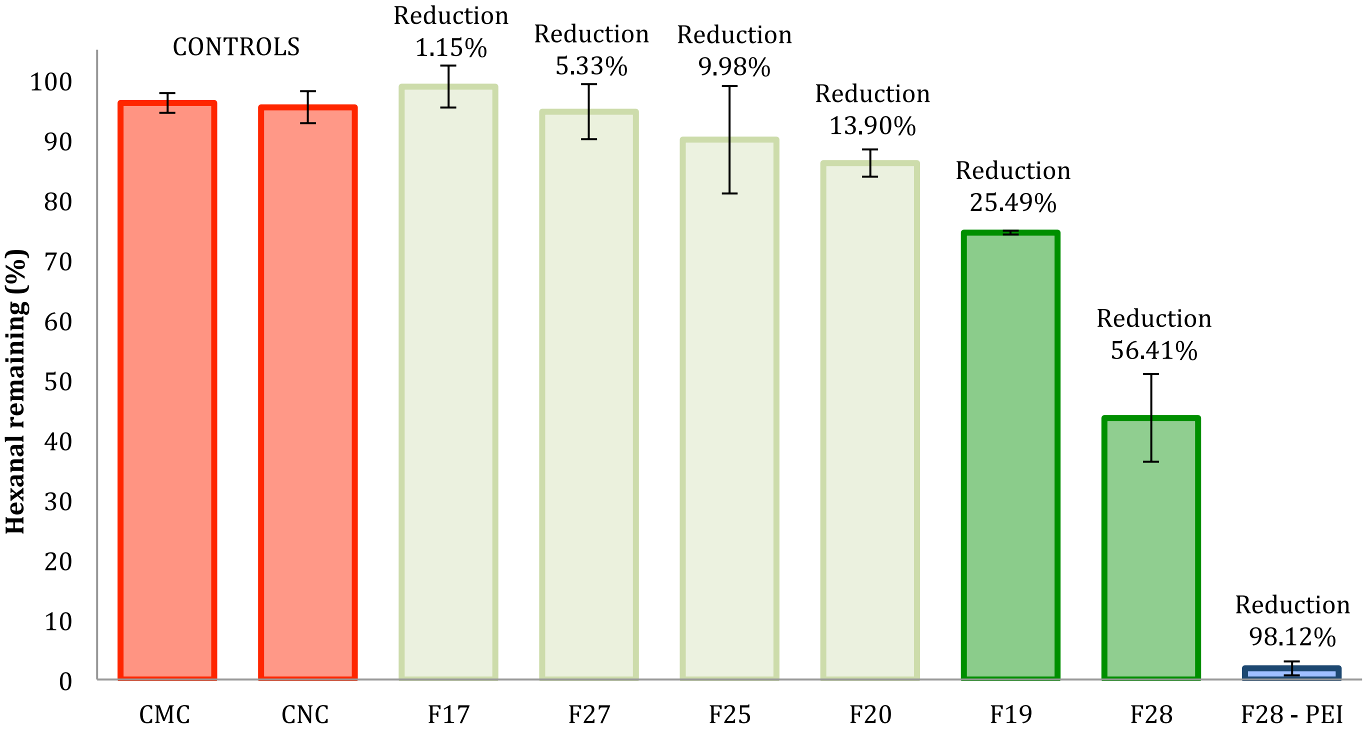


Figure 16. Percent reduction of hexanal vapors after GC experiments using unmodified, PEI-modified cellulose fibers and controls

