TOWARDS AGRICULTURAL APPLICATION OF WOOD PULP FIBRES

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By

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Abstract

Sustainable agriculture is a crucial factor to be considered in order to meet the growing demand for food production. The need for low cost and highly functional materials to provide the most efficient cultivation process has led the agriculture industry to consume petrochemical and mineral based material in an enormous amount. Thus, disposal of the used mulch materials has become a serious environmental issue. In this work, the possibility of using wood pulp fibre in two distinct applications in agriculture is investigated. First, agricultural mulching is the subject of the study and second, we focus on using wood pulp fibre as growing medium in greenhouses.

Mulching in agriculture is an essential practice in order to have high crop yield, healthy products, and more efficient cultivation process. Over the years, agricultural mulch has been made out of a variety of materials. The most common of all is plastic mulch due to its low price and high functionality. However, the problems associated with applying and removing the enormous load of plastic and their disposal have made it an option far from ideal. Therefore, there is a need to develop mulches based on biodegradable materials. Paper-based mulch is one of the candidates, In the first chapter of this work, with a review of previous works in this area, we attempt to develop a new spray-able mulch based on wood pulp fibre. A novel foam forming method is utilised to deposit wood pulp fibres in combination with other chemicals as an evenly distributed fibre network on a porous bed. Currently available paper based-mulch is of a very high basis weight. In first part of this work, application of a foam formed low basis weight paper-based mulch is investigated. Whereas, in the second chapter, the use of wood pulp fibres in a similar function as “rockwool” in soilless greenhouse farming is investigated.

Rockwool is named after fibres made of melted minerals at temperatures as high as 2000°C. Rockwool is used as blocks for seeds growth and propagation and as an alternative for soil in greenhouses. The feasibility of microenvironment control of the rockwool blocks in crop production plus its low cost have made is popular. However, their disposal has always been an environmental issue. The biodegradability of wood pulp fibres is a great advantage over mineral fibres used in rockwool. In the second chapter of current work, we study the possibility of using wood pulp fibres as carriers for agriculturally beneficial chemicals. Specifically, we focus on binding and release properties of small organic molecules from wood pulp fibres. The goal is to achieve an understanding of the capability of wood pulp fibres to be used in building biodegradable growing medium blocks in greenhouses.

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Special thanks to my family for being my backbone. To my mom and dad, for their unconditional love and support throughout my life. To Ainaz and Arjang who always encouraged me and by bringing Sam to this world they made it a brighter one for me. To my best friend, Ala, for being with me through thick and thin.

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1.1. Introduction and Literature review

1.1.1. Overview of the Current Practice

The purpose of using mulch is to retain soil moisture, control the soil temperature, reduce nutrient leaching, inhibit weed growth, and hinder pests from crops. Essentially, using mulch enhances the crop yield which contributes to a sustainable agriculture [1, 2]. Mulches allow crops to be grown in a more desirable microenvironment and climate conditions due to their ability to control moisture and temperature [3]. An ideal agricultural mulch would be made of renewable and sustainable materials while it is affordable from manufacturing to disposal. Furthermore, it has to have suitable mechanical properties comparable to that of conventional mulches and maintain functionality throughout the desired lifetime [4]. Currently, polyethylene mulches are very popular due to their excellent strength and performance. However, the high cost of removal and disposal plus their detrimental environmental effects have turned them to an option far from the ideal mulch [5]. It is currently estimated that 6.5 million tons of plastic material is used for the agricultural industry [6]. The growing demand to find an alternative mulching method can provide a profitable market opportunity for a replacement product, specifically a biodegradable mulch. Currently, the development of biodegradable mulches is facing some challenges. For instance, meeting the current standards of strength, affordability, ease of use and stability in the growing season, withstanding storage, application and a suitable degradation rate [7].

In the following sections, the various mulching methods have been introduced and their environmental sustainability is briefly discussed.

1.1.2. Types of Agricultural Mulch

1.1.2.1. Plastic Mulch

Plastic mulch usage in the agricultural industry began around the 1950s with the use of various forms of polyethylene mulching films. They enhance the crop microclimate by modifying the energy balance of the soil. Thus, they affect the growth and yield of the plants. The interactions of plastic mulches with solar radiations directly affects the soil temperature. Hence, depending on the geographical condition, mulches with specific optical properties are used in different fields. Clear and black mulches have shown the best functionality in raising the soil temperature. It is also found that the net radiation in plastic mulches is higher rather than non-plastic mulches [8]. Due to its high robustness, light weight, resiliency, flexibility, and ease of processing, the most common form of plastic mulch is low density polyethylene. Their positive impact on nutrient uptake and root growth is well documented [8, 9].

Polyethylene is an effective mulch as it excels at all of the functionality requirements, however it has many disadvantages as a sustainable agricultural product. After the crop season, removing the plastic residues from the soil is labor intensive. Furthermore, their parts that are exposed to sunlight go under photo-degradation and they break into pieces which make it impossible to fully remove the plastic from the field. On the other hand, leaving them in the soil until the next cultivation cycle leads to irreversible soil contamination. The farming microenvironment will be affected as they can prevent proper root development as well as release harmful phthalic acid esters into the soil [9]. The disposal option includes burning the used plastic mulch uncontrollably which causes emission of harmful by-products into the atmosphere. Recycling the films is not a practical option due to their high degree of contamination with organic compounds and chemical residue after the cultivation cycle [3, 9].

