Kaunas University of Technology

Faculty of Chemical Technology

Regenerated Nanofibrous Cellulose-Based Adsorbent for Water Pollutants

Master's Final Degree Project

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Environmental Engineering (6211EX003)

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Summary

In the framework of this research, an extensive two-phase study was embarked upon, focusing on investigating the adsorption capabilities of methylene blue dye using cellulose nanofibers. The cellulose nanofibers were created using the electrospinning process of regenerated cellulose polymer solution. The two phases of this research encompassed two consequential objectives. The initial phase revolved around the determination of optimal ratios within the polymer solution, that was intended for fabrication, as well as the electrospinning process parameters. Following this phase, the secondary phase centered its attention on a thorough exploration of the adsorptive capacity and the efficiency of the meticulously fabricated fibers. To provide a more comprehensive picture, a selected segment of the produced fibers, along with unprocessed raw cellulose underwent modification. This modification was undertaken using two distinct processes: ozonation modification and plasma modification.

Upon examination of the data obtained, the results demonstrated that the operational parameters that led to the most advantageous qualities were established at a voltage difference of 12 kV, coupled with a nozzle flow rate maintained at 9 mm/h, and equally balanced quantities of the employed ionic liquid and dimethyl sulfoxide. The cellulose that had undergone the ozone modification process surfaced as the front runner in terms of performance. This was evident when observing the rate of sorption and the overall adsorption capacity, as it presented significant advantages when pitted against its counterparts. In addition to the primary results, the kinetics and isotherms of the study were subjected to detailed analysis, providing additional layers of understanding and insight into the processes and results observed.

The completion of this study involved a comprehensive examination of the findings, which were compared with existing literature on this topic. The cellulose tested in this study exhibited acceptable results, but only over an extended period, characterized by high pseudo-second-order kinetic constant and Freundlich k_f and n constants values, distinguishing it from other similar cellulose adsorbents. However, the results were tempered by certain limitations and discrepancies, mainly arising from the design of the experiment, including the duration, and physical deterioration of the fibers. These factors underscore the scope for refinement and the need for continual evolution in experimental design and procedure in future studies.

Elsherif, Mahmoud Ahmed Naeem Mustafa. Regeneruotos nanopluoštinės celiuliozės vandens teršalų adsorbentai. Magistro baigiamasis projektas / Vadovas Dainius Martuzevičius; Kauno technologijos universitetas, Cheminės technologijos fakultetas.

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Santrauka

Šio darbo rėmuose buvo atliktas išsamus dviejų etapų tyrimas, skirtas ištirti metileno mėlio dažų adsorbciją, naudojant celiuliozės nanopluoštą. Celiuliozės nanopluoštas buvo pagamintos naudojant šlapiojo elektrinio verpimo procesą, kurio metu buvo naudojama celiuliozės polimerų tirpalas. Pirmasis tyrimų etapas buvo skirtas optimalių santykių nustatymui gamybai naudojamo polimerų tirpale ir elektrinio verpimo proceso parametrams. Papildomai buvo atliktas celiuliozės pluošto modifikavimas ozonavimo ir plazmos būdu. Antrojo etapo metu nustatyta pagamintų pluoštų adsorbcinės geba ir efektyvumas.

Optimalūs darbo parametrai, buvo nustatyti esant 12 kV įtampai, 9 mm/h linijiniam polimero tirpalo debitui, esant tirpalui, paruoštam iš lygių dalių joninio skysčio ir dimetilsulfoksido. Be pagrindinių rezultatų, buvo išsamiai analizuojamos tyrimo kinetika ir izotermos, suteikiant papildomą supratimo ir įžvalgų lygmenį apie pastebėtus procesus ir rezultatus. Ozonu modifikuota celiuliozė pademonstravo geriausias sorbcines savybes tiek sorbcijos greičio, tiek bendros adsorbcinės gebos atveju.

Šio tyrimo pabaigoje atlikta išsami rezultatų analizė, kuri buvo palyginama su literatūroje pateiktais duomenimis. Regeneruota nanopluoštinė celiuliozė davė patenkinamus rezultatus, tačiau tik esant ilgai eksperimento trukmei, pasižymint aukštu pseudoantrojo eilės kinetinio konstantos ir Freundlich kf bei n konstantų vertėmis, ją išskiriant iš kitų panašių celiuliozės adsorbentų. Tačiau rezultatams turėjo neigiamos įtakos tam tikri apribojimas, susiję su eksperimento dizainu, įskaitant trukmę ir pluoštų fizinį degradavimą. Šie veiksniai nurodo galimybes tobulinti ir nuolat evoliucionuoti eksperimentinį dizainą ir procedūras ateities tyrimuose.

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Abbreviations:

CN – cellulose nanofibers;

C – unmodified raw cellulose;

OCN – ozone-modified cellulose nanofibers;

OC – ozone-modified raw cellulose;

PCN – plasma-modified cellulose nanofibers;

PC – plasma-modified raw cellulose.

Introduction

Overview

The necessity of having cleaner water and rise of contaminants in both drinking and waste water are creating a crucial need for more advanced treatment methods. Methods that are not only efficient but those that offer more environmentally friendly, as well. This thesis explores the possibilities within a branch of nanotechnology that focuses on natural polymers so as to create an alternative that offers the aforementioned options. The conversion of cellulose, which exists naturally in virtually all planets, into cellulose nanofibers is the focus of this thesis.

The thesis firstly offers an article review to go through various and numerous pieces of literature that discuss the environmental aspects of using cellulose, then articles which ventured through the field of cellulose nanofiber. Afterwards, other works were reviewed to analyze methods of cellulose nanofibers fabrication, among other polymers. Finally, papers on cellulose-based adsorption mechanism were discussed.

By the end of the article review, a research gap was revealed: the lack of proper research on the adsorption efficiency of the unmodified cellulose nanofibers. Almost the entirety of research works discard the study of unmodified cellulose nanofibers, solely, as a means of efficient adsorbent. This presents a great research gap that needs to be filled.

Thereby, the thesis raises the question of: does the use cellulose nanofibers offer an efficient and viable adsorbent or not? And at what efficiency? What is the mechanism of adsorption and the rate at which adsorption occurs?

Work was conducted, and discussed in this report, to find a solution for the research questions. The work was divided into two phases. The first phase was undertaken to determine the optimal ratios of polymer solution to be fabricated, while the second phase studied the adsorption capacity and efficiency of the fabricated cellulose nanofibers.

One of the methods of creating cellulose nanofibers is using the electrospinning method. Before the beginning of electrospinning process, a solution of polymer dissolved in a solution is to be prepared. A very suitable method is the use of regenerated cellulose process to create an electrospinning polymer solution. The solution is then injected unto a collector under high voltage difference. After the process of electrospinning, post treatment operations takes place. The produced fibers are analyzed systematically to optimize the process in order to achieve the desirable quality.

The second phase of the project utilized the optimally fabricated nanofibers for the adsorption of methylene blue dye. Methylene blue dye is a basic dye commonly used in adsorption studies due to its high visibility, ease of detection and measurement, and known interaction with many types of adsorbent materials. It provides a simple yet effective means of evaluating the adsorption capabilities of a material. Furthermore, when dissolved in water, it exhibits a characteristic absorbance peak at around 664 nm in the visible light spectrum. This strong and specific absorbance allows for easy and accurate quantification using a spectrophotometer.

The resulted data from the adsorption are then analyzed to conclude the adsorption capacities, kinetics, and isotherms of the adsorption process. The results of such analysis can provide a proper judgement on the quality and mechanics of adsorption.

Aim of the thesis

To research technical feasibility of the application of regenerated cellulose nanofiber adsorbent for an efficient adsorption of water pollutants.

Thesis approach

This thesis approaches its aims through the following set of tasks:

- Review up-to-date information from the available literature to build a proper baseline in order to design the proper experiments needed for the investigation target that was set as an aim for the thesis
- Choose the optimal operating conditions to fabricate nanofibers with the suitable quality.
- Test the optimally fabricated nanofibers for the adsorption methylene blue in deionized water solution with different concentrations.
- Compare the results of each adsorbent to one another and to other similar adsorption processes from literature

1. Literature review

1.1. Cellulose

Naturally occurring and widely abundant in nature, cellulose is the most common bio-based natural polymer existing on earth; forming the structural component of plant cell walls, providing strength and rigidity to the plant. Cellulose is present in and can be extracted from a variety of sources, including plants, bacteria, and some members of the animal kingdom such as tunicates. All of this widespread availability and versatility made cellulose an extremely valuable resource for humans throughout history. From its earliest use as an essential medium for fire creation and preservation, to its modern-day applications in cellulosic-based nanotechnologies, cellulose has played a significant and an important role in the cultural and technological development of human civilization.[1–7]

The unique properties of cellulose have made it a universal material in a wide range of products and tools. For example, cellulose possesses a tensile strength which exceeds some metallic tensile strength; at a range of 4.90-7.50 GPa. Combined with its unique morphology, cellulose was coveted to be used in most of man-made products; from textiles and paper products to advanced composites and nanotechnology applications. Additionally, cellulose can be chemically modified to create new materials with unique properties. A famous example of such materials is cellulose acetate which is a versatile plastic that is commonly used in different environmental applications.[1–3, 5, 8–12]

It is possible to overlook the widespread use of cellulose in everyday products, but the importance of this biopolymer cannot be exaggerated. Not only does it provide structural support for plants and other organisms, but it has been a fundamental component of human technological progress for thousands of years, as well. As a matter of fact, the development of paper in ancient Egypt and China is one of the major turning points in human history, leading to the spread of knowledge and information as well as the creation of important components of the world economy. Nowadays, cellulose-based products are essential in everyday aspects of life, and researchers are constantly exploring new ways and methods to use these versatile biopolymers in an innovative and exciting way.[4–6]

Despite the descending popularity in the modern era of synthetic polymers, cellulose has been gaining popularity in recent few decades due to environmental and health related reasons. Cellulose is a natural polymer forming an important component of the cell walls of all plants. In other words, it is a natural and renewable resource. Another important environmental benefit of cellulose is that it is also easily decomposed. Unlike petroleum-based synthetic polymers, cellulose is biodegradable and can be degraded relatively quickly via natural processes. This makes it an environmentally friendly option for various products, from packaging materials to clothing and filters. [3, 5, 6, 11, 13–15]

Another advantageous aspect of cellulose is its minimal impact on human health. While many synthetic polymers have been linked to health issues (such as toxicity and cancer), cellulose is generally considered a health-wise safer alternative. As a matter of fact, despite their inability to digest cellulose, humans need cellulose to maintain a healthy digestive system; while herbivores and other microorganisms are capable of utilizing their digestive system to digest cellulose and use as a source of energy. This is especially of a significant importance since it eliminates the necessity to remove cellulose-based materials from any industrial or environmental processes, since it can be safely digested in a multitude of ways. [16–20]

Fig. 1. Examples of different sources of cellulose: (a) Trees; (b) Sugar canes; (c) domestic waste (d) Tunicate; (e) Rhozobium; (f) paper; (g) books; (h) clothes; (i) napkins and sheets

With the current deteriorating state of the environment and the rise of concerns about sustainability, the use of cellulose as a natural alternative to petroleum-based polymers is becoming increasingly important and targeted. Because not only is it more environmentally friendly, but it also has fewer negative impacts on human health; as previously mentioned.

1.2. Cellulose nanofibers

Among the most important methods of utilizing cellulose is through using it in the form of cellulose nanofibers (CN). Ji and Yun [9], for example, discusses the use of electrospun nanofibers (NF) for air filtration, while Sayyed et al. [21] explored the use of nanomaterials made from cellulose for water and wastewater treatment processes. Jiang and Ngai [2], on the other hand, studied the use of modified cellulose for food packaging purposes. Moreover, in the medical field, Phanthong et al. [22] tested the compatibility of CN for skin grafting with positive results. Furthermore, Wang et al. [23], Sayyed et al. [21], as well as Jain et al. [20], gave extensive examples for up-to-date utilization technologies for NF; CN included, and methods for electrospinning selective examples of such NFs.

Cellulose nanofibers are an intriguing group of bio-based polymers which have attracted the interest of researchers, in the field of nanotechnology; a branch of science that is is focused on the study of materials on the scale ranging from 1-100 nanometers. Almost the entirety of cellulose nanofibers is composed of pure cellulose molecules, making the fibers collectively possess exceptional mechanical qualities. These mechanical qualities can be attributed to the presence of hydrogen bonding between the hydrogen and hydroxyl glucose units, dispersion forces, and various stereoelectric factors which form electrical static attraction forces between molecules. The hydroxyl functional groups present in cellulose also represent a significant and pivotal role in the diverse applications of CN. The hydroxyl groups provide further potential for being functionalized to increase the active sites, creating a very versatile adsorbent and filter material. In addition to the previously mentioned advantageous properties, CN have very high surface area. Along with its exceedingly high porosity, high surface area further increase their potential utility across a range of fields as well as future innovation and technological advancements. [12, 20, 22, 24] Fig. 2 shows an illustration of cellulose molecular structure with hydrogen bonds that exist on the intermolecular level between the functional groups.

1.3. Fabrication of cellulose nanofibers

1.3.1. Extraction of cellulose from its raw sources

The aforementioned unique properties of cellulose, such as high mechanical strength, biocompatibility, and renewability cellulose fibers, made cellulose a target of significant interest in the field of nanotechnology. However, cellulose is not suitable in its natural form for utilization in nanotechnology, instead, they require extraction, processing and even restructuring.

The various methods of extraction have been ever expanding, making it a challenging mission to gather all the related information in a humble literature review without lacking the proper depth and level of details. CN are most commonly extracted from their natural form mechanically, chemically, biologically. Depending on the requirements and applications, the suitable method can be chosen. [21, 25]

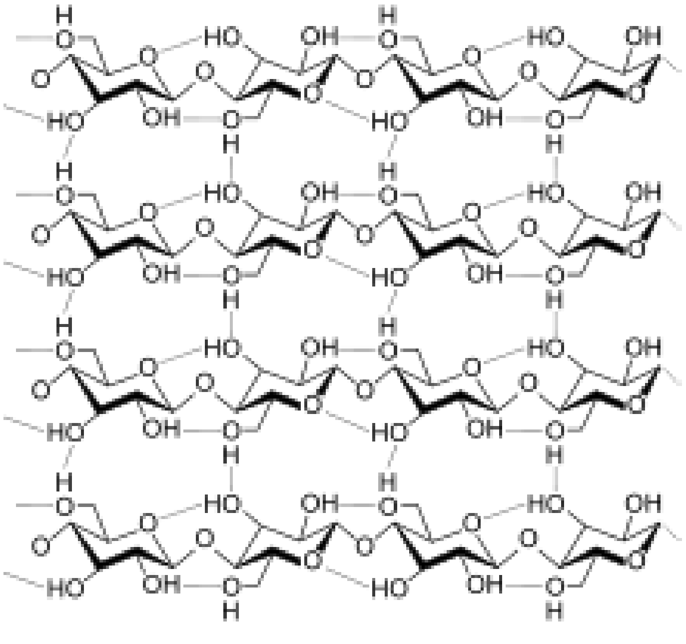

Fig. 2. Cellulose molecular structure and its intermolecular hydrogen bonds

For starters, mechanical extraction techniques include methods such as grinding, ultrasonification, microfluidization, homogenization, among others. On the other hand, chemical extraction methods (such as acid hydrolysis, extraction by a solvent, and oxidation), while being comparatively more effective, can compromise the quality of the fibers. Alternatively, the biological extraction of cellulose is an environmentally promising method that involves the use of natural enzymatic reactions to acquire CN. This method also produces high-quality cellulose fibers and is eco-friendly. [21, 25] Each of the different extraction methods has its advantages and disadvantages, edges and shortcomings; and the choice of the proper method depends on the requirements, needs and goals of the final application. The upcoming section provides a brief overview of the most commonly utilized methods.