3.2 DISCUSSION

Biopolymers are described in the literature as suitable materials for the decontamination of the environment due to their sustainable and intrinsic biological features. Cellulose is a natural polysaccharide, highly abundant worldwide with unique biocompatible, biodegradable, non-toxic, renewable, and versatile properties. Moreover, the diverse and vast biological sources present in Ecuador make this biomaterial a perfect candidate for replacing synthetic materials as aldehyde VOCs remediation agents (Luque et al., 2010; Larrea, 2013; Valencia, 1995). Six unmodified cellulose fibers were successfully extracted from six different plant sources native to Ecuador. These fibers were obtained following the same chemical protocol and characterized by a combination of FT-IR spectroscopy, thermogravimetric analysis, X-ray diffraction, BET measurements, and SEM. Importantly, the FT-IR reports indicated that the chemical composition of the cellulose samples is quite similar to commercial cellulose controls. These results proved that the fibers are mainly composed of pure cellulose with little contamination from other biopolymers, including hemicellulose and lignin. According to the XRD results, the diffraction patterns showed a typical cellulose configuration with a crystalline ($2\theta = 20 - 25$ °) and amorphous ($2\theta = 15 - 18$ °) phases. Therefore, these data suggested that the variation of the crystallinity index among samples is likely due to the different plant sources used for the extraction of the fibers, besides all samples were extracted using the exact same process. SEM images of cellulose fibers exhibited unique morphologies and structures as expected, based on their different natural sources of extraction. This fact confirms that the degree of porosity, shape, and size differ for every cellulose sample extracted from various natural sources. Further, the physicochemical characterization of PEI-F28 revealed that the cellulose fibers could be successfully surface-coated with small amounts of PEI to attach reactive amine functional groups for the covalent capture of VOCs. Previous ^{1}H NMR spectroscopy analysis carried out in 2015 by Campbell et al. demonstrated the formation of imine bonds resulting from the interaction between PEI-NPs and the common pivaldehyde VOC, thus successfully proving the potential capture mechanism of aldehydes using PEI-modified materials. Evidence of the electrostatic addition of an amino-functional coating on the fiber F28 surface was provided by the appearance of a new N-H bending band around ~1550 cm^{-1} in the FT-IR spectrum, and by the significant thermodegradable differences of the final residues of the F28 and PEI-F28 TGA thermograms. According to SEM analyses of PEI-modified and non-modified F28, the presence of the PEI polymer may alter the surface morphology of the sample.

Gas chromatography experiments revealed that some of the natural, unmodified cellulose fibers (*i.e.,* F19 and F28) demonstrated a significant, intrinsic ability to adsorb hexanal vapors (*i.e.*, up to ~57% adsorption for F28) as compared to the adsorption capability of commercially available cellulose microcrystal and nanocrystals controls (i.e., CMC and CNC). SEM and BET analyses on the cellulose samples showed that the degree of porosity and the specific surface area play a critical role in their natural VOC adsorption capacity. The two samples with the most significant efficacy for aldehyde VOC capture, isolates F19 and F28, had larger pore volumes (0.093 and 0.072 m^3/g, respectively) when compared to the other fibers and the commercial CMC/CNC samples (≤ 0.061 m^3/g). The overall specific surface area of the cellulose particle also has an essential effect on the VOC adsorption efficiency. Samples F19 and F28 possess a specific surface area of 28 m^2/g and 48 m^2/g, respectively, which are higher than the specific surface areas measured for the less-effective F17, F20, F25, and F27 fibers. Importantly, the pore volume of the fiber emerged as the main factor affecting the VOC adsorption capability of the cellulose samples. It is important to highlight that commercially available controls, CMC and CNC, which presented poor VOC adsorption capacities, exhibit smaller pore volumes. For instance, the CNC control exhibited a notable reduced VOC adsorption, despite having a large specific surface area of 22 m^2/g, while lacking sufficient pore volume (0.055 m^3/g) for effective aldehyde VOC capture. The electrostatic coating of small quantities of PEI polymer onto the surface of cellulose fiber F28 significantly increased the aldehyde VOC removal capacity of the material, reaching a performance of a 98% reduction of hexanal vapors.