Although plastic mulches have provided exceptional crop yields as opposed to mulched plots, they are harmful to the environment. Therefore, it is imperative to develop a mulching material that is comparable in effectiveness to polyethylene while it is environmentally friendly [10].

1.1.2.2. Biodegradable Mulch

Biodegradable materials are intended to fully degrade after their functional lifetime. They are designed to break down into carbon dioxide, methane, water or biomass by means of microorganisms in the soil [8]. Biodegradable materials are of high interest to the agricultural industry since degradable mulching films would eliminate the labor and disposal costs associated with traditional plastic mulches. Biodegradable mulches should show the required strength, as well as being fully degradable by the subsequent cultivation season. The method through which a biodegradable material decomposes completely is highly environmental dependent. The environmental condition where the mulch would be applied, is unpredictable which makes it a challenge from the aspect of material design. There are many factors such as rainfall, temperature, and the variety of microorganisms in the season. These are the reasons behind susceptibility of the biodegradable mulch to premature degradation. The ultimate success of a biodegradable film would be to develop a product that can relate the rate of degradation to environmental conditions, essentially solving the issue of controlled degradation [11]. Currently available biodegradable agricultural mulches can be summarized as follows.

- Aliphatic polyesters (including petrochemical and agricultural feedstock)
- Natural polymers such as blends with a base of starch, proteins or cellulose derivatives
- Blends of natural polymers and polyesters.

Polymers with hydrolysable backbones such as aliphatic polyesters, polyamides, polyurethanes, polyanhydrides, and polyamide-enamines are susceptible to biodegradation by enzymes, fungi and microorganisms found in agricultural soil. Hence, they are the common type of biodegradable polymer mulches. Polymers with carbon backbones, such as vinyl polymers (e.g. polyvinyl acid), are not generally susceptible to hydrolysis, therefore they require an oxidation reaction to occur in order to degrade. Most of these carbon-backbone polymers contain functional group that is ready for oxidation, the addition of a catalyst can increase the chance of oxidation. Polyvinyl acid is commonly chosen for degradable agricultural mulches due to its alacrity to biodegradation caused by microbial and enzymatic activity [12]. Blends of natural polymers such as starch-based mixtures can be a candidate for agricultural mulch. An adjustable property of starch-based mulches is the use of whole starch as opposed to linear amylose fractions. Whole starch is highly brittle and unstable in contact with moisture, while linear amylose fractions can produce films more similar to polyethylene [13]. However, further research needs to be conducted on improving the tensile strength, elongation and wet strength of the product so it will be comparable in mechanical strength to polyethylene and also not be prone to premature degradation [5].

1.1.2.3. Paper Mulch

Paper mulch is one of the environmentally sustainable alternatives to polyethylene mulches. However, it has shown poor mechanical properties and performance when the paper or pulp is not being used in combination with other polymers. Paper mulches are a favorable option since they originate from renewable resources and are harmless to the agricultural ecosystem. They are typically made from recycled kraft paper or newsprint in order to reduce cost and energy consumption for production [1]. The material is also generally cheaper than most biodegradable polymer materials, yet more expensive than polyethylene [9]. Paper products as agricultural mulch have some advantages over the polyethylene mulches. However, there are some weak points about the conventional paper mulches that need to be addressed when developing an effective biodegradable mulch. One of the biggest issues with paper mulch is their low elasticity and flexibility. Elasticity is important for mulching films as they must fully embrace the crop beds. Furthermore, flexibility is an important factor in case of weed penetration attempt. Paper mulches do not react well with watering cycles as they expand during watering and shrink during drying cycles [14]. The papers are therefore susceptible to get ripped easily which leads to premature degradation. Moreover, the exposure of soil to weed penetration and uncontrolled soil temperature, which essentially renders the mulch to be ineffective [4, 15]. Some paper mulches contain a resin as coating for strength and hydrophobicity. This method has led to inconsistent results which made it unreliable. Furthermore, the addition of oil or resin to the system makes it more difficult to handle. Another key factor about paper mulches is their effective thickness. Paper mulches are not very effective at increasing soil temperature at thicknesses close to conventional plastic films. They require higher thickness to regulate the soil temperature in a comparable way [9]. Additionally, paper mulches are typically two to four fold heavier than plastic mulching films. Thus, transportation costs are higher for paper products [4]. On the other hand, weed suppression showed to be an effective aspect of the paper mulches. They were observed to have equivalent or even more effective weed hindrance than plastic mulches. Shredded paper mulch was the most effective as weeds tend to come through planting holes in the mulch. Hence, the shredded paper was able to minimize exposed soil in the planting holes [9].

In general, paper mulch is not considered as the most effective mulch compared to biodegradable mulches to be a possible alternative for plastic mulch. Although the material is of low cost, the amount that must be applied to the soil to be effective is much more than other types of mulches and this increases cost per area of land [15]. Even with oil or wax coatings the paper mulches remain unstable in expose to changes of environment such as pH, soil coverage over the mulch, and rainfall. Therefore, the degradation rate and effective performance are unpredictable [9].