1.3.1.1. Mechanical Methods

Nanocellulose extraction using mechanical means is one of the most traditional methods. As self-explanatory as they sound, they involve the use mechanical forces to separate and restructure the cellulose fibers. The main concept of the mechanical process is not complex, but it can be subcategorized into conventional and non-conventional methods, each differ according to their approach and mechanism. [21]

The main mechanism behind the conventional methods, such as homogenization, microfluidization, and grinding, is the usage of form of shearing force to break down and separate the cellulosic fibers. The non-conventional methods, on the other hand, use more specialized means of refinement, such as extrusion, cryocrushing, ball milling, aqueous counter collision, blending, and extrusion. Furthermore, in some cases, using blended mechanical methods with other methods can also be beneficial; as demonstrated by Fahma et al., who combined mechanical means of fabrication with a method of chemical extraction by acid hydrolysis to prevent the coagulation of CN. [21]

The main disadvantage of mechanical extraction methods, however, is their relatively high energy consumption. Their energy consumption can reach over 25 thousand kWh per ton of processed materials, which is a significant obstacle for industrial-scale production. Despite this limitation, though, research exploring mechanical means of extraction continues to progress. The research work primarily with efforts being made to reduce energy consumption and increase efficiency in the hope of having the mechanical methods of extraction become more viable and widely used in the production of nanocellulose in the future. [21, 22]

1.3.1.2. Chemical Methods

In nature, cellulose is typically found alongside other natural fibers such as lignin. Chemical extraction of cellulose involves the use of mineral acids like sulfuric, hydrochloric acid, and phosphoric acid, to hydrolyze cellulose fibers in the natural fiber. The fibers are composed of microfibrils which contain both amorphous and crystalline regions. The amorphous sections of the fibers serve as structural weaknesses, and are responsible for the further separation of microfibrils into cellulose nanofibers. Acid hydrolysis is then used to isolate the cellulose by removing the amorphous regions, thus creating higher crystallinity fibers. However, mineral acids are not the only options for chemical fabrication, as organic acids and solvents such as N-Methylmorpholine N-oxide, Dimethylformamide, and Dimethyl sulfoxide can also be used. These solvents have the added advantage of being able to hydrolyze other natural fabrics such as lignin that exist alongside cellulose. Moreover, sodium hydroxide can additionally be used in low concentration at medium-ranged temperatures. [21]

In the previous section, it was mentioned that mechanical methods can be used as a blend with other methods of extraction; hydrolysis, too, can be used in the same manner. For example, hydrolysis can be used as a precursor step to the mechanical fabrication method. This blend can help to lower power consumption as mentioned earlier; leading to a mitigated disadvantage of the formerly mentioned method. This, however, does not come free of consequences since the use of acids ultimately leads to the inevitable need for wastewater treatment downstream. To ensure that the process remains as environmentally friendly as possible, the treatment of the downstream wastewater is an important step. This neutralization process usually starts with washing with water of low temperature and then the use of a centrifugal unit until the pH reaches an acceptable value. For this reason, chemical means of extraction remain environmentally shunned despite their promising potential as methods that are capable of producing high-quality nanocellulose materials. Their sustainability and environmental impact should be taken into consideration during the decision making process. Therefore, efforts should be made to optimize the chemical fabrication process in order to reduce its environmental footprint and to enable more widespread adoption. [21, 22, 26, 27]

1.3.1.3. Biological Methods

Nanocellulose can also be extracted via biological means. Biological means of extraction emerged as a more environmentally friendly supplement that can be merged with other means of extractions; mainly mechanical and chemical means. It is largely used as a precursor to mechanical means. This, however, is not written in stones, as a mixture of all the three methods can be used according to each case on its own. [21, 26]

The main advantage that biological means of extraction offer is that it eliminates the need for using environmentally harmful chemical; unlike in chemical hydrolysis with its widespan use of corrosive acids, for example. Instead, biological means rather utilize microorganisms to accomplish the target. [22, 28]

A rising star in the world of biological extraction is the enzymatic approach. It follows the same mechanism of chemical fabrication method but using enzymes instead. Some biocatalysts are used, however, to accelerate the process. Among those biocatalysts are cellulase and xylanase. Enzymatic hydrolysis does not only replace the chemical approach for extraction process and eliminate the need for downstream water treatment, but it offers other advantages as well. A very attractive advantage is that the produced CN using enzymatic hydrolysis have a higher aspect ratio that its counterpart which are produced via chemical hydrolysis. This results in a higher quality CN. [22, 28]

1.3.2. Cellulose preparation

The following step during the nanofibers production process is dissolving the cellulose. This is usually achieved by using a suitable solvent system that can disrupt the hydrogen bonds between cellulose molecules, thereby transforming the cellulose into a viscous solution. The choice of solvent can vary, but it is typically one that doesn't harm the intrinsic structure of the cellulose while effectively facilitating its dissolution.

1.3.2.1. Cellulose regeneration

Cellulose regeneration is a process that converts raw cellulose materials into a more ordered structure, which can be later used to produced cellulose nanofibers or be used for further alteration in the form of cellulose derivatives. The process of producing cellulose nanofibers involves several key steps, aiming to achieve the fabrication of cellulose nanofibers or derivatives with desired characteristics.

The dissolution of cellulose is achieved by employing suitable solvents, such as ionic liquids, N-methylmorpholine-N-oxide, or sodium hydroxide-urea mixtures. The dissolution process takes place where the cellulose pulp is dissolved in the liquids to obtain a homogeneous solution, paving the way for the regeneration step. Regeneration, which is the core step in the process, reorganizes the dissolved cellulose into a more ordered structure by immersing the cellulose solution in a coagulation bath, which typically contains water, alcohol, or an anti-solvent. This step leads to the formation of cellulose nanofibers or derivatives, which possess the desired structural and mechanical properties. [29–35]

After that, the separation and purification steps follow, where any residual solvents and impurities from the regenerated cellulose product are removed. This can be achieved through methods like centrifugation, filtration, or dialysis. These techniques ensure the purity of the Cellulose nanofibers, which is critical for their performance in various applications. Finally, the cellulose nanofibers are dried to reduce moisture content to achieve optimal moisture levels, which can impact their performance in various applications. The drying step can be achieved using freeze-drying (also known as lyophilization), spray drying, or air-drying techniques. The choice of the drying method depends on the desired form and properties of the final product. [29–37]

In some cases, though, cellulose can be directly dissolved in certain solvent systems, eliminating the need for a regeneration process. Solvents like N-methylmorpholine-N-oxide, ionic liquids, and a mixture of dimethylacetamide and lithium chloride, have been used successfully to dissolve cellulose directly. [29–33, 36, 37]

1.3.2.2. Cellulose derivatization

Cellulose on its own might not be the optimal form for utilization in some applications. Cellulose derivatization, therefore, can be undertaken to convert cellulose into a derivative that possesses increased solubility and processing capacity compared to the original cellulose structure. It involves the chemically transformation of the cellulose structure by reacting cellulose with specific reagents and introducing new functional groups into the cellulose structure. The resulting cellulose derivatives exhibit enhanced solubility in a wide range of solvents, thereby significantly improving their processing capabilities for techniques such as electrospinning. Some of the most commonly used cellulose derivatives include cellulose acetate and cellulose nitrate. These derivatives readily dissolve in selected organic solvents and can form nanofibers through electrospinning. If needed, these derivatives can be converted back to cellulose by deacetylation or denitration. Despite the fact that modifications can alter the inherit properties of cellulose, it can be ultimately useful in some applications. [34–36, 38]

1.3.2.3. Indirect approaches

In some cases, cellulose can be directly used without the need for an actual preparation. Blend electrospinning involves the mixing of cellulose with other polymers that are more soluble and easier to process. In this method, the additional polymer serves as a matrix or carrier for the cellulose during the electrospinning process. This approach proves particularly useful when it is challenging to directly dissolve or process cellulose on its own. Following the electrospinning, the carrier polymer can be selectively removed, leaving behind cellulose nanofibers. Blend electrospinning offers a means to produce cellulose nanofibers without the need for complex dissolution or regeneration processes. Moreover, the choice of polymer mixture can be used to tailor the properties of the resulting nanofibers according to specific requirements. However, achieving a homogeneous mixture and controlling the final morphology of nanofibers can be challenging. It is also crucial to ensure that the carrier polymer can be completely removed without causing damage to the cellulose nanofibers. [39–41]

Another method is coaxial electrospinning which is an advanced technique used in electrospinning to create a core-shell structure, where cellulose is incorporated in one phase. This method enables the production of composite nanofibers that contain cellulose within the fiber structure, even when direct electrospinning of cellulose is challenging. Coaxial electrospinning offers the ability to encapsulate cellulose within another polymer, eliminating the need for direct dissolution or regeneration of cellulose. This technique provides significant versatility in the properties of the resulting nanofibers. It allows for the creation of fibers with a specific core-shell structure or the inclusion of other substances within the fiber core alongside cellulose. However, achieving a stable core-shell structure in coaxial electrospinning requires careful control of process parameters, typically necessitating advanced equipment and process control beyond what is typically required in conventional electrospinning. [40–42]

1.3.3. Fibers production

Nanofibers can be produced via a multitude of methods. To each there are advantages and disadvantages; as well as a method of application. The coverage of all methods of fabrication is an impossible mission to be done in a single study. Therefore, the following sections will provide a brief description of selected common methods. Furthermore, Fig. 3 shows the most commonly used methods for the production of nanofibers.

1.3.3.1. Electrospinning

A very common approach for CN production is an effective method that has risen into use since the beginning of the 21st century. It is a method that utilizes high voltage to spray out polymer droplets which in turn are collected on a substrate. The way the droplets are dispersed and later post-treated leads to the spinning of cellulose fibrils into a membrane of CN that span from the micron scale to the nanoscale.

Electrospinning (Fig. 5) operates through the following mechanism: Initially, a polymer solution is prepared, typically consisting of a polymer and one or more solvents. This polymer solution is then discharged from a nozzle under pressure and subjected to a high voltage differential. The high voltage endows the solution droplets with sufficient charges across their surfaces. As the electric field strength achieves a specific threshold, which naturally varies between solutions, the electric field force overcomes the surface tension of the liquid surface. This leads to a stable liquid flowing from the tip of a cone shape, known as Taylor's cone, with the tip situated at the nozzle and the base at the collector. [1, 3, 8, 13]

This liquid progresses towards the target, acquiring a charge in the process. As it moves, the solvent extends and evaporates, causing the liquid to become thinner and drier. As the diameter of the stream narrows, the power density escalates, and due to substantial resistance, the stream is fragmented into smaller streams. This process can recur several times, yielding a vast number of small streams. Eventually, the liquid solidifies, and the fiber is randomly deposited on the target's surface, forming a non-woven mat of nano-scaled, intricate spinning of the polymer in the form of fibrils [1, 3, 8, 13].

A range of synthetic and natural polymers can be employed for nanofibers fabrication via ES. Common examples of the utilized polymers include polyvinyl pyrrolidone, poly lactic acid, poly glycolic acid, poly vinyl alcohol, polyurethane, collagen, gelatin, and chitosan, cellulose; which is the scope of this thesis. A mixture of polymers is sometimes also used. [20]

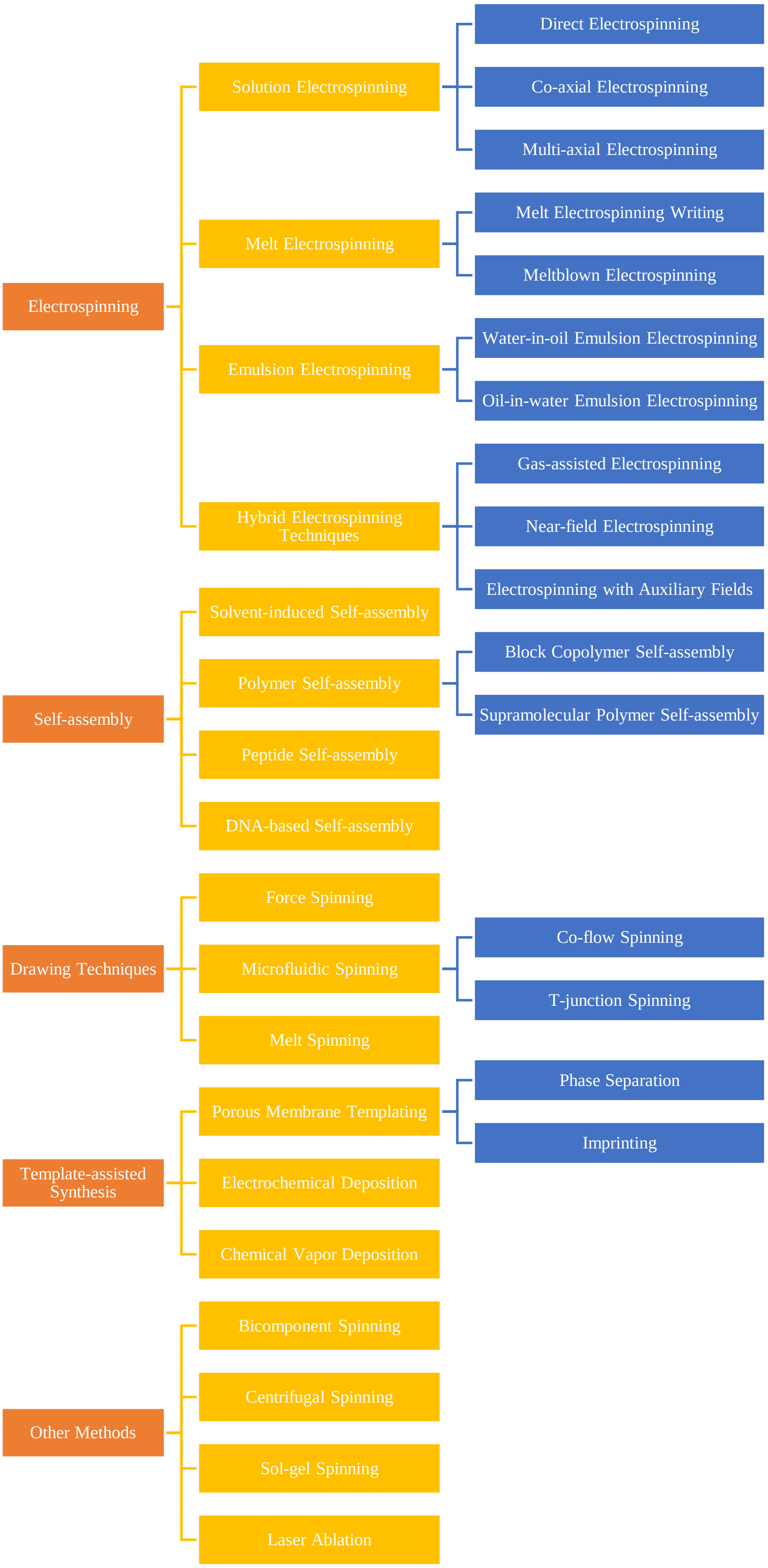

Fig. 3. The most commonly used methods of fabricating nanofibers

Electrospinning is widely regarded as one of the most effective methods for producing high-quality nanofibers due to its ability to generate nanofibers with superior mechanical properties, larger total surface area, and fewer defects when compared to other techniques. The success of ES largely hinges on certain parameters, including the polymer concentration in the polymer solution, the presence of additional components in the solution, the solution's fluid properties (e.g., viscosity, surface tension), the flow rate through the nozzle, the distance between the nozzle and the collector, and the voltage difference applied between the nozzle and the grounded collector. [1, 3, 13]

During the electrospinning process, there are some key parameters that affect the morphology and properties of the resulting nanofibers. Each of these parameters can be fine-tuned to produce nanofibers with specific properties. These parameters can be broadly divided into solution parameters, process parameters, and ambient parameters. Solution parameters include the properties of the solution that's being electrospun, such as its viscosity, conductivity, surface tension, and the concentration of the polymer. The solution's viscosity affects the size of the resulting nanofibers, as a higher viscosity results in thicker fibers. Conductivity plays a role in the jet initiation and its stability during the electrospinning process, with higher conductivities generally facilitating the electrospinning process. Surface tension is critical for the formation of the Taylor cone, the point at which the solution jet is ejected. Lastly, the concentration of the polymer in the solution can also influence the diameter and uniformity of the nanofibers. [13, 40, 41, 43]

As for the process parameters, they are related to the setup of the electrospinning process itself; such as the applied voltage difference, the injection flow rate of the solution, and the distance between the nozzle and the collector. A higher applied voltage leads to smaller fiber diameters, while a higher flow rate tends to produce larger diameters. The distance between the nozzle and the collector also affects the drying and solidification of nanofibers, and thus their shape. On the other hand, indoor parameters include factors such as temperature and humidity. The ambient temperature can influence the solvent's evaporation from the solution jet, while humidity can affect the solvent's evaporation rate and thus the diameter and shape of the resulting nanofiber. Finally, collector properties can also influence the electrolytic process, with parameters such as the geometry, movement, and conductivity of the collector being involved. For example, rotating collectors can produce a nanofiber aligned to the axis, while stationary collectors produce randomly oriented fibers. [13, 40, 41, 56]

Another critical aspect of ES is the hydrophilicity or hydrophobicity of the polymer being electrospun. This factor is especially significant when it comes to the electrospinning of CN. Adjusting these parameters allows researchers to fine-tune the process and achieve the desired properties in the resulting CN fibers, making electrospinning a versatile and highly customizable method for CN production. [3]

In recent years, a variety of hydrophobic and hydrophilic polymers have been employed in the electrospinning process to create fibers with adjustable properties for a diverse set of applications. Şimşek M. (2020) [44] examined the impact of solvent systems and relative humidity on the surface texture of electrospun hydrophobic polycaprolactone fibers, revealing their potential in tissue engineering and filtration industries. In a separate study, Liu et al. (2021) [45] investigated the reinforcement of electrospun hydrophilic polyvinyl alcohol nanofibers with cellulose nanocrystals, resulting in mechanically robust and environmentally friendly nanofibers with promising applications in packaging, water treatment, and tissue engineering.