The characterization results described in this study indicate that while the fiber samples are structurally and chemically similar each other, small differences in their intrinsically physicochemical properties are still evident arising from the six different unique natural sources of the samples. More importantly, the data demonstrate that these physicochemical properties of each cellulose sample present (*i.e.,* such as specific surface area, surface morphology, and pore volume) directly affect the efficiency of VOC remediation. It was reported in the literature that the area-to-volume ratio and porosity parameters play an important role in the effectiveness of materials for the cleanup of organic pollutants in water and air (Wu et al., 2019; Ruminski et al., 2011; Salman et al., 2019). Nonetheless, the correlation for the absorption of hexanal vapors is not linear. The twin features of large specific surface area coupled with a large pore volume of cellulose particles F19 and F28, as compared with commercially available controls, make the fibers uniquely useful for the capture of aldehyde VOCs. The magnitude of the specific surface area can determine the density and pore size distribution on the surface of the materials, thus explaining why isolates with large pore sizes but little specific surface areas perform poorly in VOC capture studies.

CHAPTER 4

4.1 CONCLUSIONS

- Six unique unmodified cellulose fibers were successfully extracted and purified from six different natural biodiverse sources of Ecuador.
- Extensive physicochemical characterization was performed on each cellulose fiber, as well as on the cellulose crystal controls, using FTIR, XRD, SEM, and BET, and proved that the natural source of extraction directly affects physicochemical properties, and, in turn, their intrinsic VOC decontamination capacity.
- Surface area and pore volume of cellulose fibers are critical factors that directly affect their VOC adsorption capacity. Higher surface area results in higher degree of porosity, which, in turn, yields better VOC adsorption capability.
- There are optimal natural cellulose physicochemical properties, such as high specific surface area and abundant pore volume that directly affect the intrinsic ability of the material to capture VOCs.
- Amine surface electrostatic coating of the cellulose fibers dramatically increases their adsorption capacity. Moreover, surface coating of cellulose fibers by electrostatic interactions results on the modification of cellulose avoiding several chemical steps and the use of a wide variety of reagents, thus, abstaining from creating more pollution.
- The inherent sources of biodiverse rich countries, such as Ecuador, present a potential for the exploration and creation of novel, sustainable, and structurally diverse cellulosic platforms for remediation of the environment.

4.2 RECOMMENDATIONS

In the present study work I focused on the determination of the physicochemical properties of six cellulose natural fibers through the use of a series of characterization methods such as FTIR, TGA, XRD, SEM and BET measurements. As well, I studied the capacity of these fibers for the proper capture of hexanal vapors by the development of gas chromatography assays. The results I presented here demonstrated that these fibers present different physicochemical properties, which in turn explain the differences in their aldehyde VOC capture, ability. The conclusions stated above well described the goals of this research and thus, I highly recommend that future work can be focused on the study and comparisons of other biopolymers obtained from plant cell walls such as lignin or hemicellulose as air pollution remediation agents, but more importantly, their interactions with air contaminants in order to degrade them.

Moreover, research projects can be oriented on the evaluation of these materials capacity to remediate other toxic molecules present in air or water pollution, and thus test their application versatility for further decontamination of the environment worldwide. Furthermore, based on the results analyze in this work I highly recommend to deeply investigating the effects of natural extraction source, and the physicochemical parameters, of the biomaterials utilized, that control the efficient capture of not only aldehyde VOCs, but also other contaminants present in all forms of pollution.

BIBLIOGRAPHY

Abdou E. S., Nagy K. S. A. & Elsabee M. Z. (2008). Extraction and characterization of chitin and chitosan from local sources. *Bioresour Technol. 99,* 1359–1367.

Ahmad S., Pandey A. & Pathak V. V. (2020). Phycoremediation: Algae as Eco-friendly Tools for the Removal of Heavy Metals from Wastewaters. *Bioremediation Ind. Waste. Environ. Saf.* X, 53–76.

Aider M. (2010). Chitosan application for active bio-based films production and potential in the food industry: Review. *LWT - Food Sci. Technol. 43*(6), 837–842.

Aigner T.B., DeSimone E. & Scheibel T. (2018). Biomedical applications of recombinant silk-based materials. *Adv. Mater. 30*(19), 1–28.