1.1.3. Properties of Mulches

The performance of mulches varies depending on the geographical location, weather, and the type of crop and soil. In this section a few of the most important properties, namely mechanical and physical, will be outlined. The colour of the mulch is important depending on the pests being deterred, or if weed inhibition or increase of soil temperature is more important. Many studies have focused on the colour of mulches and their effect on performance and yield [16]. Generally, black mulch is more effective for inhibiting weed growth but clear mulch is more effective for increasing soil temperature as it allows more light to transmit to the soil [8]. Pure starch mulching films are too brittle to be solely used. Thus, in order to adjust the properties of starch as a film while maintaining the strength, organic or synthetic degradable polymers can be blended with starch. When discussing starch as an amorphous extruded film product, it exhibits poor mechanical strength at 15% water content, which makes it unsuitable for an agricultural environment. The extruded product at 20% humidity after only a few hours has shown a decreased elongation at break value. The mixture of starch with other polymers would decrease brittleness and increase elasticity [12].

1.1.4. Application Methods of Mulch

The application of mulch on the field can be done through different methods. Current methods are in the form of a film or mat. The product is mixed and developed beforehand, transported to the field and then rolled on the soil either by hand or a machine. The film is then tucked under the soil on the edges to make it stable on the crop bed [7]. Another method of application is spray or foam mulch. Spray technology is available, but few mulches are currently applied using this technique. The method is to have a slurry or pulp suspension in a mixing tank that will be sprayed onto the soil to dry and harden into a film that will stick to and cover the entire crop area [17-19]. One of the materials that is suitable for spray mulch, is in form of a foam slurry which creates an evenly distributed film after application.

1.1.5. Fibre Network Deposition by Foam

Foaming has shown promising results as a carrier phase for fibers. It provides an excellent homogeneity compared to the watery medium. The fibers are separated because of air bubbles; hence, by means of foaming long fibers at high consistency can be handled. The reduced density and the microporous structure as the result of foaming is other advantages of this method [20].

1.1.5.1. Overview of Foam Forming

Foam structure is defined as gas bubbles dispersed in a liquid medium. Based on their air content, foams are categorized into dry foam and wet foam. Generally, foam with an air content of ≥80% is considered as dry foam. While foam with an air content of 40-60% is considered as wet foams. Pure liquids do not have the tendency to create foams; hence, surfactants are used to induce foaming. Surfactants are used because of their unique structure of a hydrophilic head group and hydrophobic tail. There are four types of surfactants that can be used: anionic, cationic, zwitterionic and non- ionic. A popular anionic surfactant is Sodium Dodecyl Sulfate (SDS). SDS is an efficient choice to be used in large scale industries due to its low cost and high functionality [20]. Sheet forming by means of foaming was introduced to paper making industry as early as 1972 [21]. In this method of sheet making, fibers are dispersed homogenously between air bubbles. The foam collapses as vacuum is applied and leaves a consistent fiber network. The drawback of this method is that foaming reduces the fiber network strength. The most common method to introduce air into the water, fiber, surfactant, and other chemicals mixture is to use a mechanical mixer. Various designs of the mixer propeller and the mixing vessel are available to reach the desired air content and bubble size distribution. It should be noted that mixing speed also affects the foam characteristics [22].

1.1.5.2. Properties of Foam Formed Paper

Mechanical properties of the paper sheets are evaluated through measuring tensile strength, compressive testing, and delamination force. The total strength of the sheets depends on both individual fiber strength and the fiber-fiber bonds strength [23].

In order to cover the weakening effect of foaming on the sheet strength without increasing the basis weight of the sheets, a variety of chemicals have been used by researchers. The choice of surfactant and its dose affect the sheet properties. It was found that using an anionic surfactant like SDS resulted in sheets with higher tensile index compared to a non-ionic surfactant like alkyl polyglucoside. Polyvinyl alcohol (PVA) was used as a surfactant as it offers the surfactant properties once the force is applied. The sheets made with PVA dried faster than the ones made with SDS hence it reduced the process time [24]. Studies from Al-qararah *et al.*, Lappalainen *et al.* and Madani *et al.* showed that the tensile index decreases with increasing bulk and surfactant dose [25]. One of the major factors affecting the sheet strength is the mean pore radius of formed sheets. Both foam medium and mixing speed affects the mean pore radius of the sheets. It was found that by increasing the mixing speed the mean pore radius decreases [20]. Madani *et al.* investigated methods to increase the strength of the foam formed paper without pressing. It was found that similar to standard paper, in case of foam formed paper the mechanical failure occurs in the network first. They used the PFI refiner to fibrillate the long fibres without cutting them. Refining the fibers increase the fiber-fiber bonding strength. Hence, the refined pulp fibers lead to a stronger foam paper sheet. They also utilized Valley Beater to beat the fibres to cut them in very short length and form fines. In which, the strength increased by a different mechanism. As the ratio of small fibers to the long ones increase, the bulk decrease and it improves the strength [25, 26].

1.1.5.3. Effective Additives in Fiber Network Formation

Here, a few number of additives that are found to be effective in paper strength improvement are briefly reviewed. Based on the intended final application as agricultural mulch, additives that result in an increase in the inter-fibre bonding are more of interest. We are looking at the possibility of fixing the lack of pressing and heat treatment by using strengthening additives.

1.1.5.3.1. Polyamideamine-epichlorohydrin (PAE)

PAE is a cationic polymer which is widely used to increase wet strength. By creating covalent bonds between 3-hydroxy-azetidinium groups on PAE and the carboxyl groups on the fibers after thermal treatment [27].