Furthermore, Toriello et al. (2020) [46] explored the fabrication of electrospun hydrophilic polyacrylonitrile nanofibers with tunable wettability using binary and ternary solvent systems, showcasing the potential of these fibers in filtration, water treatment, and tissue engineering applications. Additionally, Reddy et al. (2019) [47] developed antibacterial electrospun hydrophobic polyurethane nanofibers by incorporating bioactive glass nanoparticles, which led to enhanced antibacterial activity against specific strains of bacteria, making them ideal for wound dressing and tissue engineering purposes. [40, 41, 48, 49]

Once electrospinning is completed, it's important to remove any residual solvent from the electrospun fibers. This is generally accomplished by drying the fibers, which can occur under ambient conditions, in a vacuum, or at elevated temperatures. The choice of method depends on the solvent used in the electrospinning process and the stability of the fibers. In some cases, the fibers may undergo a heat treatment to enhance their mechanical properties or stability, or to induce structural changes. For example, heat treatment can lead to crystallization of the fibers, improved alignment, or crosslinking of the polymer chains. This step can greatly influence the final characteristics of the nanofibers. For fibers produced from a solution containing salts, acids, or other undesirable substances, washing might be required. This step can be done using water or a suitable solvent to ensure the purity of the final product. In processes where electrospinning involved a blend of cellulose and a carrier polymer, the carrier polymer may need to be removed. This is often achieved through a selective dissolution process, where a solvent is used that can dissolve the carrier polymer but not the cellulose. This leaves behind pure cellulose nanofibers. [40, 41, 48, 49]

Another important step can be the functionalization of nanofibers. This step involves adding specific properties or functionality to the nanofibers. Methods of functionalization can vary widely, including coating the fibers with other materials, grafting functional groups onto the fiber surface, or incorporating other substances into the fiber structure. This allows for the tailoring of nanofibers to suit specific applications. In conclusion, the specific post-treatment steps can greatly vary depending on the materials used for electrospinning and the intended application of the nanofibers. [48, 49]

1.3.3.2. Non-spinning methods

1.3.3.2.1. Mechanical drawing

The drawing technique is an alternative method for the generation of fibers, bearing similarity to the process of dry spinning. The primary advantage of this technique lies in its minimal equipment requirements, which essentially consist of a sharp tip or a micropipette. This approach involves utilizing a sharp tip to pull a droplet of a pre-deposited polymer solution into liquid fibers. The subsequent evaporation of the solvent, facilitated by a large surface area, results in the solidification of these fibers. An alternative to the use of a sharp tip is a hollow glass micropipette that can continuously dispense the polymer to counteract issues of volume shrinkage. This shrinkage impedes the uninterrupted drawing of fibers and influences their diameter. After immersing the micropipette into the droplet with the aid of a micro-adjustor, the pipette is gently pulled from the liquid and moved at a low velocity. This movement pulls the nanofibers, which are then deposited onto a surface by contacting it with the pipette's tip. This process is repeatedly executed on each droplet to create nanofibers. [50–52]

This technique allows for the creation of continuous nanofibers in any configuration, while maintaining precise control over key parameters such as drawing viscosity and speed. This control enables consistency and manipulability over the dimensions of the produced fibers. Despite the simplicity of the process, its application is typically limited to the laboratory scale due to the one-at-a-time formation of nanofibers, a characteristic that restricts productivity. However, the ability to control the dimensions of the fibers remains a benefit of this method. Its application is restricted to viscoelastic materials capable of enduring the stress generated by pulling, and fibers with diameters of at least 100 nm can be produced, contingent on the size of the orifice. [50–52]

1.3.3.2.2. Template synthesis

The template synthesis method is a technique used to fabricate polymeric, metallic, semiconductor, or ceramic nanofibers. It leverages chemical or electrochemical oxidative polymerization and employs a nonporous membrane with numerous cylindrical pores, typically ranging from 5 to 50 mm in thickness. The essence of this approach is the usage of templates to produce the desired material structure and thus produce nanofibers. In this context, the word template refers to metal oxide membranes. In this method, the nanofiber is generated by forcing the polymer solution to enter the nanopore under the pressure of water on one side. As a result, polymers are extruded and solidified by contact with solidifying solutions into fibers. [50, 53]

However, it is noteworthy that this method has limitations regarding the production of long nanofibers; It usually produces fibers of only a few micrometers in length. The diameter of the fibers is determined by the size of the membrane pore. Nevertheless, this method offers the advantage of being able to fabricate nanofibers of various diameters by employing different templates. [50, 53]

1.3.3.2.3. Self-assembly

Self-assembly is a fabrication method where molecules fit into structured patterns, autonomously, through intermolecular, non-covalent forces like hydrogen bonding, hydrophobic forces, and electrostatic interactions. This technique can generate extremely small nanofibers, ranging from less than 100 nm to a few nanometers. This process takes place by forming supramolecular hydrogels through the self-assembly of small molecules via weak interactions such as hydrogen bonding and hydrophobic interactions. The principal mechanism of this method is founded on intermolecular forces that bring small molecular units together. The shape of these small molecular units ultimately determines the overall shape of the macromolecular nanofiber. Despite its unique approach and capabilities, self-assembly has its limitations. It is a complex, time-consuming, and highly intricate technique with relatively low productivity. Additionally, it doesn't offer fine control over the dimensions of the fiber. Also, the method is limited to creating nanofibers from small active molecules that can self-assemble either independently or under an external stimulus.[50, 53]

1.3.3.3. Electrospinning versus Alternative Methods

Every method employed in the production and processing of nanofibers possesses unique advantages and disadvantages when compared to other techniques. These differences can be observed in terms of efficiency, effectiveness, and overall quality. The selection of the most appropriate method from various alternatives is heavily influenced by factors such as the specific polymer being processed, the time constraints for the project, the desired quality of the nanofibers, as well as the environmental and energy impacts associated with the process. By carefully considering these factors, manufacturers and researchers can optimize their approach and ensure the best possible outcomes for their endeavors. In this section, the main points of comparison are highlighted to give a general brief overview.

As aforementioned, electrospinning process of nanofiber fabrication has been on the rise. Not only do recent research efforts focus on the utilization of electrospinning technologies and its development, with publications and citations rising from mere few ones in 2000 up to approximately 4000 publications and 160 thousand citations by 2021 [54]; but immense efforts are also being exerted to achieve large-scale industrial level of nanofibers production using modified electrospinning. [20]

Furthermore, electrospinning products can be repeatable. This is especially helpful when it comes to experimenting with different polymers and their complex forms. It is true that the chemical method of phase separation can achieve comparable repeatability; however, unlike electrospinning, fiber diameter is difficult to be predicted and controlled in phase separation. Self-assembly, chemical disintegration, cyrocrushing, and template synthesis can, indeed, control the diameter of the produced nanofibers, but when compared to electrospinning, other factors can be of important values. For instance, unlike electrospinning and template synthesis, self-assembly does not possess the same potential of scaling up. Moreover, electrospinning remains superior when it comes to financial feasibility. Ball milling is another cost-efficient method, yet the resulted quality is inferior to electrospinning quality products. Another important aspect which makes electrospinning an attractive option for nanofibers fabrication is that different mixtures of polymers and solutions can be employed. This advantage is shared with other methods such as mechanical drawing; however, each has its own drawback. Mechanical drawing for example is very limited when it comes to the continuity of the fabrication process; which is a strong point of electrospinning process that can be left semi unattended over a long span of time. [20, 21, 49]

On the other hand, there are some shortcomings of electrospinning. First of all, electrospinning process is relatively unstable. If the process parameters change (for example: relative ambient humidity), the process can be disrupted, giving a very undesirable product characteristics. Another main drawback of using electrospinning is the dependency on solvents. As discussed in 1.3.3.1, polymers cannot be used in electrospinning on their own; instead, they need to be mixed with other chemicals to be suitable for spraying. From the engineering and technical points of view, this might not be as impactful as it is from the environmental point of view. Chemicals released to air during the process or wastewater in post treatment processes remain a strong negative point against electrospinning. Novel processes such as enzymatic and bacterial nanofibers fabrication are researched as attractive competitors to chemicals-dependent processes like electrospinning. In spite of the fact that enzymatic and bacterial processes eliminate the need for environmentally harmful solvents, they remain relatively niche compared to electrospinning. This can be attributed mainly to some issues such as low yield and productivity rates, cost feasibility, and adaptability; the three of which are not a weakness of electrospinning. [20, 21, 49]

1.3.4. Pore formation

Explaining the steps of cellulose nanofibers fabrication and the methods followed is important, but it is crucial to understand the core concepts of pore formation when creating the nanofibers. This understanding can be of a great assistance when deciding which parameters to modify during the fabrication process and what quality is expected from the fabricated nanofibers. There are different concepts of pore formation which can be either solely responsible for the pore formation or collectively with other mechanisms.

1.3.4.1. Chemical etching

Chemical etching is a post-processing method of pore formation. It usually follows a fabrication method such as mechanical disintegration or electrospinning. CN are treated with specific chemicals that selectively remove parts of the material. Sodium hydroxide can be used to remove the amorphous regions of cellulose, leaving behind a porous structure. This method exploits the heterogeneity in cellulose, particularly the difference between crystalline and amorphous regions. The amorphous regions, which are less tightly packed and organized, are more susceptible to the action of chemicals. On the other hand, the more robust crystalline regions remain intact, leading to a porous structure. The size and distribution of the pores depend on the concentration and treatment time of the etching chemical. [40, 48, 55]

1.3.4.2. Lyophilization

Lyophilization or freeze-drying is often applied to CN fabricated through methods like mechanical disintegration, bacterial synthesis, or electrospinning. In this technique, a CN suspension is quickly frozen, followed by sublimation of the ice under vacuum conditions. This leaves a network of CN with pores where the ice crystals were located. The porosity can be controlled by adjusting the freezing rate: a fast freezing rate generates small ice crystals and thus small pores, while a slow freezing rate results in larger ice crystals and pores. In addition, freeze-drying prevents the collapse of CN upon drying, which often occurs in air-drying or oven-drying, helping to maintain the network structure and high surface area. [40, 48, 56]

1.3.4.3. Phase separation

Phase separation is often used after the mechanical disintegration of cellulose into CN. A homogeneous mixture of CN and a solvent undergoes phase separation (either by temperature, chemical, or concentration changes), leading to the formation of a two-phase system. Upon removal of the solvent, a porous structure remains. This method allows for the control of porosity by adjusting the phase separation conditions, such as the cooling rate or the concentration of CN. [57, 58]

1.3.4.4. Pore formation by spinning

Electrospinning is a method that is often used to create CN with inherent porosity. The size and distribution of the pores can be adjusted by modifying the spinning parameters, such as the solution concentration, voltage, and collector distance, and by post-processing methods like lyophilization or chemical etching.

1.3.4.5. Combinations

Many pore formation methods in cellulose nanofiber fabrication can be combined for optimal results, such as electrospinning and freeze-drying. In the electrospinning process, a cellulose solution is electrically charged to form a nonwoven mat of nanofibers with inherent macro-porosity. This mat is then freeze-dried, where it's first frozen, then the ice is sublimated under vacuum. This avoids the pore structure collapsing due to surface tension effects, enabling the creation of additional porosity within and between the nanofibers. By carefully adjusting these processes, it's possible to create a cellulose nanofiber mat with a complex, hierarchical pore structure suitable for a variety of applications.[54][20][20, 21, 49][20, 21, 49]

1.4. Adsorption via cellulose nanofibers

The adsorption mechanisms of cellulose and cellulose nanofibers are primarily attributed to their large surface area, porous structure, and the presence of functional groups, such as hydroxyl groups, which can interact with various molecules and ions.

Cellulose nanofibers exhibit various adsorption mechanisms that enable them to remove pollutants from water and other media. Some of the primary mechanisms of adsorption for cellulose nanofibers include:

1. Van der Waals forces: Non-specific attractive forces between the cellulose nanofibers and the pollutant molecules due to the fluctuation of electron densities in their structures. This mechanism is primarily driven by the proximity of the adsorbate to the adsorbent surface.

1. Hydrogen bonding: The presence of hydroxyl groups in cellulose nanofibers allows for the formation of hydrogen bonds with pollutant molecules that have polar functional groups. These bonds can significantly contribute to the adsorption of polar pollutants.
2. Electrostatic interactions: Cellulose nanofibers can be charged or functionalized to exhibit positive or negative surface charges. This allows for electrostatic interactions with oppositely charged pollutants, leading to enhanced adsorption capacity.
3. π-π stacking interactions: They are attractive forces between pi electron clouds of adjacent aromatic rings or conjugated systems, play a role in the adsorption of water pollutants containing aromatic or conjugated structures by cellulose nanofibers. Despite the lack of aromatic rings in their structure, cellulose nanofibers possess electron-rich regions in their backbone due to oxygen atoms in hydroxyl groups and ether linkages. These regions enable π-π stacking interactions with the electron clouds of aromatic rings in the pollutants, enhancing the adsorption capacity of cellulose nanofibers for such contaminants and providing an additional mechanism for their removal from water or other media.
4. Chelation: In some cases, cellulose nanofibers can be functionalized with specific chemical groups that can form coordination bonds or chelate with pollutant ions, such as heavy metals. This mechanism can significantly increase the adsorption capacity for targeted pollutants. [59–61]

Different pollutants and environmental conditions will influence the relative importance of each of these mechanisms in the adsorption process involving cellulose nanofibers. By understanding these mechanisms, researchers can tailor the properties of cellulose nanofibers to improve their adsorption capacity and selectivity for specific contaminants. Fig. 4 show illustrations for some of the aforementioned mechanisms.

Liu et al. [62] developed cationic cellulose nanofibers for efficient anionic dye adsorption and salt-free dyeing of paper. The primary adsorption mechanism involved in this study is electrostatic attraction between the cationic cellulose nanofibers and the anionic dye molecules. Ma et al. [63] developed hybrid cellulose acetate/titania nanoparticles for the photocatalytic degradation of organic pollutants in water. The adsorption mechanism in this study is predominantly based on physical adsorption, where the pollutant molecules are attracted to the surface of the cellulose acetate/titania nanoparticles.

Moreover, Štefelová et al. [64] prepared cellulose nanofiber-based aerogels for the removal of heavy metal ions from water. The adsorption mechanism discussed in this work involves complexation between the carboxylate groups of the cellulose nanofibers and the heavy metal ions. Furthermore, Araga et al. [65] synthesized cellulose-based hydrogels reinforced with cellulose nanocrystals for the removal of methylene blue dye from water. The main adsorption mechanisms in this study are hydrogen bonding between the hydroxyl groups of cellulose nanocrystals and the dye molecules, and π-π stacking interactions between the electron-rich regions of cellulose and the aromatic rings in the dye.

1.5. Scope of the thesis

In this thesis report, the development and exploration of cellulose nanofibers derived from unprocessed cellulose will be thoroughly examined. Cellulose preparation method utilized is cellulose regeneration in a ternary solution of cellulose, ionic liquid and a co-solvent. The selected fabrication technique is electrospinning, with a particular focus on nozzle solution electrospinning, which is widely recognized as the default method in the electrospinning field. [13] The formation of pores within the resulting fabric can be attributed to removal of solvent as well as the drying steps.

Subsequent to the production of these fibers, an investigation into the adsorption capabilities of methylene blue dye was conducted. The methodologies employed, the outcomes, and a detailed discussion of the findings will be presented throughout the subsequent chapters. It is worth mentioning that this thesis is considered as a continuation of ongoing research that is taking place in Kaunas University of Technology during and before the writing of this thesis. Some of the choices that were made as a baseline for this research were made based on the precursor experiments conducted by the researchers at the department of environmental technology in Kaunas University of Technology.

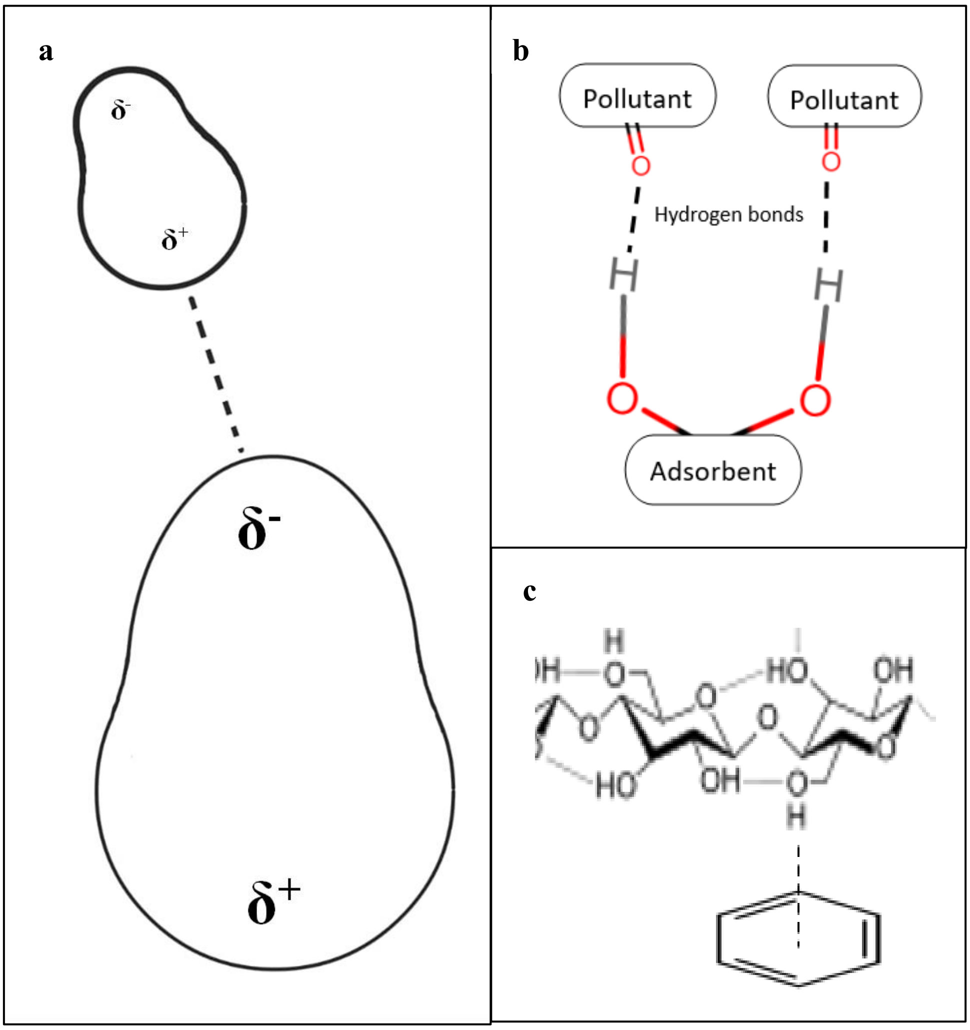

Fig. 4. (a) Van der Waal adsorption mechanism between pollutants and adsorbents; (b) Hydrogen bond adsorption mechanism between adsorbents and pollutants; (c) π-π stacking-based adsorption illustrated between a benzene ring and cellulose

2. Research methodology

The research for this thesis was conducted in two phases. The first phase involved the development of the fabrication of optimized cellulose nanofibers. This included changing the parameters of the fabrication process in a feedback loop manner until the desired optimal outcome was achieved. The second phase involved experimenting on the adsorption of methylene blue dye using the produced optimal cellulose nanofibers.

2.1. Phase I: Nanofibers fabrication

2.1.1. Raw cellulose preparation

The source of cellulose that was chosen to fabricate cellulose nanofibers in the research for this thesis was raw cellulose (Mw= 53.000, CAS 90004–34-6). Raw cellulose was shredded manually into tiny shreds to increase the contact area in the solution which in turn improves its mixing. Following the shredding, shredded cellulose was put in a ceramic dish to be placed in an oven for drying. The drying process took place at 210 °C and for a time period of 24 hours.