Al-manhel A. J., Al-hilphy A. R. S. & Niamah A. K. (2018). Extraction of chitosan, characterisation and its use for water purification. *J. Saudi Soc. Agric. Sci. 17,* 186-190.

Almeida M. A. (2007). Extraction of Bioactive Compounds from Latin American Plants.

Babu K.M. (2019). Chapter 1: Introduction to silk and sericulture. In Babu K.M., *Silk, procesing, properties and applications* (pp. 1–32). Woodhead Publising.

Barakat M. A. (2011). New trends in removing heavy metals from industrial wastewater. *Arab. J. Chem. 4*(4), 361–377.

Bates M. E., Grieger K. D., Trump B. D., Keisler J. M., Plourde K. J. & Linkov I. (2016). Emerging Technologies for Environmental Remediation: Integrating Data and Judgment. *Environ. Sci. Technol. 50*(1), 349–358.

Bethke K., Palantöken S., Andrei V., Roß M., Raghuwanshi V. S., Kettemann F., Greis K., Ingber T. T. K., Stückrath J. B., Valiyaveettil S. & Rademann K. (2018). Functionalized Cellulose for Water Purification, Antimicrobial Applications, and Sensors. *Adv. Funct. Mater. 28*(23), 1800409.

Bhandari G. (2018). Environmental Nanotechnology: Applications of Nanoparticles for Bioremediation. Approaches in Bioremediation. 301–315.

Bismarck A., Aranbefwi-Askargorta I., Springer J., Lampke T., Wielage B., Stamboulis A., Shenderovich I. & Limbach H. H. (2002). Surface characterization of flex, hemp and cellulose fibers; surface properties and the the water uptake behavior. *Polym. Compos. 23*(5), 872–894.

Boehm F. (2006). Nanotechnology in Environmental Applications. *Report NAN039A, BCC Research*, Wellesley, MA.

Boerjan W. Ralph J. & Baucher M. (2003). Lignin biosynthesis. *Annu. Rev. Plant Biol. 54,* 519–546.

Campbell M.L., Guerra F.D., Dhulekar J., Alexis F., & Whitehead D.C. (2015). Target-Specific Capture of Environmentally Relevant Gaseous Aldehydes and Carboxylic Acids with Functional Nanoparticles. *Chem - A Eur Journ. 21*(42), 14834-1484.

Cao Y. & Wang B. (2009). Biodegradation of silk biomaterials. *Int. J. Mol. Sci. 10*(4), 1514–1524.

Carpenter A. W., De Lannoy C. F. & Wiesner M. R. (2015). Cellulose nanomaterials in water treatment technologies. *Environ. Sci. Technol. 49*(9), 5277–5287.

Carvalho I. C., Medeiro-Borsaglio F. G. L., Mansur A. A. P., Caldeira C. L., Haas D. J., Lage A. P., Ciminelli V. S. T. & Mansur H. S. (2019). 3D sponges of chemically functionalized chitosan for potential environmental pollution remediation : biosorbents for anionic dye adsorption and “antibiotic-free” antibacterial activity. *Environ. Technol.,* 1–21.

De Souza M.M., & Borsali R. (2004). Rodlike Cellulose Microcrystals: Structure, Properties, and Applications. *Macromol Rap Commun. 25*(7), 771-787.

Elham F. M. (2017). Nanotechnology: Future of environmental air pollution control. *Macrothink Institute Online Journal. 6*(2), 429-454.

George J. & Sabapathi S. N. (2015). Cellulose nanocrystals: synthesis , functional properties , and applications. *Nanotechnol. Sci. Appl. 8*, 45–54.

Guerra F.D., Campbell M.L., Attia M.F., Whitehead D.C., & Alexis F. (2018b). Capture of Aldehyde VOCs Using a Series of Amine-Functionalized Cellulose Nanocrystals. *Chem Sel. 3*(20), 5495–5501.