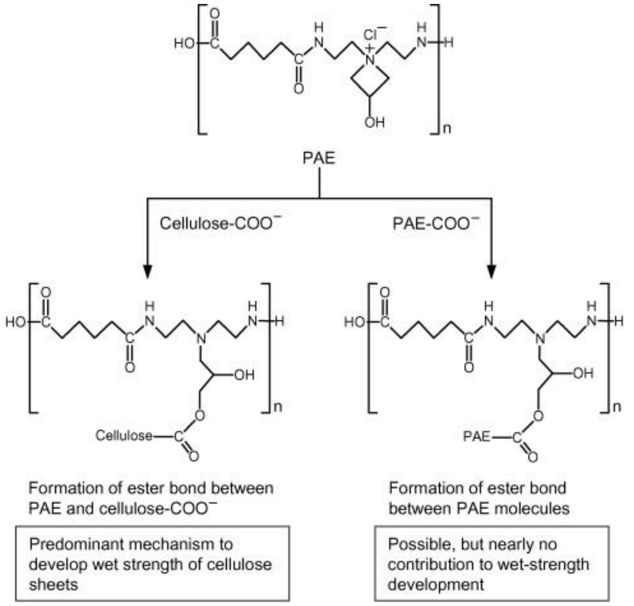


Figure 1.1 Formation of ester bonds between azetidinium groups of PAE and either carboxyl groups of cellulose fibers in sheets or carboxylate groups of PAE molecules [28]

Examples of its industrial use include household paper since it produces good wet strength. PAE does not help with softness of fibers and usually leave dried sheets very coarse and brittle at high concentrations. The common concentration of PAE is 0.1-1% of dry weight of pulp. Molecular weight of PAE is an effective factor in increasing wet strength in paper sheets. The higher the molecular weight, the more PAE contribute to the wet strength development [28]. Pulp fibers with carboxyl groups available on their structure, are able to form more bonds with PAE. Both wet and dry strength found to increase as the result of the formation of covalent bond [29]. Obokata also found that the ester bonds that form between azetidinium groups in PAE and carboxyl groups of cellulose are responsible for wet strength development. Homo-crosslinking in PAE structure as a result of heat treatment, do not contribute to increasing wet strength [28].

1.1.5.3.2. Cationic Starch

Cationic starch is a conventional dry-strength additive that is used widely in the paper industry. High molecular weight starch has been found to work much better than low molecular weight starch due to higher bonding strength [30]. Cationic starch is widely used both as an internal and external additive. Its external or surface sizing use is for the purpose of increasing the paper resistance against liquid penetration. Due to its positive charge, cationic starch bonds with the negatively charged cellulose fiber. This will result in a more surface oriented coating on the fiber network [31].

1.1.5.3.3. Carboxymethyl Cellulose

Carboxymethyl cellulose (CMC) is a water soluble negatively charged cellulose derivative that can be used with a cationic component to form polyelectrolyte multilayers. Cationic starch is the most commonly used cationic substance in combination with CMC. The formation of polyelectrolyte multilayer led to improvement in tensile strength in paper sheets [32]. CMC has also been used in conjunction with PAE to further improve the wet strength of fibers. They form a spherical shape complex which contribute to the wet strength due to its bridging ability [33].

1.1.5.3.4. Gelatin

Gelatin is a mixture of proteins and peptides which is resulted from partial hydrolysis of collagen. The collagen source can be skin, bone, or connective tissues in animal bodies [34]. Gelatin is water soluble and its film forming properties made it a favourable candidate in making foam formed paper sheets. Due to its low cost and availability, it was suggested by researches to form biodegradable polymeric mulch mat on the surface of the soil [35].

1.2. Objective

Here, we are seeking the feasibility of developing a low basis weight paper based material for agricultural mulch application. The distinct characteristic of this material compared to similar biodegradable mulches, would be the low amount of wood pulp fibers. In the previous studies [9] the basis weight of the solid part of the mulch is 60-150g/m^2 which is not feasible to transport and spray on large areas of application. We try to cut down the fiber usage to half of the reported basis weight, 60g/m^2, and report the results. Furthermore, this study tracks the deposition of wood pulp fiber foam network on a porous bed. To determine the functionality of on-site application of paper mulch, the arrangement of wood pulp fibers on sand was investigated.

1.3. Experiments

1.3.1. Materials and Methods

Northern softwood bleached kraft (NSBK) pulp fibers were used in this study. No prior modification was performed on the fibers. Sodium Dodecyl Sulfate (SDS) is an anionic surfactant used for foam making and bought from Sigma Aldrich. Gelatin from bovine skin analytical grade was purchased from Sigma Aldrich. Partially hydrolyzed (88-89%) Polyvinyl Alcohol (PVA) with average molecular weight of 146-186 kDa was purchased from Sigma Aldrich and used as received. Polyamide-epichlorohydrin (PAE) was received under the name of Kymene 5221 provided by Solenis.

A rotary mixer with high speed (maximum speed 7000 RPM) was used to make foam. In cases where other chemicals are used in addition to the foaming agent, they were added to the mixture prior to the foaming agent. A cylinder with three identical baffles inside was provided as the container for mixing. After adding the desired amount of pulp to make 30 g/m^2 sheets of paper, different doses of foaming agent were added to the slurry in sequential trials. Following by 10 minutes mixing of the slurry, the foam was carefully poured on the specific substrate. Samples were dried at room temperature both in presence and absence of vacuum. Buchner funnel with stainless steel 200 mesh wire cloth fritted disc used to apply vacuum filtration.