2.1.2. Polymer solution preparation

Following the drying process, dry cellulose, along with an ionic liquid of 1-butyl-3-methylimidazolium acetate (IL) (concentration> 95%, CAS 284049-75-8) and Dimethylsulfoxide (DMSO)[1] (CAS no. 67-68-5). A scale was used to measure the quantities of each component being added into a 10 ml glass vial. The ratios and quantities are discussed in 2.1.7. The glass vial was then taken to be magnetically stirred using a magnetic stirrer (ChemLand SH-4C). The stirring took place a rotation speed of 600-800 rpm[2] and at a temperature of 80 °C for 24 hours.

2.1.3. Electrospinning process

A vertical electrospinning device was especially designed by the department's researchers for electrospinning processes. Fig. 5 shows an illustration of the used equipment. Prior to the electrospinning process, a collector of aluminum foil was manually perforated using sandpaper, then it was fixed on the collector wheel. The perforated aluminum foil was used as a collector. Furthermore, a solution of diluted bioethanol was prepared by mixing bioethanol (96.6%) and deionized water (DI) at a ratio of 1:1. The purpose of this solution is to remove the IL from the electrospun fibers; otherwise, it will continue dissolving the nanofibers leading to the formation of a membrane instead.

Upon the initiation of the process, the mixed polymer solution was put inside a glass syringe. The needle gauge used was 23 (outer diameter= 0.64 mm, inner diameter= 0.34 mm). The syringe was set up in the equipment as seen in Fig. 5, and the flow was set (see 2.1.7). A hot air blower was used to increase the temperature to 100-130 °C in order to decrease the viscosity and thus facilitate the flow of the polymer solution in the syringe. A decoy aluminum foil was used during the initial stage of the electrospinning where the high voltage generator was turned on to allow the commencement of the

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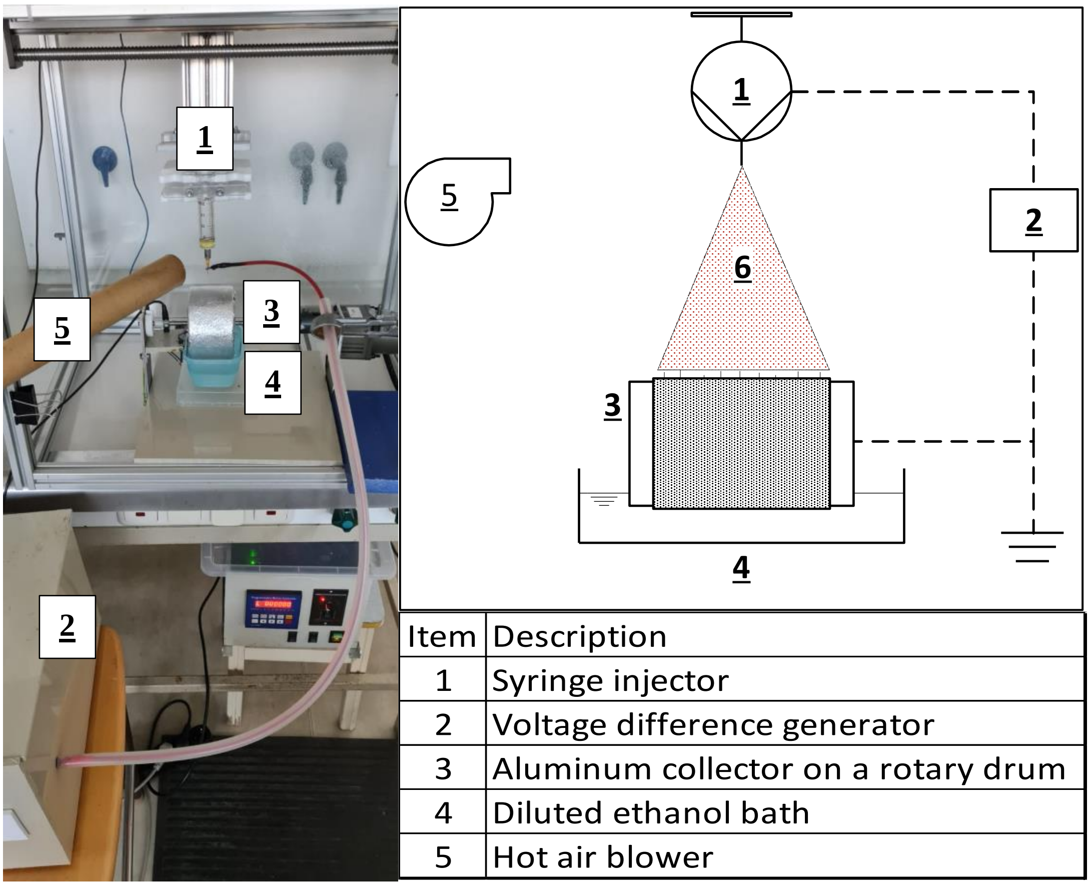
[1] DMSO and ionic liquids are used together in electrospinning cellulose nanofibers to enhance cellulose dissolution, improve spinnability, enable tunable solvent properties, facilitate pore formation, and promote green chemistry. [81]

[2] The variation in speed was due to the change of viscosity of the solution across time. This is because both heat and dissolving solid cellulose change the viscosity of the whole solution gradually.

electrospinning. After the stabilization of the flowing process, the generator was paused until the decoy foil was removed and then the actual electrospinning process started.



Item	Description
1	Syringe injector
2	Voltage difference generator
3	Aluminum collector on a rotary drum
4	Diluted ethanol bath
5	Hot air blower

Fig. 5. (left) Electrospinning equipment used for the experiment; (top right) A diagram for the equipment; (lower right) Legend

2.1.4. Post-electrospinning operations

After the end of the electrospinning process, the collector, along with the fiber on it, was removed and left in a 96.6% bioethanol bath for 24 hours. This is to ensure the complete removal of the solvent mixture from the electrospun fibers; thus, ensuring the prevention of membrane formation as aforementioned.

The formed fibers were then moved to inert polymer mesh for further washing processes. The process is delicate since moving from a medium to another can result in dwindling fibers that become of a small width which results in the impossibility of analysis (see 5.1.7). This washing step involves moving the inert mesh with the cellulose nanofibers into warm DI bath in a one-liter beaker at 80 °C. The washing bath is changed every 45 minutes. This was to ensure that the driving force between the concentration of solvents and bioethanol in the nanofibers and the washing water remains large enough; thus, increasing the leaching rate. The operation took place over eight baths after which the mesh was left in a cold DI bath for another 24 hours to ensure the removal of any traces of foreign chemicals from the cellulose nanofibers.

2.1.5. Freezing and drying

The washed cellulose nanofibers were then transformed unto solid dry covered surfaces to be left for freezing for at least 24 hours[3]. Following this step, the sample was moved to a soft, porous carrier and then taken to be dried. The initial choice for drying was lyophilization; however, oven drying was tried during the optimization process (see 2.1.7). Lyophilization, or freeze-drying, is a dehydration technique that removes water from a sample through sublimation, transitioning water molecules directly from solid (ice) to gas (water vapor). The process involves freezing, primary drying under vacuum with heat, and secondary drying to create a porous, dried matrix for preservation and easy rehydration.

2.1.6. Analysis

For the analysis step, scanning electron microscopy (SEM) (SEM S-3400 N, Hitachi Ltd, Japan) image analysis was used. SEM image analysis refers to the process of extracting quantitative and qualitative information from images obtained using a scanning electron microscope. SEM is a powerful microscopy technique that uses a focused beam of electrons to generate highly detailed images of a sample's surface at a nanometer scale. SEM image analysis involves various methods, such as measuring particle size and distribution, evaluating surface morphology, identifying elemental composition, and quantifying specific features or structures within the image. Image processing and analysis software tools are typically used to assist in SEM image analysis. For this thesis, ImageJ software (v. 1.53t).

Manual measurements were taken using ImageJ software for the diameters of the fibers. Diameters of the cellulose fibers were measured using a method that involved dividing SEM images into four equal sections and examining all fibers in one section. The distribution of fiber width was plotted using Microsoft Office Excel. This helped with giving a proper judging of the quality of the fibers.

2.1.7. Parameters and optimization

In the electrospinning process, there are several parameters that heavily influence the process. Those parameters can be divided into 3 groups: solution parameters, electrospinning process parameters, and ambient conditions. The first group are: the voltage difference between the needle tip and the collector, distance from the needle tip to the collector, collector type, and flowrate at which the polymer solution flows from the syringe. The second group parameters are: the polymer solution components concentrations, fluid properties, and conductivity. Lastly, the ambient parameters are humidity and temperature at which the process takes place. [13, 43]

Some of these parameters were fixed while other parameters were tested. Constant parameters were the distance between the needle and the collector (2.25 cm), collector type (aluminum foil, manually perforated using sandpaper), and ambient conditions (temperature at 20 °C, RH= 65%); the rest of the parameters were tested. There were other factors that should be mentioned, though. Despite the variation in the ratio of IL:DMSO:cellulose, cellulose quantity was kept at 0.2 g. The size of the sample was 7 ml, and the rotational speed of the collector drum was 50 rpm. Furthermore, the temperature of hot air flow from the air blower was kept at 100-130 °C.

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[3] "At least" was used because it was more practical to collect all samples for later processes since waiting time would not affect the specimen quality starting from the freezing step.

It is also worth mentioning that the drying method was tested limitedly. A vacuum dryer (ChemLand DZ-2BCI) was used to dry a portion of the produced samples (at 30 °C) to study the effect of the difference in drying methods.

In order to reach the decision for the optimal conditions, 14 samples were produced. Table 1 summarizes the aforementioned parameters changes per each trial. After that, 10 more optimal samples were fabricated to further assist with adsorption experiments.

Table 1. Main constant and variable parameters of the thesis experiment

Constant parameters	**D, cm**	**Temperature, °C**	**RH, %**	**Cellulose mass, g**	**Sample size, ml**	**Collector drum rotation speed, rpm**	**Blower temperature, °C**
	2.25	20	65	0.2	7	50	100-130

Variable parameters	Sample no.	IL:DMSO	Syringe flow rate, mm/h	Voltage difference, kV	Drying method
	1	1:1.5	7	12	Lyophilization
	2	2:1	7	12	Lyophilization
	3	1:1.5	16	12	Lyophilization
	4	1:1.5	7	15	Lyophilization
	5	2:1	16	12	Lyophilization
	6	1:1	7	12	Lyophilization
	7	1:1.5	7	12	Lyophilization
	8	1.25:1	9	10	Lyophilization
	9	2:1	9	12	Lyophilization
	10	2:1	9	13	Vacuum drying
	11	1:1	9	13	Vacuum drying
	12	1:1.5	9	12	Vacuum drying
	13	1.25:1	9	12	Vacuum drying
	14	1:1	9	12	Vacuum drying
	15	2:1	9	12	Lyophilization
	16	1:1	9	12	Lyophilization
	17	1:1.5	9	12	Lyophilization
	18	1.25:1	9	12	Lyophilization
	19	1:1	9	12	Lyophilization

2.2. Phase II: Adsorption trials

2.2.1. Materials used

2.2.1.1. Adsorbate

Methylene blue dye was used as a test dye in the adsorbing trials. It was chosen as the initial targeted adsorbate because it is a popular choice for testing adsorption properties due to its easy detection and measurement, with a characteristic absorbance peak at around 664 nm; cationic nature; water solubility; and stability over a wide range of pH values and temperatures. As a common representative of synthetic organic dyes and a significant water pollutant, Methylene blue allows researchers to evaluate the potential of adsorbents in removing similar dye pollutants from wastewater. Additionally, its well-established adsorption mechanisms, including hydrogen bonding, electrostatic interactions, and π-π stacking, facilitate comparisons between different adsorbents and their performance, making methylene blue a convenient and informative model compound for adsorption studies.

Three solutions were prepared for each of the adsorbents to test the adsorption of each at different concentrations. The three solutions were of concentration of 1 mg of methylene blue per 1 liter of DI.

2.2.1.2. Adsorbents

The main targeted adsorbent was the fabricated cellulose nanofibers; however, more adsorbents were used to have a comparative overview. The amount of each adsorbent used was 10 mg per 1 liter of the methylene blue solution. The quantity was measured by cutting the cellulose nanofibers into bits of a total weight that satisfied the mentioned concentration. The measurement took place using a sensitive scale.

2.2.1.2.1. Nanofibers

2.2.1.2.1.1 Cellulose Nanofiber

The produced nanofibers were measured on the scale and used in their fabricated form without any modifications.

2.2.1.2.1.2 Ozone-modified Cellulose Nanofibers

Ozonation is a powerful oxidation process that modifies cellulose fibers' surface properties, including hydrophilicity, charge density, and roughness. This affects their interactions with substances like dyes or chemicals and their overall application. The process enhances fiber swelling and processability, making them suitable for further treatments or blending with other materials. Ozonation alters the chemical structure of cellulose nanofibers by oxidizing hydroxyl groups on the surface, forming carbonyl or carboxyl groups while maintaining the overall linear chain structure.

A portion of the cellulose nanofibers were modified using an ozonation device. The device involves passing ozone through a DI water bath that contains fragments of cellulose nanofibers; with each fragment of 1 mg have been separately ozonized for technical feasibility. The water in the bath ensures a high level of homogeneity and mixing to have a high degree of ozonation uniformity. The ozonation process took place for 3 hours. The resulted fibers were slightly swollen yet maintained the overall structure.

2.2.1.2.1.3 Plasma-modified Cellulose Nanofibers

Plasma modification of cellulose nanofibers involves generating plasma by applying energy to a gas and exposing the nanofibers to the reactive plasma environment. The reactive species interact with the nanofibers' surface, causing physical and chemical changes that modify their properties. This process improves the nanofibers' performance in various applications. The way it does is by altering their surface properties. It introduces new functional groups that improve interactions between nanofibers and adsorbate molecules. The treatment also increases hydrophilicity, promoting better dispersion and contact with the adsorbates in aqueous environments. Furthermore, plasma modification boosts surface area and porosity, offering more adsorption sites for improved adsorption performance.

Plasma modification took place using a device developed by researchers of KTU that was designed specifically for plasma modification of different substances. The operation was conducted by placing the nanofibers on a rotary drum which was subjected to plasma on a segment of it. The aim for the temporary subjection is to reduce the time of direct exposure thus reducing the chance of overheating; and consequently specimen damage. The drum rotational speed was 100 rpm and the plasma modification took place over 5 minutes (i.e. 500 overall rotations). Fig. 6 shows the used device.

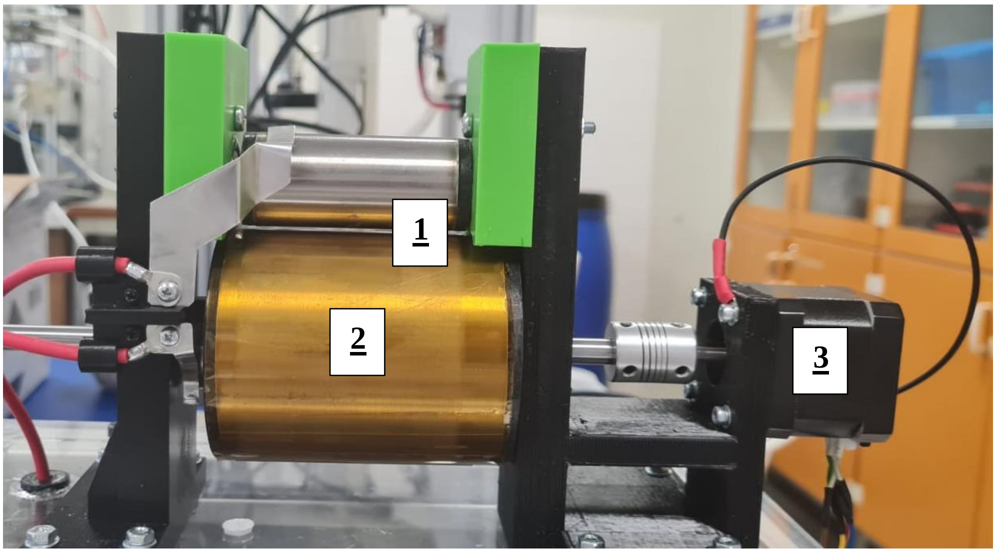


Fig. 6. Plasma modification equipment; whereas: 1- plasma exposure zone; 2- rotary drum; 3- rotary motor

2.2.1.2.2. Raw Cellulose

The raw cellulose that was used to create the cellulose nanofibers was also put to adsorption experimentation. Using the same methodology and applications that were followed with cellulose nanofibers, three types of adsorbents were produced: cellulose, ozone-modified cellulose, and plasma-modified cellulose.

2.2.2. Adsorption process

The prepared adsorbents were inserted into the prepared adsorbate solutions; with 10 mg of adsorbent per 1 liter of adsorbate solution. A spectrophotometer (Spectronic GENESYS 8, wavelength range= 190-1100 nm) was used to measure the concentration of methylene blue at time= 0. The device is shown in Fig. 7. After this, as shown in Fig. 8, the solution were put in a shaker (IKA LABORTECHNIK HS250 basic), for different intervals of time; between which measurements were taken to measure the concentration of methylene blue. The intervals were 30 minutes, 1 hours, 2 hours, 3 hours, 4 hours, 5 hours, and 24 hours.

Fig. 7. Spectrophotometer (Spectronic GENESYS 8)

Fig. 8. IKA LABORTECHNIK HS250 basic shaker with a special mount to keep the vials in position

3. Research results and discussion

Adhering to the two-phase categorization established in the methodology, the study's findings were systematically determined. The first phase was focused on the determination of the most optimal conditions for the fabrication of cellulose nanofibers. This involved careful examination and experimentation to identify the ideal parameters and conditions under which the highest quality cellulose nanofibers could be produced.