Guerra F.D., Campbell M.L., Whitehead D.C., & Alexis F. (2017). Tunable properties of functional nanoparticles for efficient capture of VOCs. *Chem Sel. 2*(31), 9889-9894.

Guerra, F., Attia, M., Whitehead, D., & Alexis, F. (2018a). Nanotechnology for Environmental Remediation: Materials and Applications*. Molecules, 23*(7), *1760-1783.*

Harrison, P. (2002). Indoor environmental quality: *By T Godish. 2001. Boca Raton, FL, USA: Lewis, CRC Press. ISBN: 1 56670 402 2. Occupational and Environmental Medicine, 59(3), 201–204.*

Haseena M., Malik M. F., Javed A., Arshad S. & Asif N. (2017). Water pollution and human health. E*nviron. Risk. Assess. Remediat. 1*(3),16–29.

Hatakeyama H. & Hatakeyama T. (2009). Lignin structure, properties, and applications. In A. Abe, K. Dusek & S. Kobayashi (Eds.), *Biopolymers. Advances in Polymer Science*, (pp. 1-63) Springer, Berlin, Heidelberg.

Hokkanen S., Bhatnagar A. & Sillanpää M. (2016). A review on modification methods to cellulose-based adsorbents to improve adsorption capacity. *Water Res. 91,* 156–173.

Ion V. A., Pârvulescu O. C. & Dobre T. (2015). Volatile organic compounds adsorption onto neat and hybrid bacterial cellulose*. Appl. Surf. Sci. 335,* 137-146.

Kampa M. & Castanas E. (2008). Human health effects of air pollution. *Environ. Pollut. 151,* 362–367.

Kampa M., & Castanas E. (2008). Human health effects of air pollution. *Environ. Pollut. 151*(2), 362-367.

Khan S., Garg M., Chockalingam S., Gopinath P. & Kundu P. P. (2019). TiO2 doped chitosan/poly (vinyl alcohol) nanocomposite film with enhanced mechanical properties for application in bone tissue regeneration. *Int. J. Biol. Macromol. 143,* 285-296.

Khin M. M., Nair A. S., Babu V. J., Murugan R. & Ramakrishna S. (2012). A review on nanomaterials for environmental remediation. *Energy Environ. Sci. 5,* 8075–8109.

Kim S. Y., Yoon Y. H. & Kim K. S. (2016). Performance of activated carbon-impregnated cellulose filters for indoor VOCs and dust control. *Int. J. Environ. Sci. Technol. 13,* 2189-2198.

Kishi, R., Norbäck, D., & Araki, A. (Eds.). (2020). Indoor Environmental Quality and Health Risk toward Healthier Environment for All*. Current Topics in Environmental Health and Preventive Medicine.*

Klemm D. , Heublein B. , Fink H. & Bohn A. (2005). Polymer Science Cellulose : Fascinating Biopolymer and Sustainable Raw Material Angewandte. *Chemie Int Ed. 44*(22), 3358–3393.

Kumar M. & Turner S. (2014). Plant cellulose synthesis: CESA proteins crossing kingdoms. *Phytochemistry. 112,* 91-99.

Kumar V. & Ioan S. (2016). Recent advances in cellulose and chitosan based membranes for water purification: A concise review. *Carbohydr. Polym. 146,* 148–165.

Larrea C., September 12-13, 2013. Extractivism, economic diversification and prospects for sustainable development in Ecuador. Paper presented to the "Latin America and the Shifting Sands of Global Power" Conference, Australia National University, Canberra.

Li Z., Ge Y. & Wan L. (2014). Fabrication of a green porous lignin-based sphere for the removal of lead ions from aqueous media. *J. Hazard Mater. 285,* 77-83.

Luque S., Mart G., Echeverr C. & Pacha M. J. (2010). Chapter 15: Overview of Biodiversity Loss in South America: A Landscape Perspective for Sustainable Forest Management and Conservation in Temperate Forests. In C. Li, R. Lafortezza & J. Chen, *Landscape Ecology in Forest Management and Conservation*. (pp. 357-384). Elsevier.