1.3.1.1. Glass Beads

The first round of trials for fibre network deposition with foam were tested on the uniform 3mm glass beads. The experiment setup is shown in Figure 1.2. Different recipes were used and their appearance characteristics were observed. This setup was useful to measure the drainage time for each recipe and to determine the effect of each ingredient on drainage time.

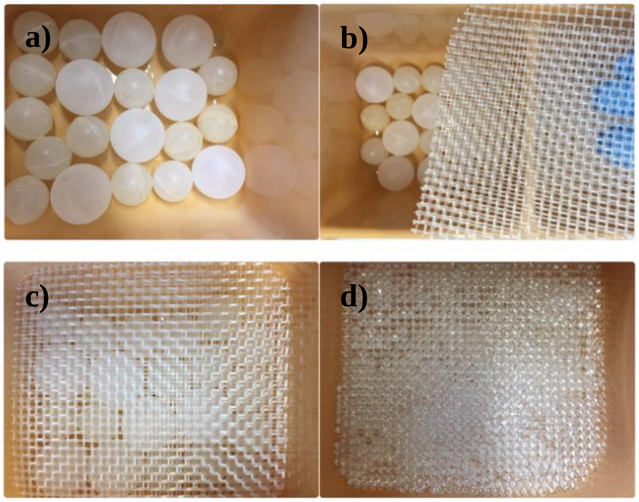


Figure 1.2 The apparatus for foam paper deposition on glass beads, a) the compartment tray is filled with hollow polyethylene balls and c) covered with plastic mesh screen d) on top of screens the 3mm glass beads are placed

Figure 1.3 The fiber network detached from the glass bead bed (5%SDS, 10% gelatin, 30g/m^2)

Although the glass bead substrate is helpful for some preliminary purposes, in order to measure the strength of the fibre network the sheets need to be detached from the substrate. Hence, next trials were performed stainless steel 200 mesh wire cloth.

1.3.1.2. Stainless Steel Wire Cloth

The setup for this section of experiments contains the wire cloth screen, Buchner funnel, and a vacuum pump. The fibre slurry was made separately and deposited on the wire cloth, vacuum was applied to accelerate the drainage. The target basis weight of the sheets was 30g/m^2 and the rotation speed for foam making was chosen to be 4500 RPM.

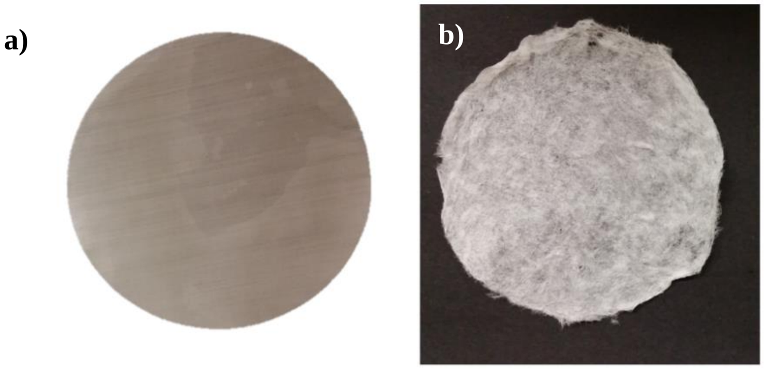


Figure 1.4 a) a circular wire cloth, b) the peeled foam paper made on the wore cloth after drainage on the Buchner funnel under mild vacuum

The effect of using PVA as foaming agent, cationic starch as dry strength additive, and gelatin as a film forming additive was investigated. Several recipes were used and the fibre networks were detached for further testing. The challenge in this part was peeling the fragile foam network after drying from wire cloth. Sheet making started with using SDS as foaming agent. Due to the negative of foam forming method on sheet strength, it was not possible to peel the samples with more than 5% SDS. When PVA was used as the foaming agent, the sheets were not as fragile as in case of SDS and much higher percentages were investigated.

1.3.1.3. Coarse and Fine Sand

Based on the particle size, sand is classified in four categories and it is shown in Table 1.1. Two types of sand were used in this set of experiments, one is "desert sand" which is considered as fine sand and the other type "pool filter sand" and its particle size falls in the range of coarse sand. They were used to mock the porous bed for mulch application. Microscopic pictures were taken using SWIFT M5 optical microscope, with 100X magnification.

Table 1.1 Sand type classification based on particle size [36]

Type of sand	Average diameter of the particles
Very Fine Sand	0.05-0.1 mm
Fine Sand	0.1-0.25 mm
Coarse Sand	0.5-1.00 mm
Very Coarse Sand	1.00-2.00 mm

1.4. Results and Analysis

1.4.1. Foam on Glass Beads

Experiments that were performed using glass bead apparatus did not result in quantitative data. Observations from this section of experiments helped us recognize the important ingredients in foam stability and the foam behavior upon changing each of them. It was found that by increasing the surfactant a more stable foam is resulted and a more uniform arrangement of fibers on the glass bead bed. What's more, using gelatin resulted in more stable foam even at low SDS dose.