Following this, the second phase of the study was dedicated to the investigation of the adsorption capacities of methylene blue by various selected adsorbents. These adsorbents were carefully chosen to represent a wide range of materials with different properties and modifications. These included:

- Unmodified cellulose: The base material in its raw form.
- Unmodified cellulose nanofibers: Nanoscale cellulose without additional modifications.
- Ozone-modified cellulose: Cellulose treated with ozone to alter its properties.
- Ozone-modified cellulose nanofibers: Nanofibers treated with ozone.
- Plasma-modified cellulose: Cellulose treated with plasma for modification.
- Plasma-modified cellulose nanofibers: Nanofibers that have undergone plasma modification.

Through this two-phase approach, the study aimed to provide a comprehensive understanding of the factors influencing the adsorption of methylene blue and to identify the most effective materials and modifications for this purpose.

3.1. Phase I: Fabrication of the optimal nanofibers

3.1.1. Preliminary trials

During the first trial, two operating conditions were tested. The first set of operating conditions were with an IL:DMSO ratio of 1:1.5, syringe flow rate of 7 mm/h, and 12 kV of applied voltage difference. The second set of operating conditions were the same as the first ones but with an IL:DMSO ratio of 2:1. The chosen criteria were to check the effect of the ratio on the final product. This was especially important not only because of the dissolution properties of both DMSO and IL, but also due to technical reasons. Despite playing a crucial role in the process, DMSO is a very viscous liquid (2 cp at 20 °C. For reference, water is 0.01 cp at the same temperature). This poses a challenge to the process of electrospinning due to the need to provide the proper pressure to keep the flow in a continuous state. Furthermore, this is the main reason for the dependency on the hot air blower.

During the commencement of the experimental process, two distinct samples, labelled as sample number 1 and 2, were produced. These preliminary samples were crafted with the specific purpose of setting a foundational benchmark. This benchmark would then serve as a reference point around which the variable parameters could be manipulated and altered for further trials, thereby allowing for a systematic and comparative analysis of the results.

During the experiment, some observations were made. Among these observations, it was noted that the voltage difference applied was actually sufficient for the process. However, other factors may pose a potential challenge during the experiment. In particular, the relatively low flow rate and the high viscosity of the solution have led to some technical problems that have a negative impact on the smooth operation. It was pointed out that these conditions did not allow the operation to proceed as smoothly and robustly as expected.

Upon encountering these issues, potential alternatives were considered to address these challenges. These alternatives were constrained by the experimental setup and the need to maintain certain conditions. One potential solution could have been to increase the heat flow. However, this parameter was already established as a fixed parameter and hence, could not be manipulated in this context. Another potential alternative considered was the possibility of increasing the voltage difference. This approach was deemed feasible and was taken into consideration for the subsequent trials. The idea was that by adjusting the voltage, the issues caused by the low flow rate and high viscosity could be alleviated, thereby leading to a smoother and more stable operation.

In the ensuing phase of the experiment, the second set of trials led to the production of samples numbered 3, 4, and 5. This particular phase of the study focused on investigating the influence of alterations in flow rate and voltage difference on the previously established IL:DMSO ratio of 1:1.5. Moreover, a significant adjustment was made during this trial, wherein the injection flow rate was amplified from the original 7 mm/h to a value more than double, reaching 16 mm/h, specifically for the IL:DMSO ratio of 2:1.

As the trial progressed and observations were recorded, some intriguing patterns emerged. In the case of samples 3 and 4, it was discerned that the augmentation in the flow rate led to the increased presence of beads in the final products. This outcome was notably tied to the relatively high viscosity of the solution. The elevated viscosity seemed to facilitate the formation of a substantial number of beads within the fibers.

Alongside this, the impact of escalating the voltage difference, while keeping the injection flow rate constant, was also evaluated. Under these conditions, the final product was deemed of superior quality, characterized by fewer beads. Despite the reduction, the beads were still markedly present. However, the overall process was not entirely stable. There were instances of intermittent pauses, stemming from improper heating, which consequently led to the discontinuation of the flow process.

Lastly, for sample number 5, which was produced under the IL:DMSO ratio of 2:1, the increase in voltage rendered favorable results. Yet, it is important to note that the difference brought about by this adjustment was relatively minor, indicating that while the change had a positive impact, its degree was somewhat limited.

From the first two preliminary trials, it was concluded that massively increasing the flow would have adverse effects on the final quality. The voltage difference, though, was left to be subjectable to slight modification (10-15 kV) depending on the processes circumstances. For the final three repeated sets of trials, four ratios of IL:DMSO were put under experimentation; 1:1, 1:1.5, 1.25:1, and 2:1. Furthermore, the syringe flow was set to be at 9 mm/h.

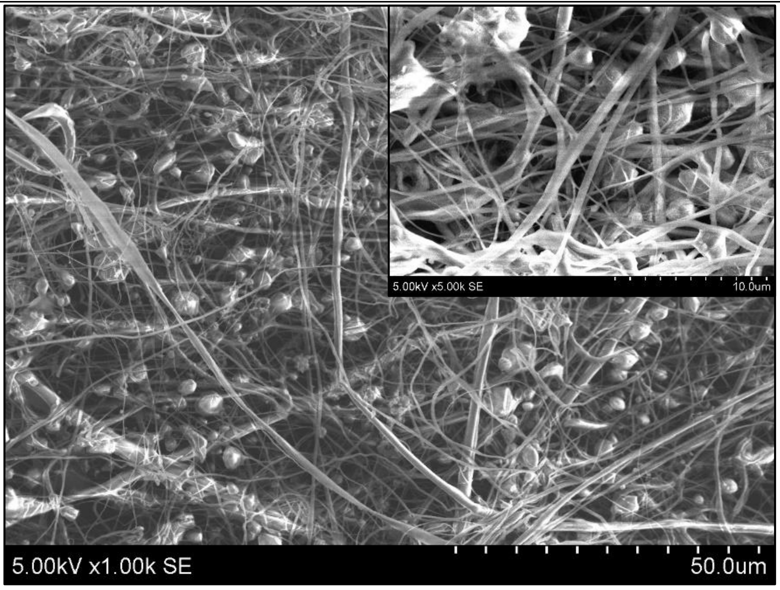
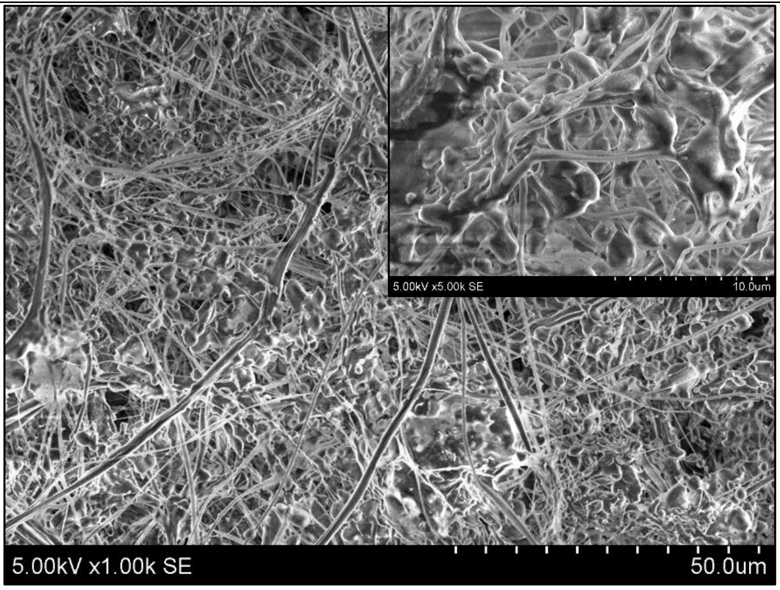
3.1.2. Final trials

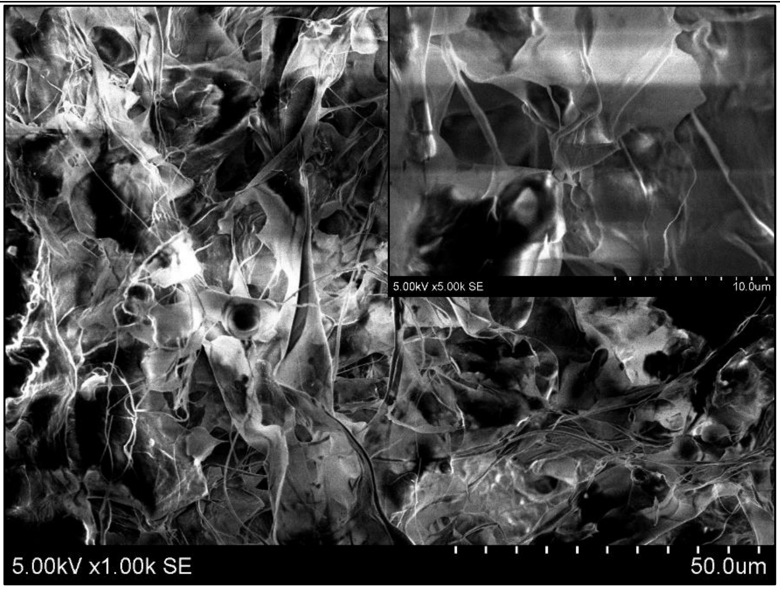
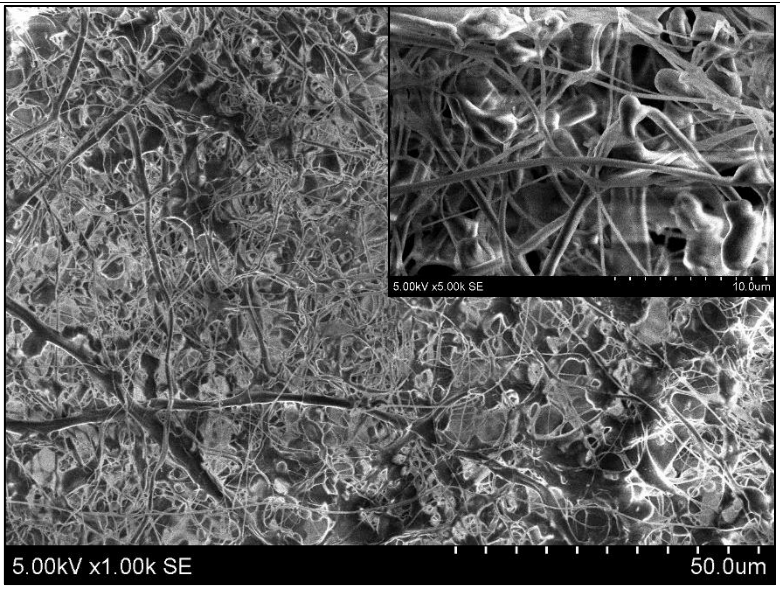
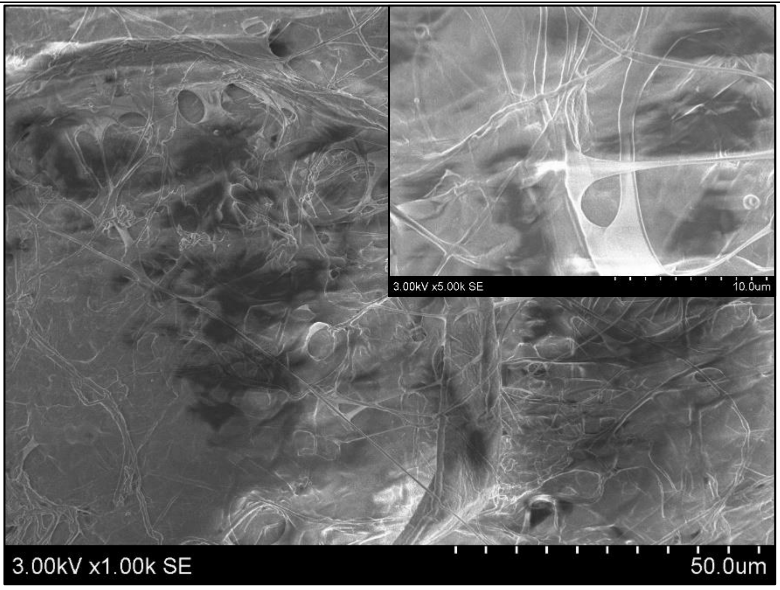
The purpose of those trials was to test the chosen operational conditions as well as repeatability of the experiment of producing cellulose nanofibers under those conditions.

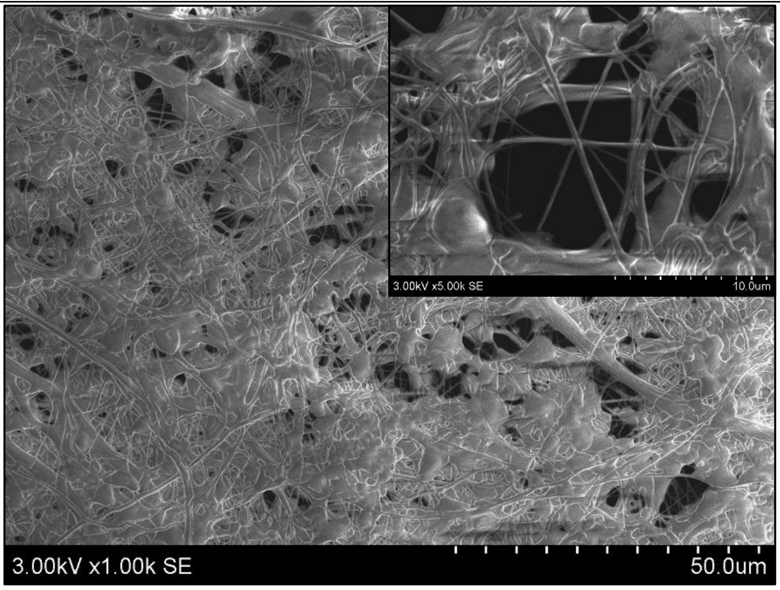
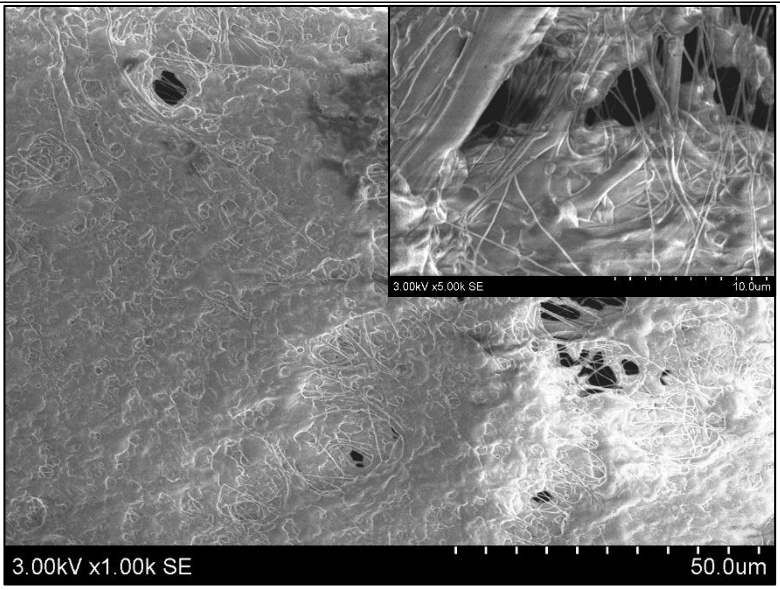
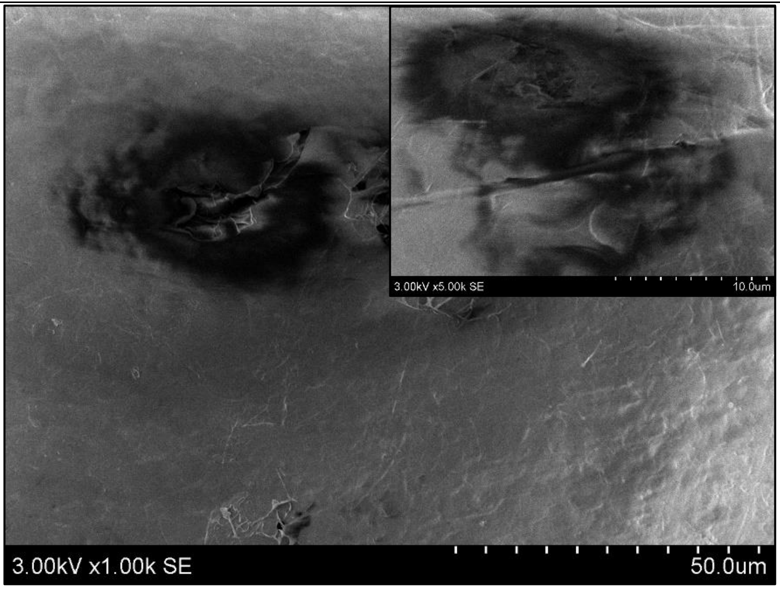
Four samples number 6, 7, 8, and 9 were produced using the chosen conditions. The voltage difference values were 10, 12, 13, and 13 kV for samples number 6, 7, 8, and 9; respectively. Those chosen values were due to the optical observation of the process flow which aimed towards having less splashes and having a proper spraying of Taylor’s cone. The produced samples were analyzed using SEM imaging as seen in Table 2.