Ma H., Burger C., Hsiao B. S. & Chu B. (2011). Ultra-fine cellulose nanofibers: New nano-scale materials for water purification. *J. Mater. Chem. 21*(21), 7507–7510.

Maleki S. S., Mohammadi K. & Ji K. (2016). Characterization of Cellulose Synthesis in Plant Cells. *Sci. World J. 2016,* 1-8.

Manjarrez L., Ballinas M. L., Solís-Canto O., Celzard A., Fierro V., Ibarra R. & Gonzalez

G. (2011). Biopolymers-based nanocomposites: Membranes from propionated lignin and cellulose for water purification. *Carbohydr. Polym. 86*(2), 732–741.

Mcnamara J. T. & Morgan J. L. W. (2015). A Molecular Description of Cellulose Biosynthesis. *Annu Rev Biochem. 84*(1), 895–921.

Moon R. J., Martini A., Nairn J., Simonsen J. & Youngblood J. (2011). Cellulose nanomaterials review: Structure, properties and nanocomposites. Chem. Soc. Rev. 40(7), 3941-3994

Morán J. I., Alvarez V. A., Cyras V. P. & Vázquez A. (2008). Extraction of cellulose and preparation of nanocellulose from sisal fibers. *Cellulose. 15*(1), 149–159.

Mueller, N. C., & Nowack, B. (2010). Nanoparticles for Remediation: Solving Big Problems with Little Particles*. Elements, 6*(6), 395–400.

Muralikrishna V. I., & Manickam V. (2017). Chapter one: Introduction. In V. I. Muralikrishna, & V. Manickam, *Environmental Management: Science and Engineering for Industry* (pp. 1-4). Elsevier.

Nabili A., Fattoum A., Passas R. & Elaloui E. (2016). Extraction and characterization of cellulose from date palm seeds *(Phoenix dactylifera L.). Cellulose Chem.Technol. 50*(9–10), 1015-1023.

O'Connell D. W., Birkinshaw C. & O'Dwyer T. F. (2008). Heavy metal adsorbents prepared from the modification of cellulose: A review. *Bioresour. Technol. 99*(15), 6709–6724.

Osseiran N., & Chriscaden K. (March 6th, 2017). The cost of a polluted environment: 1.7 million child deaths a year, says WHO. *World Health Organization.* Available at: https://www.who.int/news-room/detail/06-03-2017-the-cost-of-a-polluted-environment-1-7-million-child-deaths-a-year-says-who

Parajuli D., Inoue K., Ohto K. & Oshima T. (2005). Adsorption of heavy metals on crosslinked lignocatechol: a modified lignin gel. *React. Funct. Polym. 62,* 129–139.

Peng B., Yao Z., Wang X., Crombeen M., Gsweene D. & Tam K. C. (2019). Cellulose-based Materials in Wastewater Treatment of Petroleum Industry. *Green Energy Environ. In Press.*

Rickerby D., & Morrison M. (2007). Report from the Workshop on Nanotechnologies for Environmental Remediation. *JRC Ispra*. Available at: www.nanowerk.com/nanotechnology/ reports/reportpdf/report101.pdf

Rinaudo M. (2006). Chitin and chitosan: Properties and applications. *Prog. Polym. Sci. 31*(7), 603–632.

Ruminski A. M., Jeon K. J. & Urban J. J. (2011). Size-dependent CO2 capture in chemically synthesized magnesium oxide nanocrystals. *J. Mater. Chem. 21*(31)*,* 11486-11491.

Salman M., Jahan S., Kanwal S. & Mansoor F. (2019). Recent advances in the application of silica nanostructures for highly improved water treatment: a review. *Environ. Sci. Pollut. Res. 26*(21), 21065-21085.

Schweitzer L., & Noblet J. (2018). Chapter 3.6 – Water contamination and pollution. In B. Török, & T. Dransfield (Eds.), *Green Chemistry* (pp. 261-290). Boston, MA, USA: Elsevier.