1.4.2. Paper Making on Wire Cloth

Sheets were collected from foam paper made on wire cloth and their tensile strength were measured. By, increasing the foaming agent percentage a more uniform fibre network was developed. However, the weakening effect of surfactant on the sheets was severe and it was not possible to peel the sheets for tensile strength test when the SDS dose was higher than 5%. When the foaming agent switched to PVA, much higher doses were explored and results are presented here.

Tensile index of PVA foam formed sheets are plotted in Figure 1.5, the drop in strength is observed as expected. However, the weakening effect of PVA is not as significant as SDS reported in literature [20]. It should be noted that here the basis weight of the fiber network is 30g/m^2 which is one third of the amount used in earlier works.

The effect of PAE addition on tensile index values was investigated and compared with samples with no PAE in Figure 1.6. As it is presented in the graph, PAE significantly improved the weakening effect of foaming. Results show that when using 1% PAE, by increasing the foaming agent dose, tensile index increases. This is favorable from the application perspective since foaming improves the uniformity of the fiber network after deposition.

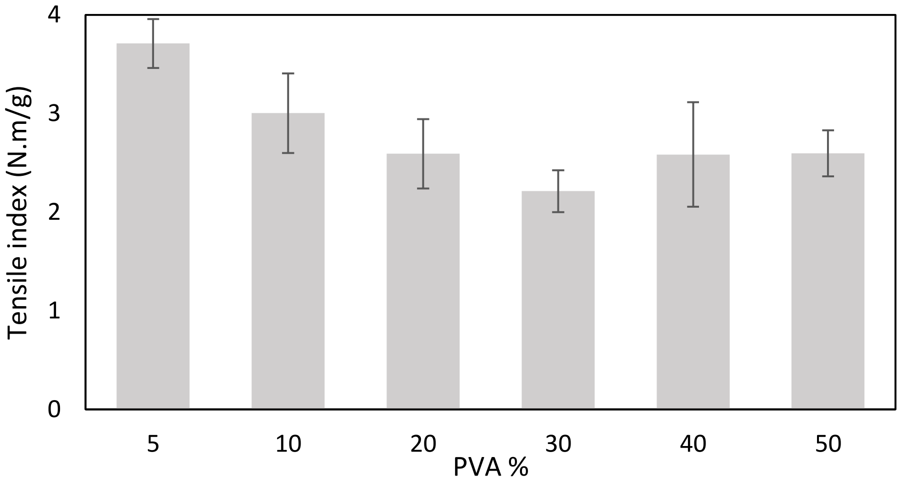


Figure 1.5 Tensile index of sheets with increasing dose of PVA as foaming agent, target basis weight of sheets is 30g/m^2, standard deviation from average was calculated from multiple strips cut from the sheet

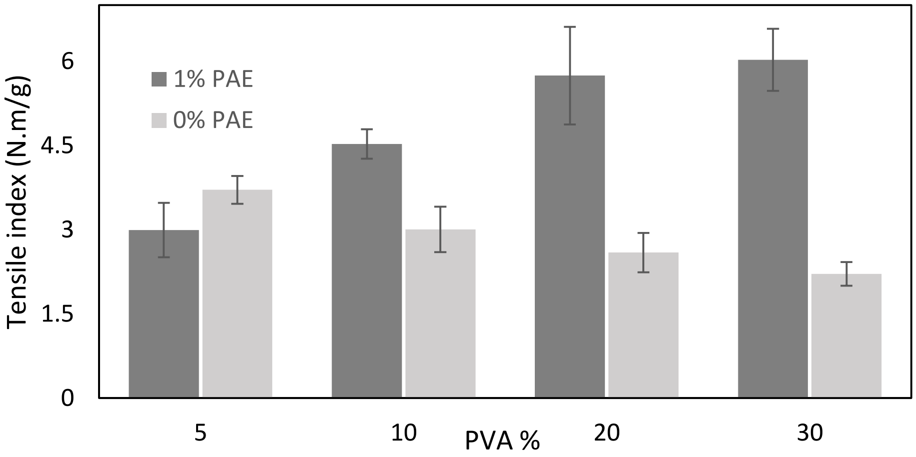


Figure 1.6 Effect of 1% PAE on sheet samples while increasing PVA as foaming agent at target basis weight of 30g/m^2, standard deviation from average was calculated from multiple strips cut from the sheet

The addition of gelatin resulted in an increased tensile index at constant dose of SDS. Cationic starch has also shown to be effective in combination with gelatin when using

SDS as foaming agent. Data provided in Table 1.2 depict the strength improvement in foam formed sheets at the same basis weight by changing the recipe.

Table 1.2 Summary of the samples recipe, comparison of their tensile index and errors for sheets at target basis weight of 30g/m^2, standard deviation from average was calculated from multiple strips cut from the sheet

Recipe	**Tensile Index (N.m/g)**	
	Mean value	**Error**
5% SDS	2.55	0.21
5% PVA	4.28	0.29
5% SDS, 5% gelatin	3.82	0.65
5% SDS, 12.5% gelatin, 40% Starch	5.66	0.50
30% PVA, 1% PAE	6.02	0.55

At 5% dose of foaming agent, tensile index for the PVA-made sample is approximately 70% higher than when SDS is used. Furthermore, the addition of gelatin and cationic starch led to stronger sheets although SDS was used as the foaming agent.