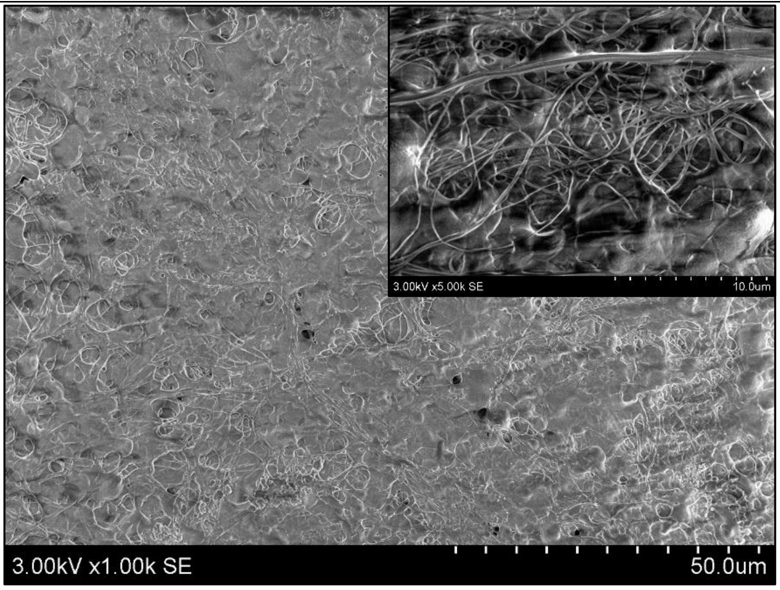
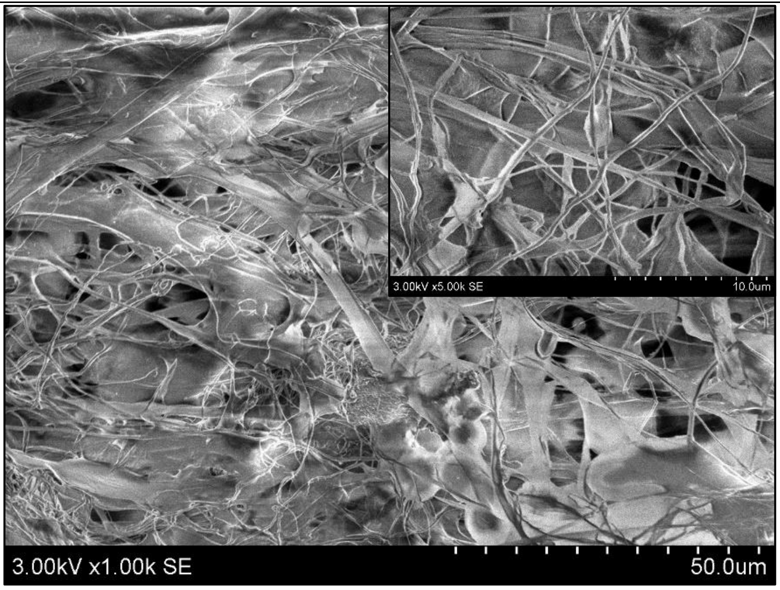
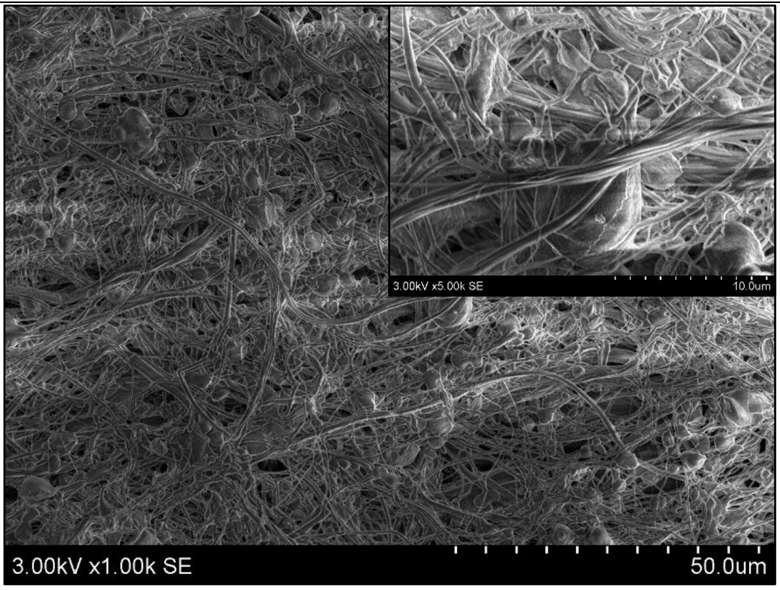
Following the analysis and the study of the distribution of samples number 6, 7, 8, and 9 (see 3.1.3.2), the voltage difference was chosen to be set on the average between 10 and 15 kV at the value of 12 kV. Despite being advantageous, raising the voltage difference can have adverse complications; hence the average-value approach. On the other hand, the syringe flow of 9 mm/h was found to be suitable for all concentrations. The concluded conditions were used to produce 10 more samples; labeled from 10 to 19. Table 2 shows SEM images of the 19 samples produced repeatedly after the preliminary trials.

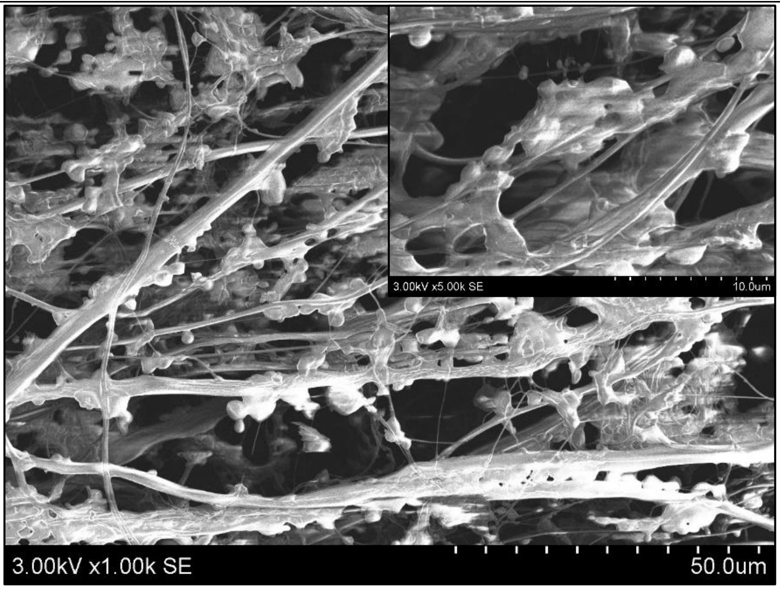
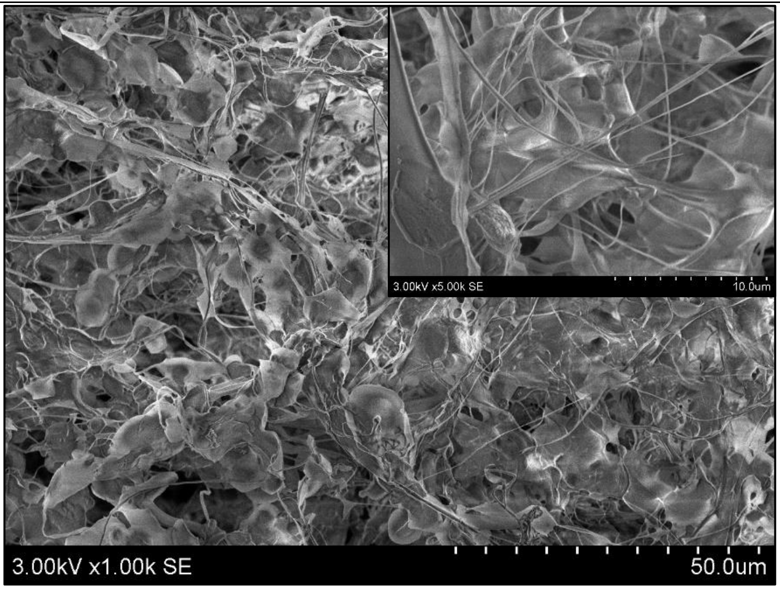
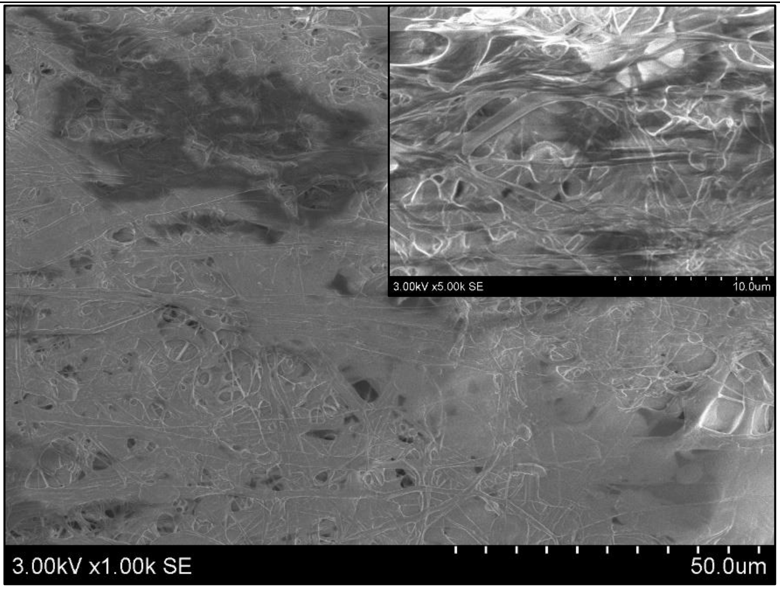
Table 2. The scaled SEM images of the 19 samples produced repeatedly after the preliminary trials alongside their numbers, DMSO:IL ration and methods of drying

SEM image	**Sample number**	**IL:DMSO**	**Drying method**
	Sample #6	1:1	Lyophilization
	Sample #7	1:1.5	Lyophilization

SEM image	**Sample number**	**IL:DMSO**	**Drying method**
	Sample #8	1.25:1	Lyophilization
	Sample #9	2:1	Lyophilization
	Sample #10	2:1	Vacuum drying

SEM image	**Sample number**	**IL:DMSO**	**Drying method**
	Sample #11	1:1	Vacuum drying
	Sample #12	1:1.5	Vacuum drying
	Sample #13	1.25:1	Vacuum drying

SEM image	**Sample number**	**IL:DMSO**	**Drying method**
	Sample #14	1:1	Vacuum drying
	Sample #15	2:1	Lyophilization
	Sample #16	1:1	Lyophilization

SEM image	**Sample number**	**IL:DMSO**	**Drying method**
	Sample #17	1:1.5	Lyophilization
	Sample #18	1.25:1	Lyophilization
	Sample #19	1:1	Lyophilization

3.1.3. Fiber analysis

3.1.3.1. Visual analysis

Despite being inaccurate, visual analysis provided a preliminary indication of the quality of the final product. It is possible as soon as the fabricated nanofibers are out of the drying step. Throughout the final trials, all produced fibers were of an acceptable form. The only exception, however, were the fibers dried using vacuum dryer. Those fibers seemed to be lighter in structure and fragile; lacking the plasticity of their counterparts that were dried using lyophilization. This was confirmed using SEM analysis. As it can be seen in Table 2, samples 10, 11, 12, and 13 show clear signs of damage in the fibers.

3.1.3.2. Statistical analysis

Microsoft office Excel and IBM SPSS software were used to produce statistical data of fibers diameter for them to be statistically analyzed. The analysis was mainly conducted for the repeated samples since they were the main focus. In the upcoming section, the quality of the fibers will be determined based on different statistical approaches depending on their diameters that were measure using the methodology followed in section 2.1.6. It is important to note that the comparative pivotal point will be mainly the IL:DMSO ratio. This is because the variation in voltage difference in samples 6, 8, and 9 were within the same range of voltage difference of 10-15 kV.

3.1.3.2.1. Percentiles

Upon the examination of the diameter percentiles of various nanofiber samples (Table 3), it is evident that samples produced from IL:DMSO ratio of 1:1, encompassing samples 6, 11, 14, 16, and 19, consistently demonstrated superior performance in maintaining smaller diameters across all percentiles. This implies greater control over the manufacturing process and possibly higher quality outcomes in applications where smaller nanofiber diameters are preferable. Outstandingly, sample 6 set a promising start with a mere 0.1238 µm at the 5th percentile, increasing only slightly up to 0.2728 µm at the 95th percentile. Sample 16 also exhibited competitive diameters, displaying the smallest diameter within this group at the 75th percentile, with a measurement of 0.188 µm. Similarly, samples 11 and 14 held their ground in the face of competition, maintaining their diameters predominantly under 0.2 micrometers until the 75th percentile.

As for the samples produced from IL:DMSO ratio of 1:1.5 (7, 12, and 17) generally comprised larger diameters. Despite the larger diameters, Sample 7 stood out due to its tight control over diameter growth, with only a 0.0646 micrometer increase from the 5th to 95th percentile. Furthermore, samples 8, 13, and 18, demonstrated a broader range in terms of their diameter percentiles. The diameters in this group are noticeably larger, especially in the higher percentiles. Interestingly, sample 8 presents the smallest 5th and 10th percentile measurements across all samples, which might be of interest depending on the particular application.

Finally, samples 9, 10, and 15, reflected a broad spectrum of diameters, with Sample 10 showing particularly less favorable results. The diameter measurements for Sample 10, especially in the higher percentiles, are among the highest, indicating a lack of control in achieving smaller diameters. It also underperforms when compared to its counterparts within other samples that were produced using the same IL:DMSO ratio.

Comparatively, samples 10, 13, and 14 show less favorable results within their respective groups. Sample 10's 90th and 95th percentiles in its group are notably larger than those of other samples in the group, which suggests it may have more inconsistency in maintaining small diameters. For sample 13, it is noted 75th and 90th percentile values are remarkably higher than samples 8 and 18, indicating a steep increase in diameter compared to other samples. Lastly, within compared to samples 6, 11, 16, and 19; sample 14's 90th and 95th percentiles are larger than the rest, although this group generally has smaller diameters.

In conclusion, the percentile data showed favorable results of using an IL:DMSO ratio of 1:1. Additionally, the data analysis supported the visual analysis of how samples dried using vacuum drying had compromised fiber quality.

Table 3. The 5th to 95th percentile for the diameters of the nanofibers categorized by IL:DMSO ratio. Cells of each column are colored in gradient to compare with the values of other samples within the same percentile.

IL:DMSO	Sample number	Percentile						
		5	10	25	50	75	90	95
1:1	6	0.1238	0.1382	0.1510	0.1700	0.1990	0.2436	0.2728
	11	0.1452	0.1532	0.1630	0.1870	0.2030	0.2388	0.2566
	14	0.1342	0.1438	0.1590	0.1800	0.2020	0.2966	0.3258
	16	0.1226	0.1460	0.1530	0.1690	0.1880	0.2328	0.2662
	19	0.1350	0.1502	0.1630	0.1930	0.2360	0.3236	0.3764
1:1.5	7	0.1426	0.1520	0.1620	0.1750	0.1890	0.2000	0.2072
	12	0.1366	0.1462	0.1610	0.1890	0.2460	0.3122	0.3212
	17	0.1348	0.1410	0.1570	0.1980	0.2520	0.3350	0.4076
1:1.25	8	0.1176	0.1334	0.1670	0.2080	0.2650	0.3484	0.3890
	13	0.1338	0.1524	0.1720	0.2020	0.3680	0.6028	0.6976
	18	0.1380	0.1472	0.1550	0.1730	0.2150	0.2470	0.2660
2:1	9	0.1426	0.1484	0.1630	0.1770	0.2020	0.2398	0.2986
	10	0.1364	0.1554	0.1720	0.1920	0.2570	0.3598	0.4164
	15	0.1302	0.1406	0.1620	0.1850	0.2270	0.3086	0.4070
	Legend	Smallest ø						Largest ø

3.1.3.2.2. Box-whisker Plot

By examining the box-whisker plot for the diameters of the produced samples in Fig. 9, we can conclude the following statements. For samples 6, 11, 14, 16, and 19, showcase impressive median nanofiber diameters which range between 0.1690 µm and 0.1930 µm. For instance, sample 6 displays a median diameter of 0.17 µm, and its smallest diameter was seen as low as 0.11 µm, an indication of this sample's quality nanofibers; diameter-wise. The larger diameters for this group, despite being outliers, such as 0.30 and 0.39 for samples 6 and 14 respectively, demonstrate a wider range in their diameter values. Even in the presence of larger outliers, such as 0.30 and 0.39 for samples 6 and 14 respectively, the overall analysis indicates the superiority of the samples produced from a ratio IL:DMSO of 1:1 in producing finer nanofibers compared to their counterparts which were produced by different ratios of IL:DMSO. This can be easily seen in the box-whisker plot since on the 75th all of these samples were below 0.21 µm; with the exception of sample 19.

On the other hand, the median values of the diameters for samples 7, 12, and 17, were recorded as 0.1750, 0.1890, and 0.1980 respectively. The lowest diameters in this group are also satisfactory with values down to 0.13 for sample 7. Meanwhile, samples 8, 13, and 18 had medians ranging from

0.1730 to 0.2080 which reflect a slightly larger nanofiber diameter tendency. For instance, sample 8 has its median diameter as 0.2080, and its outliers reach as high as 0.80. Nonetheless, it's noteworthy that even in this group, the smallest diameters go down to 0.11. Finally, samples 9, 10, and 15 had median diameter values range from 0.1770 to 0.1920. Sample 10, despite its higher median value of 0.1920, has been seen to produce nanofibers as fine as 0.12.

However, it's worth noting that samples from 10 to 14 seem to fall behind when compared to other samples within their respective groups. For instance, samples 11 and 14 had a relatively high median diameter and larger outliers when compared to other samples (6 and 16) which were fabricated using an IL:DMSO ratio of 1:1. This trend, present across those samples (10-14) within their respective groups.

In conclusion, the data, once again, show the edge that samples produced using IL:DMSO ratio of 1:1 over other samples. Moreover, samples dried using vacuum method were of poorer qualities; most notably, sample number 18 which had an outlier reaching as large as 1 μm.