Segal L., Creely J. J., Martin A.E., & Conrad C. M. (1959). An empirical method for estimating the degree of crystallinity of native cellulose using the x-ray diffractometer. *Text Res J. 29*(10), 786–794.

Swasy M.I., Campbell M.L., Brummel B.R., Guerra F.D., Attia M.F., Smith G.D., Alexis F., & Whitehead D. C. (2018). Poly(amine) modified kaolinite clay for VOC capture. *Chemosphere*. *213*, 19–24.

Taylor P., Yunus I. S., Kurniawan A., Adityawarman D. & Indarto A. (2012). Nanotechnologies in water and air pollution treatment. *Environ. Technol. Rev. 1*(1), 37–41.

Tchounwou P. B., Yedjou C. G., Patlolla A. K. & Sutton D. J. (2012). Heavy Metal Toxicity and the Environment. *Exp Suppl. 101,* 133–164.

Thakur V. K. & Thakur M. K. (2014). Processing and characterization of natural cellulose fibers/thermoset polymer composites. *Carbohydr. Polym. 109,* 102-117.

Tian Y., Wu M., Liu R., Li Y., Wang D., Tan J., Wu R. & Huang Y. (2011). Electrospun membrane of cellulose acetate for heavy metal ion adsorption in water treatment. *Carbohydr. Polym. 83*(2), 743–748.

Tursi A., Beneduci A., Chidichimo F., De Vietro N. & Chidichimo G. (2018). Remediation of hydrocarbons polluted water by hydrophobic functionalized cellulose. *Chemosphere. 201,* 530–539.

Valencia R., June 21-26, 1995. Composition and structure of an Andean forest fragment in eastern Ecuador. Paper presented to the "Biodiversity and Conservation of Neotropical Montane Forests" Symposium, The New York Botanical Garden, Brooklyn, NY, USA.

Van Toan N. & Hanh T. T. (2013). Application of chitosan solutions for rice production in Vietnam. *Afr. J. Biotechnol. 12*(4), 382–384.

Vanholme R., Morreel K., Ralph J. & Boerjan W. (2008). Lignin engineering. *Curr. Opin. Plant Biol. 11*(3), 278–285.

Wang B., Wan Y., Zheng Y., Lee X., Liu T., Yu Z., Huang J., Ok Y. S., Chen J. & Gao B. (2019). Alginate-based composites for environmental applications: a critical review. *Crit. Rev. Environ. Sci. Technol. 49*(4), 318-356.

Wang C., Wu S., Jian M., Xie J., Xu L., Yang X., Zheng Q. & Zhang Y. (2016). Silk nanofibers as high efficient and lightweight air filter. *Nano. Res. 9*(9), 2590–2597.

Wang D., Pillai S. C., Ho S. H, Zeng J., Li Y. & Dionysiou D. D. (2018). Plasmonic-based nanomaterials for environmental remediation. *Appl. Catal. B. 237*, 721–741.

Wang R., Guan S., Sato A., Wang X., Wang Z., Yang R., Hsiao B. & Chu B. (2013). Nanofibrous microfiltration membranes capable of removing bacteria, viruses and heavy metal ions. *J. Membr. Sci. 446,* 376-382.

Wang S., Sun H., Ang H. M. & Tadé M. O. (2013). Adsorptive remediation of environmental pollutants using novel graphene-based nanomaterials. *Chem. Eng. J. 226,* 336-347.

Wu Y., Pang H., Liu Y., Wang X., Yu S., Fu D., Chen J. & Wang X. (2019). Environmental remediation of heavy metal ions by novel-nanomaterials: A review. *Environ. Pollut. 246,* 608-620.

Yong K. & Mooney D. J. (2012). Alginate: Properties and biomedical applications. *Prog. Polym. Sci. 37*(1), 106–126.

Zhang W. X. (2003). Nanoscale iron particles for environmental remediation: An overview. *J. Nanopart. Res. 5*(4), 323–332.