1.4.3. Foam Forming on Sand

After pouring the foam slurry on top of the sand, a two phase system was constructed. fibres were divided in two separate phases, and upper layer of foam and fibres and the watery phase that included fibres as well. The fibers in watery phase formed the first layer of sheet structure on the sand. It normally took 2-7 minutes for drainage to complete depending on the foaming agent dose and type of chemicals. The fact that fibres existed in both phases suggest that foam is only capable of holding a certain amount of fibres in its structure of air bubbles and water.

By increasing the foaming agent dosage, 5-20% of dry pulp weight, more stable foam structure was produced followed by a longer drainage time. Type of the foaming agent was also effective in this matter, increasing the percentage of PVA had more contribution in foam stability compared to SDS. The addition of gelatin combined with SDS showed improvement in foam stability and also in keeping the 3D structure of fibres after the drainage was completed. After samples were dried and the fibre network peeled off the surface, samples made with PVA included a thicker layer of sand compared to SDS made samples. Using gelatin as the foam stabilizer agent resulted in forming a thin layer of flexible gelatin film engaging cellulose fibres. Furthermore, the addition of cationic starch resulted in a more uniform placement of fibres within the network. For a limited number of samples, vacuum force was applied for drainage. The effect of using vacuum appeared in the adhesion between sand surface layer and the paper sheet. Fiber layer detached easier and the layer of fibres peeled off with lower amount of sand attached to it compared to the air drying. Another effective factor is the sand particle size. Sand particle size affected the amount of sand that stuck to the fibre layer, larger particles are heavy and fibres could not include as many particles in their structure as they did in smaller sand particle size.

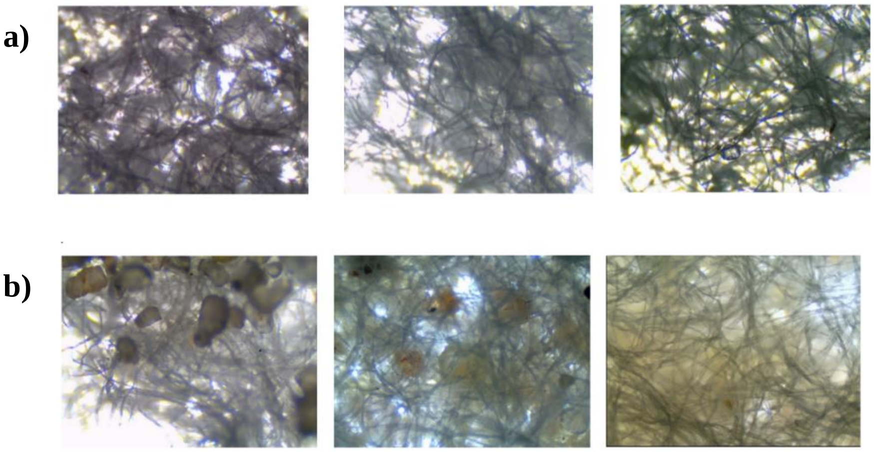


Figure 1.7 Fibre network formed on **a)** Coarse sand and **b)** fine sand, ×100 magnification, target basis weight is 30g/m^2

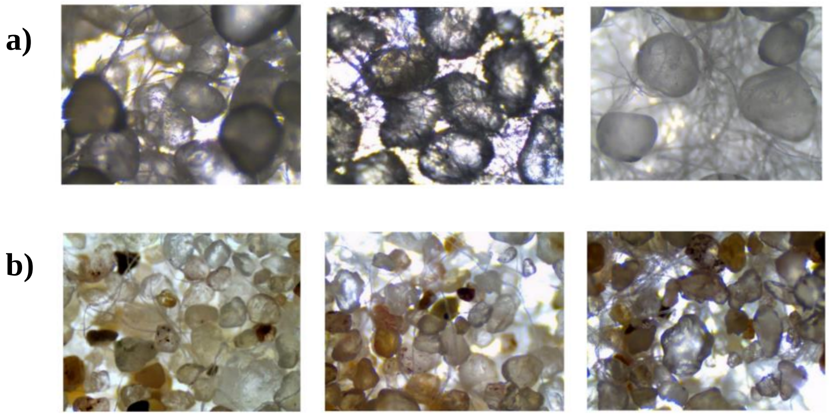


Figure 1.8 Sandy side of the fiber-sand network with **a)** Coarse sand and **b)** fine sand, ×100 magnification, target basis weight is 30g/m^2

Fibre flocculation is an undesirable phenomenon in conventional papermaking that is controlled through a variety of methods. However, here in this application, increased flocculation is an asset to have an engaged network of fibres. Accelerating the drainage of the liquid phase by applying vacuum, addition of gelatin and cationic starch, and switching to PVA as foaming agent are expected to affect the flocculation of fibres in different ways.

Generally, in a typical experiment of paper making on sand, an effective factor in fibre formation on the surface of sand is assumed to be fibre flocculation. The addition of gelatin leads to the formation of a gelatinous layer on fibres which reduces the friction between fibres. Hence, less fibre flocs are formed and the fibrous network is more evenly formed. On the other hand, using cationic starch encourages the formation of fibre flocs by neutralizing the surface charge of fibres. Furthermore, cationic starch tends to improve the inter fibre bonding by increasing the bonding area. Thus, cationic starch alters the fibre network structure in two different ways.