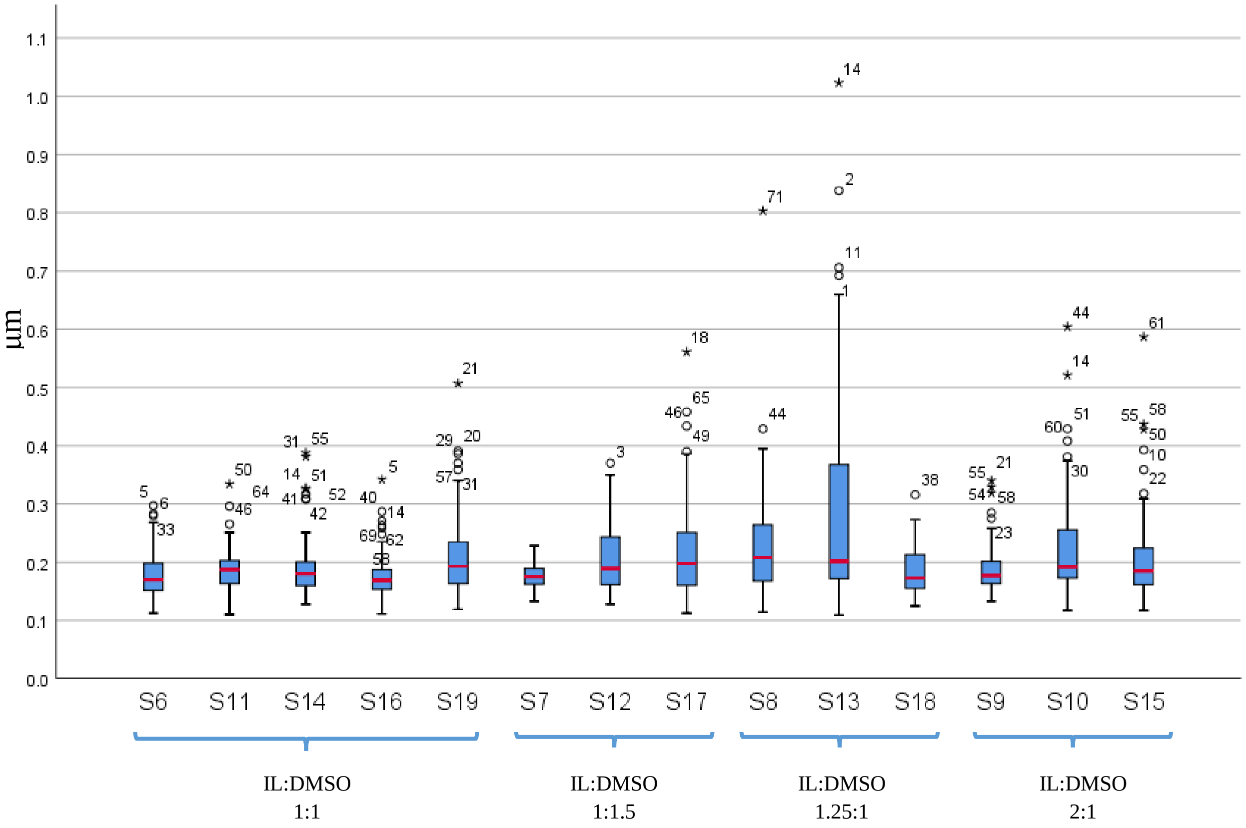


Fig. 9. Box-whisker plot of the diameters of the produced samples

3.1.3.3. Analysis Outcomes

The statistical data analysis showed that the fibers produced from the electrospinning of an equal amounts of IL and DMSO in the presence of 2% w/w cellulose possess higher quality in regards with fibers diameters. Electrospinning a polymer solution with increasing amount of IL results in the alteration of two parameters: solution electrical conductivity, and viscosity. IL leads to increasing the of the overall solution electrical conductivity. According to several literature findings, this should result in the formation of generally finer diameters. [66, 67] This was the case with samples 6, 9, 11, 14, 16, and 18. However, there were other samples which did not conform to the aforementioned literature findings by having relatively much thicker diameters than the rest of their counterparts; those samples were 8, 10, and 13. On the other hand, the overall finding can be justified by literature in the sense that few articles suggest that the electrical conductivity of the solution does not affect the diameters of the electrospun fibers. An example of such findings is what Naseri et al. [68] suggested in their research which investigated how solution properties and nanoparticle surface chemistry impact the electrospinning of a chitosan/polyethylene oxide with a high concentration of chitin and cellulose nanocrystals.

On the other hand, a polymer solution with higher concentration of IL in comparison to DMSO has a reduced viscosity. According to Li et al., Ciuzas et al., and Luraghi et al. [13, 66, 67], elevated viscosity results more continuous diameters, but also results the beads formation and even the clogging of the nozzle if the heating and injection piston rate are not sufficient (for example samples 6 and 16 in Table 2). This does not mean that the decreasing the viscosity is the absolute answer, this is because decreasing it results in shorter more fragile fibers and even, in some cases, excessive flow and therefore failure to form a fibrous product; both cases were evident during the experiments precursing this research. In conclusion, a fine tuning of viscosity is necessary to have a proper quality of produced nanofibers.

In addition to the previous parameters, there are two more important factors that were taken into consideration when deciding the optimal operation conditions: applied voltage difference, and drying method. Zeng et al. [69] in their efforts to investigate how different drying methods affect the porosity of regenerated cellulose fibers, concluded that using lyophilization is advantageous for the case of cellulose nanofibers. Meanwhile, despite the absence of a global default value of applied voltage difference during the process of electrospinning, this research's values of voltage differences (in the range of 10-15 kV; and primarily 12 kV) go in line with other research papers that worked on similar electrospinning process; such as da Mata et al. (20 kV) [70], and Ramos et al. (11-15 kV) [71].

The outcome of the previous discussion and analysis resulted in settling on using a polymer solution of 2% w/w cellulose dissolved in a 1:1 IL:DMSO for the electrospinning process under a voltage difference of 12 kV.

3.2. Phase II: Adsorption of methylene blue

After the adsorption process was completed, the data from the spectrophotometer were put into calibration curve to obtain concentration data. The results are shown in Fig. 10. Multiple conclusions can be deducted from the plots available.

First of all, most of the methylene blue adsorption occurred in the first 30 minutes of the experiment; regardless of the adsorbent type, and initial concentration of methylene blue. Another important note is that OC showed the best adsorption results among all adsorbents. The difference between all other adsorbents is not evident in the processes of adsorbing MB with initial solution concentrations of 5 and 10 mg/l; however, the difference is slightly more evident in the solution with the initial solution concentration of 1 mg/l. At this initial concentration, ozone-modified adsorbents were superior to their counterparts. On the other hand, CN, PC, and PCN show mediocre results; while raw cellulose adsorbent was in the middle between both sides.

The graphs, though, showed consistency with some principles of adsorption. As it is seen in Fig. 11, the amount of adsorbed MB per unit mass of the adsorbent rose consistently as the initial concentration of MB increases. According to Freundlich isotherm equation (3.2.2.3), as the initial concentration increases, the amount of adsorbate adsorbed also increases. Furthermore, the pseudo-second-order kinetic model (3.2.1.1.1) shows the same concept based on the driving force. This was also approved by many other works; such as Chen et al. [72] in their work for the MB removal using cellulose-graphene oxide fibers from water.

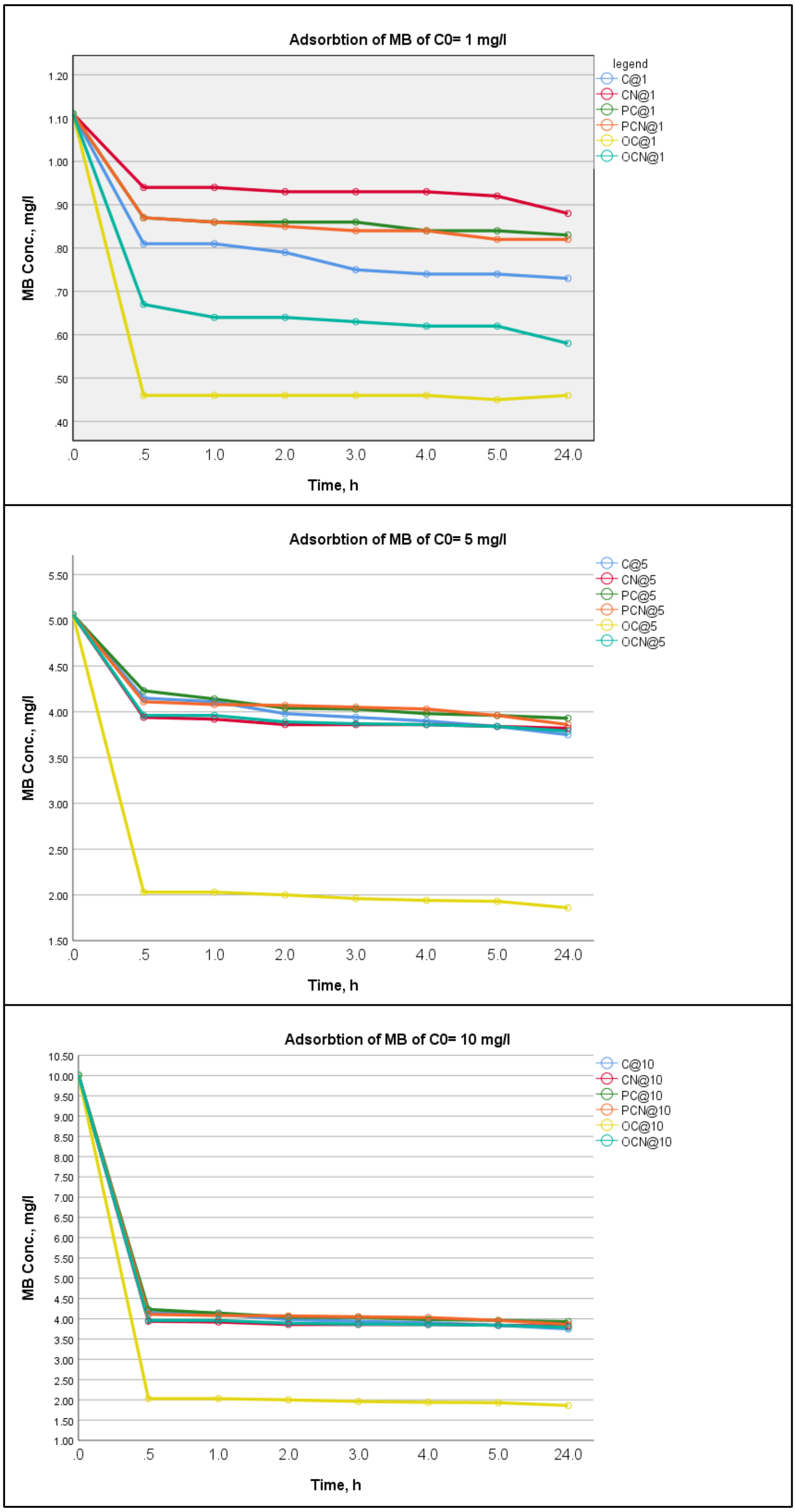


Fig. 10. The concentration of methylene blue at different intervals of time in the presence of different adsorbents with initial concentrations of methylene blue of 1 mg/l (top), 5 mg/l (middle), and 10 mg/l (bottom)

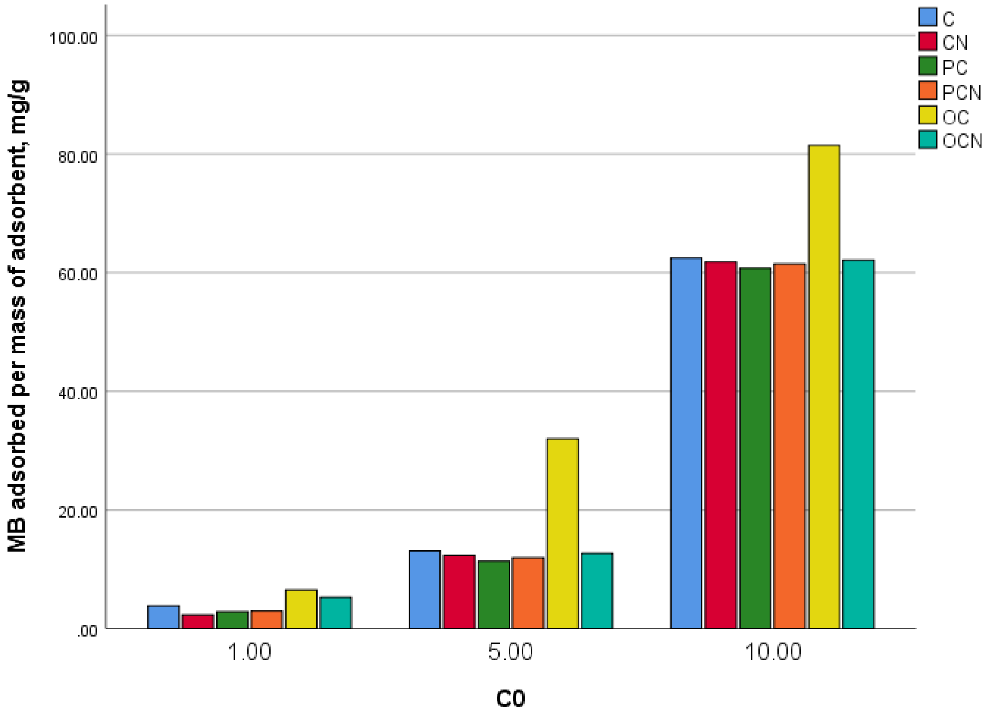


Fig. 11. The amount of adsorbed MB by each adsorbent at different initial concentrations of MB

Moreover, as previously mentioned, in Fig. 10, the rate of adsorption during the first 30 minutes was the highest; regardless of the initial concentration of MB and adsorbent. The effect of contact time on adsorption is described by adsorption kinetics models, such as the pseudo-second-order kinetic model. The pseudo-second-order equation (3.2.1.1.1) shows that as the contact time increases, the amount of adsorbate adsorbed at that time also increases, until it reaches the equilibrium amount.

3.2.1. Adsorption kinetics

3.2.1.1. Kinetics investigation

For the investigation of adsorption kinetics, pseudo-second-order equation was used; as it was found to be the most fitting kinetics model to the experimental data. The main concept of pseudo-second-order can be expressed as:

$$\frac{dq}{dt} = k'(q_e - q_t)^2 \qquad (3.2.1.1.1)$$

In order to plot the data for fitting, linearization is done to the above equation. The pseudo-second-order equation becomes as follows:

$$\frac{t}{q_t} = \frac{1}{k'q_e^2} + \frac{1}{q_e}t \qquad (3.2.1.2)$$

Where:
t (min) is time.
q_t (mg/gm) is the amount of adsorbed adsorbate at a given time,
k' (g/mg.min) is the rate constant,
q_e (mg/gm) is the amount adsorbed at equilibrium,

By plotting t/qt versus t, the resulted k’ value can be calculated, and were found to be as follows:

Table 4. k’ values of the adsorbents at different initial concentrations of MB

MB Initial Concentration, mg/l	k’ value, g/mg.min					
	C	**CN**	**PC**	**PCN**	**OC**	**OCN**
1	0.22	0.11	0.31	0.28	0.75	0.13
5	0.03	0.16	0.06	0.03	0.06	0.07
10	0.03	0.17	0.07	0.04	0.06	0.08

The k’ values show similar results to the conclusions deducted from Fig. 10, where OC showed the fastest adsorption rates. However, some of the k’ values do not describe what happened in Fig. 10. Primarily, the main difference between Table 4 and Fig. 10 is that increasing initial concentrations of MB did not affect the adsorption rate in a directly proportional manner; conversely, with the exception of CN, the k’ value decreased. Furthermore, CN, at higher initial concentrations of MB showed higher rates than that of its counterparts.

Although data might seem contradictory to one another at the first glance, there is a good explanation for this. Because plotting a pseudo-second-order equation requires dividing by either t or q_t, both of which are of a zero value at the beginning of the experiment, it is not possible to plot the adsorption process between the very beginning of the process and after 30 minutes of the beginning of the process. By taking into consideration that, according to the data from Fig. 10, most of the adsorption process occurred during the first half hour, this means that the k’ values solely describe what happened afterwards when the adsorption process had already slowed down.

Since pseudo-second-order kinetics assumes that the rate-limiting step may be of a chemisorption nature, involving valency forces through sharing or exchange of electrons between the adsorbent and the adsorbate, this means that the lack of modifications of cellulose nanofibers did indeed prolong the adsorption rate. This is why the k’ value of CN was directly proportional with the increasing initial concentrations of MB. Moreover, this also goes with why the k’ value of CN was relatively higher at initial concentrations of 5 and 10 mg/l.

3.2.1.2. Literature overview

Various other researchers investigated the adsorption of various cellulose-based adsorbents as well as of MB adsorption using various other adsorbents. Tong et al. [73] conducted research focused on the adsorption of methylene blue from an aqueous solution using porous cellulose-derived carbon/montmorillonite nanocomposites. Their analysis revealed a k’ value of 0.002 g/mg.min. Interestingly, the adsorption rate did not increase with the increasing concentration, similar to observations in your current research.

Furthermore, Gago et al. [74] turned their attention towards the use of dicarboxymethyl cellulose for the efficient removal of methylene blue. Their experiments resulted in a comparatively high k' value of approximately 6 g/mg.min, indicating a more rapid adsorption process under the conditions they tested. Wang et al. [75] took a different approach by investigating methylene blue adsorption using a polyacrylic acid-grafted, quaternized cellulose adsorbent. Their k' values were found to be concentration-dependent, starting at 3.510^{-4} g/mg.min at the lowest initial concentration and increasing to 1.410^{-4} g/mg.min when the initial concentration was sextupled. Shi et al. [76] conducted an evaluation of a nitriloacetic acid-modified cellulose film for the adsorption of methylene blue. Their work resulted in a k' value of 0.33 g/mg.min, providing another perspective on the range of possible rates in such adsorption processes.

Continuing this exploration, Liu et al. [77] synthesized a high efficiency and eco-friendly porous cellulose-based bioadsorbent by grafting acrylic acid and acrylamide, with the intent of removing methylene blue from both single and binary dye solutions. Their measured k' value stood at a notably low $1.3*10^{-5}$ g/mg.min, indicating a slower adsorption rate under their specific experimental conditions. Lin et al. [78] utilized TEMPO-oxidized cellulose beads for the adsorption of methylene blue. Their research resulted in a k' value of 0.0370 g/mg.min, adding yet another data point to the broader understanding of how different adsorbents and conditions can influence adsorption kinetics. Lastly, Chen et al. [72] aimed at removing methylene blue from water using cellulose/graphene oxide fibers. Their determined k' was found to be 0.00003 g/mg.min, suggesting a relatively slow adsorption rate for their system.

As for other adsorbates, Saravanan et al. [79] have demonstrated the use of a new chemically modified cellulose, known as DTD, for heavy metal ion adsorption and antimicrobial activities. Their experimentation led to the determination of two separate pseudo-second order rate constants (k'), one each for lead and copper ions. The values, 0.002 g/mg.min and 0.0015 g/mg.min respectively, highlight different rates of adsorption for these two metals, which could be consequential in understanding the efficiencies of different types of ion removal. In parallel, Pan et al. [80] also explored the use of chemically modified cellulose for heavy metal ion adsorption and antimicrobial activities. Their study revealed the k' value to be dependent on the initial concentration of the adsorbates, measuring at 0.001 g/mg.min at lower concentrations, and increasing to 0.014 g/mg.min at higher concentrations. This distinction offers valuable insight into how adsorption rates may change depending on the initial concentration of contaminants.

Lastly, Pottathara et al. utilized TEMPO-oxidized cellulose nanofibrils-graphene oxide composite films, with a particular focus on improving dye adsorption properties. Their research led to the determination of k' values for two dyes: basic violet and rhodamine. For both dyes, the k' value was found to be $1.3*10^{-4}$ g/mg.min, indicating a uniform adsorption rate under their experimental conditions. This uniformity could point to similarities in the interaction between the adsorbent and these two different dyes.

Table 5. Comparison of different k’ values from literature and this study

Adsorbent	**Adsorbate**	**k' at different initial concentrations (g/mg.min)**	**Source**
C	MB	at C0=1: 0.22, at C0=5: 0.03, at C0=10: 0.03	This study
CN	MB	at C0=1: 0.11, at C0=5: 0.16, at C0=10: 0.17	This study
PC	MB	at C0=1: 0.31, at C0=5: 0.06, at C0=10: 0.07	This study
PCN	MB	at C0=1: 0.28, at C0=5: 0.03, at C0=10: 0.04	This study
OC	MB	at C0=1: 0.75, at C0=5: 0.06, at C0=10: 0.06	This study
OCN	MB	at C0=1: 0.13, at C0=5: 0.07, at C0=10: 0.08	This study
Carbon/Montmorillonite nanocomposite	MB	0.002	Tong et al.
Dicarboxymethyl Cellulose	MB	Approximately 6	Gago et al.
Polyacrylic Acid-Grafted Quaternized Cellulose	MB	At lowest conc.: 3.510-4, at 6 times initial conc.: 1.410-4	Wang et al.

Adsorbent	Adsorbate	k' at different initial concentrations (g/mg.min)	Source
Nitriloacetic Acid Modified Cellulose Film	MB	0.33	Shi et al.
Acrylic Acid & Acrylamide Grafted Cellulose	MB	$1.3*10^{-5}$	Liu et al.
TEMPO-Oxidized Cellulose Beads	MB	0.037	Lin et al.
Cellulose/Graphene Oxide Fibres	MB	0.00003	Chen et al.
DTD	Pb2+	0.002	Saravanan et al.
DTD	Cu2+	0.0015	Saravanan et al.
Cellulose	Metal Ion	Low Conc.: 0.001, High Conc.: 0.014	Pan et al.
TEMPO-CN	Basic Violet	1.3*10-4	Pottathara et al.
TEMPO-CN	Rhodamine	1.3*10-4	Pottathara et al.

3.2.2. Adsorption isotherms

3.2.2.1. Isotherms investigation

As in adsorption kinetics, the resulted data were put into investigation in order to study the adsorption isotherms that occurred during the experiment. Since adsorption isotherms study requires multiple initial concentrations of MB, the experimental data obtain for this study were not sufficient. This resulted in a relatively average value of R^2 which describe the fitness of a model to the experimental data. The model which was found of the best fit was Freundlich isotherm model.

A linearized form of Freundlich isotherm equation was used (3.2.2.3), where $\log(q_e)$ was plotted against $\log(C_e)$ to find the values of Freundlich constants.

$$\log(q_e) = \log(k_f) + \frac{\log(Ce)}{n} \qquad (3.2.2.1.3)$$

Where:
q_e (mg/g) is the quantity of adsorbate adsorbed per unit weight of adsorbent
C_e (mg/l) is the equilibrium concentration of the adsorbate
k_f (mg/g) and n are Freundlich constants, indicative of adsorption capacity and intensity, respectively.

For the C adsorbent, the value of k_f was found to be 0.49 mg/g. This value indicates a moderate adsorption capacity for MB. Furthermore, the heterogeneity factor (n) for C was determined to be 1.79. Being greater than 1, this value suggests the occurrence of cooperative adsorption[4]. The CN adsorbent showed a notably high adsorption capacity for MB, having the highest k_f value of 0.77 mg/g among the tested adsorbents. It also displayed a stronger cooperative adsorption effect, which was reflected in its n value of 2.23, the highest among the group.

As for the PC adsorbent, it demonstrated an adsorption capacity of k_f of 0.68 mg/g; which is lower than that of CN but higher than the remaining adsorbents. Its n value stood at 2.05, indicating a

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[4] Cooperative adsorption is a process where the adsorption of one molecule enhances the likelihood of subsequent molecules to bind to the same surface, effectively making the adsorption process more efficient with increasing concentration of the adsorbate.

cooperative adsorption effect, albeit weaker than CN. The PCN adsorbent's k_f value was 0.65 mg/g, suggesting a slightly lower adsorption capacity for MB than PC. Nevertheless, the n value was nearly similar at 2.01, indicating a nearly equivalent level of cooperative adsorption.

Contrastingly, the OC adsorbent displayed the lowest adsorption capacity for MB, having a k_f value of 0.18 mg/g. Additionally, it exhibited a cooperative adsorption effect, reflected in its n value of 1.72. Although cooperative adsorption was present, the effect was weaker than in the other adsorbents. Lastly, the OCN adsorbent, with a k_f value of 0.32 mg/g, showed a low adsorption capacity for MB, higher only than OC. Its n value was also the lowest among all tested adsorbents, at 1.50, indicating the least cooperative adsorption effect.

3.2.2.2. Literature overview

Upon checking the literature, Tong et al. [73] focused on the adsorption of methylene blue from an aqueous solution using porous cellulose-derived carbon/montmorillonite nanocomposites. The Freundlich adsorption constants recorded were k_f= 111.5 mg/g and n= 9.09, indicative of a high adsorption capacity. The fit of the model to the experimental data was found to be very good, with an R^2 value of 0.9192. Another work by Gago et al. [74] investigated the use of dicarboxymethyl cellulose for the efficient removal of methylene blue. In their research, the Freundlich adsorption constants were approximately k_f= 0.05 mg/g and n= 3. These values suggest a lower adsorption capacity in comparison to the study by Tong et al. However, the model still demonstrated a good fit, as indicated by an R^2 value of 0.8. Another paper by Wang et al. [75] examined methylene blue adsorption using a polyacrylic acid-grafted quaternized cellulose adsorbent. The Freundlich adsorption constants reported were k_f= 192 mg/g and n= 3.2, suggesting a high adsorption capacity. The R^2 value for this study was 0.816, indicating a good fit between the model and the experimental data.

Liu et al. [77] put forth a study where they synthesized a high-efficiency and eco-friendly porous cellulose-based bioadsorbent. This was achieved by grafting acrylic acid and acrylamide for the removal of the cationic dye methylene blue from single and binary dye solutions. The Freundlich adsorption constants for this study were k_f= 16 mg/g and n= 1.4, and the model fit was excellent with an R^2 value of 0.9736. Moreover, Chen et al. when focusing on the removal of methylene blue from water using cellulose/graphene oxide fibers, they found the Freundlich adsorption constant to be k_f= 230 mg/g. The R^2 value was high at 0.98, indicating a very strong correlation and an excellent fit of the model. However, the heterogeneity factor, n, was not provided in their study. Lastly, Saravanan et al. worked with a newly chemically modified cellulose, referred to as DTD, for heavy metal ion adsorption and antimicrobial activities. For the adsorption of lead ions, the Freundlich constants were k_f= 41 mg/g and n= 3.7, while for copper ions, they were k_f= 38 mg/g and n= 3.6.

Upon comparing results of this study with the literature, the cellulose adsorbent (C) showed a k_f value of 0.49 mg/g and an adsorption intensity (n) of 1.79. Comparatively, Tong et al. [73], who also used a cellulose-based adsorbent, had a considerably higher k_f of 111.5 mg/g. This suggests that C adsorbent had a lower adsorption capacity for methylene blue. The CN, on the other hand, showed a k_f of 0.77 mg/g and an n of 2.23 which was higher than the values produced by Gago et al [74]. who used dicarboxymethyl cellulose with a k_f approximately 0.05 mg/g. For the OC and OCN, the k_f values are lower than those from the selected literature. As for the PC and PCN, the k_f values are lower than those in the literature; however, the n values are within the range of the studies, suggesting similar adsorption intensity.

Table 6. Comparison of different Freundlich constants values from literature and this study

Adsorbent	**Adsorbate**	**Kf (mg/g)**	**n**	**R2**	**Source**
Raw Cellulose (C)	MB	0.49	1.79	0.69	This study
Cellulose Nanofibers (CN)	MB	0.77	2.23	0.76	This study
Plasma Modified Raw Cellulose (PC)	MB	0.68	2.05	0.70	This study
Plasma Modified Cellulose Nanofibers (PCN)	MB	0.65	2.01	0.71	This study
Ozone Modified Raw Cellulose (OC)	MB	0.18	1.72	0.87	This study
Ozone Modified Cellulose Nanofibers (OCN)	MB	0.32	1.5	0.56	This study
Porous Cellulose-derived Carbon/Montmorillonite Nanocomposites	MB	111.5	9.09	0.92	Tong et al.
Dicarboxymethyl Cellulose	MB	0.05 (approx.)	3 (approx.)	0.8	Gago et al.
Polyacrylic Acid-grafted Quaternized Cellulose	MB	192	3.2	0.82	Wang et al.
Acrylic Acid and Acrylamide-grafted Cellulose	MB	16	1.4	0.97	Liu et al.
Cellulose/Graphene Oxide Fibers	MB	230	N/A	0.98	Chen et al.
DTD (Chemically Modified Cellulose)	Lead ions	41	3.7	N/A	Saravanan et al.
DTD (Chemically Modified Cellulose)	Copper ions	38	3.6	N/A	Saravanan et al.
DTD (Chemically Modified Cellulose)	Basic Violet	$1.3*10^{-4}$	N/A	N/A	Saravanan et al.
DTD (Chemically Modified Cellulose)	Rhodamine	$1.3*10^{-4}$	N/A	N/A	Saravanan et al.

3.2.2.3. Limitations

During the adsorption experiment, some of the adsorbent fibers started to loosen resulting in floating fibers. This certainly affected the measurements of the spectrophotometer by mistakenly measuring obstacles as MB presence. It might have caused some inconsistencies and errors that will be reflected in section 3.2.3.

3.2.3. Discrepancies and discussion

Despite the empirical results that were obtained in (3.2.2.1), they do not go hand in hand with the data found in Fig. 11. At a low initial MB concentration (1 mg/L), the OC adsorbent shows the highest adsorption capacity, followed by the OCN adsorbent. The remaining adsorbents (C, CN, PC, PCN) exhibit significantly lower adsorption capacities. Interestingly, as the initial MB concentration increases to 5 mg/L, the OC adsorbent still exhibits the highest adsorption capacity, whereas the capacities for the C, CN, PC, and PCN adsorbents increase but are still lower than OC and OCN. However, at an even higher initial concentration (10 mg/L), the OC adsorbent now shows the highest adsorption capacity. The other adsorbents, including OCN, exhibit similar capacities, which are significantly lower than that of OC.

Comparing these observations with the previously discussed Freundlich constants, the OC adsorbent, which had the lowest k_f value, surprisingly shows the highest adsorption capacity (Fig. 11) at different MB concentrations. Meanwhile, the CN adsorbent, which had the highest k_f value, did not show a proportional increase in adsorption capacity. These discrepancies could be attributed to the fact that the Freundlich isotherm is an empirical model and may not accurately describe all adsorption systems, particularly at higher concentrations. Furthermore, the highest fitting of the model to the data was in the case of OC, having a mere value of R^2= 0.87; as it can be seen in Table 6. Moreover, the value of k_f cannot be directly translated to higher adsorption capacity. The whole model is better at describing the adsorption process than giving capacity values; especially with a low fitting to the experimental data. Another important note is the adsorption rate. From the kinetics investigation 3.2.1.1, it was noted that time period during which the highest rate of adsorption occurred was the first 30 minutes which was not investigated thoroughly. It is possible that by designing an experiment with more detailed and prolonged timespan, the data can be more fitting with models.

Nevertheless, the Freundlich model was not by any means useless. The constant 'n' can give some insights into the affinity of the adsorbent for the adsorbate, particularly how this affinity changes with the concentration of the adsorbate. This is termed as cooperative adsorption. Cooperative adsorption is a phenomenon that occurs when the binding of one molecule to a surface facilitates the adsorption of subsequent molecules. In this process, the initial adsorption event changes the surface properties, making it more favorable for other molecules to adsorb. This means that as more adsorbate molecules bind to the adsorbent, the easier it becomes for additional adsorbate molecules to bind, indicating a positive cooperative effect. This cooperative behavior is often reflected in adsorption isotherms, like the Freundlich isotherm, where a heterogeneity factor greater than 1 suggests cooperative adsorption.

According to the values of constant (n) in Table 6, CN, PC, and PCN adsorbents exhibit highly cooperative adsorption of the adsorbate, while the C and OC adsorbents show cooperative adsorption, and OCN demonstrates a moderate level of cooperativity. This suggests that the initial binding of molecules to CN, PC, and PCN greatly facilitates the subsequent adsorption of more molecules, and this effect is less pronounced but still present for C and OC. OCN has the least cooperative effect among the tested adsorbents. This explains the rise of adsorption capacities with higher initial concentrations of adsorbate. However, it is important to note that this constant does not directly measure affinity; rather, it's an empirical parameter that describes how adsorption varies with concentration.

From the previous statistical analysis, several conclusions were made. Firstly, unmodified CN showed inadequate adsorption capabilities in comparison with other investigated adsorbents. Despite possessing similar adsorption capacities, the kinetics showed that the adsorption process of MB in CN was rather slow. On the other hand, OC was found superior in terms of kinetics and adsorption capacity. It surpassed all other adsorbents; performance-wise.

Furthermore, the study showed that ozone modification was a promising method of modifying adsorbents. Both OC and OCN were faster to adsorb MB and had high capacities to adsorb the MB dye. This can be explained by the fact that ozonation added additional functional groups which provided better affinity towards MB, better adsorption capabilities. As for plasma modification, PC and PCN showed relatively average results. This can be explained by the fact that the adsorbents which were modified by plasma were frail in structure.

As a conclusion, the outcome of this thesis resulted in finding an answer to the hypothesis of whether the unmodified cellulose will be an efficient adsorbent or not. The thesis came to the conclusion that the adsorption rate of CN is slow in comparison to other studied adsorbents over short period of time but has higher rates over prolonged times. The thesis also points out that CN can be of competent adsorptive capacities at elevated initial concentrations of adsorbate. Moreover, further improvements to the structure of the fibers are important to have intact and resilient CN adsorbents.

Conclusions

1. Electrospinning process was used as a method of producing cellulose nanofiber in order to test their adsorptive capabilities. Some of the operating parameters (voltage difference, nozzle flow, the ratio of the used ionic liquid to dimethyl sulfoxide) were tuned to find the optimal conditions that produce the fiber with the most favorable qualities. The experiments concluded that the parameters that gave the most favorable qualities were at a voltage difference of 12 kV, nozzle flow of 9mm/h, and equal quantities of the used ionic liquid and dimethyl sulfoxide.
2. The ozone modified cellulose had the best performance in terms of the rate of adsorption as well as the adsorptive capacity; achieving 58%, 63%, and 81% removal efficiencies in methylene blue solutions with initial concentrations of 1, 5, and 10 mg/l, respectively. Cellulose nanofibers, on the other hand, achieved removal efficiencies of 21%, 25%, and 62% for each methylene blue solution. With the exception of the solution of 1 mg/l of methylene blue, other adsorbents showed similar efficiencies with a variation of ±1.5%. As for the 1 mg/l solution, the efficiencies of the adsorbents ozone modified cellulose, ozone modified cellulose nanofibers unmodified cellulose, plasma modified cellulose nanofibers, plasma modified cellulose, and unmodified cellulose nanofibers were 58%, 48%, 34%, 27%, 26%, and 21%; respectively. This again showed the advantage of ozone modification over using unmodified cellulose nanofibers.
3. Upon investigation of the adsorption kinetics and isotherms, cellulose nanofibers showed favorable results within a longer span of time; having both high kinetic constant and Freundlich k_f constant values in comparison with other tested adsorbents. This meant that cellulose nanofibers can be acceptable adsorbents but in case of the usage for prolonged time periods; which is might not be technically nor economically feasible.
4. However, the adsorption kinetic and isotherms models are not very descriptive of the processes tested. This is because of two main reasons. The first one is that most of the adsorption process occurred during the first half hour of the experiment which was not investigated. The second reason is that the number of trials were not sufficient for the isotherm model to be descriptive of the process.

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