Using vacuum to force a faster drainage and drying, led to decrease in flocculation. Thus, the appearance of fibre network on sand was different and less fibre flocs were formed. The adhesion between the fibre layer and sand surface was decreased since the fibre engagement was lower compared to air drying.

1.4.4. Drawback of Foam Forming Method

Although some results from the previous section are promising, the method that was being used to deposit the fibre network on different substrates is not efficient from the water consumption aspect. A very dilute slurry (0.1%) was used in all the experiments in order to reach desirable foam properties. This method of application requires 0.6 L water for a surface area as small as 0.027 m^2. Scale up of this method for a 1hectare farm field, leads to the required volume of approximately 222 m^3 water. Transportation of this mass of slurry is not viable with available agricultural equipment. Furthermore, it is not an economically and environmentally sustainable method.

1.5. Conclusions

1. Increasing the foaming agent dose reduces the inter fibre bonding in the network which leads to loss of mechanical strength. However, PVA as foaming agent showed less weakening effect compared to SDS. This can be correlated with the high molecular weight of PVA which contributes to the sheet strength.

2. The low basis weight fiber network showed satisfactory values of tensile strength compared with literature. This means that choosing the chemicals plays a vital role in the final properties. Here, PAE and gelatin are shown to have a positive impact on maintaining the strength in the foam formed fibre network.

3. Fibrous network on sand deposited by foam showed the engagement of sand particles with the network. Changing the recipe affected the flocculation of fibres, which determined the appearance of fibre network on the porous bed of sand particles.

4. A scale-up calculation for this particular method of application with low basis weight, showed the requirement of an enormous volume of water. Spray application of this volume of fibre slurry is labor intensive and its high energy cost makes it an inefficient method.

2. **Chapter Two:** Cellulose fibers as Medium for Plant Growth

2.1. Introduction and Literature Review

2.1.1. Plant growth medium

Soilless culture or hydroponic is a popular trend in greenhouse agriculture. Hydroponic can be defined as the process of growing plants without soil in substrates that are made of a supporting material flooded with nutrient solutions. This method has enabled farmers to: reach the maximum yields, grow crops where there is no suitable soil, and reduce the labor for traditional cultivation practices. Different types of medium have replaced soil for crop production in greenhouses. Rockwool is known to be the most widely used growing medium in hydroponic for growing pepper, cucumber and tomato [37]. Rockwool, sometimes referred to as stonewool, is named after a fibrous form of material that is originated from mineral rocks. The mineral fibers are prepared by molten Basaltic rocks at 1500-2000˚C that is spun to form single filament fibres. The fibres are then pressed to from loosely woven sheets which are used to form rockwool slabs. Rockwool has some advantages over other similar materials that are used for crop production. Due to the high temperature of rockwool manufacture, they are essentially sterilized and have shown to be chemically and biologically inert. Because of the nature of the process, a very consistent product is resulted. Furthermore, it is feasible to keep the air to water ratio at the optimum amount by freely watering and draining the rockwool. In addition to the mentioned benefits, using rockwool is economically efficient [38]. Rockwool has excellent water holding capacity which is a determining factor in choosing the growing substrate [39]. There are water absorbent and water repellent types of rockwool and a mixture of them can be used when preparing the blocks for plant growth. Based on the type of plant and growing conditions, rockwool is used with different density, porosity, and fiber orientation [38]. In this method of production, the root-zone nutrient concentration as well as the leaching fraction has to be carefully controlled for crop cultivation. Nutrient shortage or fertilizer accumulation are both harmful to the plant root and should be avoided. In case of using rockwool, the high water-holding capacity of rockwool leads to a less frequent irrigation. Thus, the water soluble fertilizers are applied less and the run-off decreases. In order to prevent a shortage of nutrient from happening, the dose of fertilizer is increased in each irrigation [40].

The disadvantage of using rockwool is its harmful environmental impact. There is no sustainable second usage for this material and also no environmentally safe method to dispose this material. After usage, the rockwool block is too contaminated to be used for another cultivation cycle. It is also not possible to burn or destroy this type of material, hence their disposal is turning into a major problem [38].

In the current research work, wood pulp fibres are treated and modified to be used as a potential replacement for rockwool. The biodegradable cellulose fibres are environmentally friendly and they are from renewable sources. Also the unique structure of wood pulp fibre is favorable for treatment with agriculturally beneficial materials and high water holding capacity.

2.1.2. Wood Pulp Fiber Structure

Wood cell structure can be explained as a composite of micro-fibrils in a matrix of hemicelluloses and lignin. The 3-4 nm diameter cellulosic micro-fibrils gather together to make 20-25 nm diameter components called cellulose fibrils or aggregates [41]. A closer look to the cell wall of the fiber in wood system, reveals its layered structure centered around the cell wall axis. The outer layer, called middle lamella, is mostly made of lignin marked as “M” in the schematic Figure 2.1. It is because of this layer that individual fibers are glued to each other within the wood structure. The Primary wall (P), contains micro-fibrils arranged in a crisscross pattern. The secondary layer is called S and contains three individual layers within itself, shown as S_1, S_2, and S_3. They are slightly different in chemical composition but have distinct variety in micro-fibrils placement angles. The lignin concentration is the highest in S_1 layer. In both softwood and hardwood cell wall structure, the S_2 layer is usually the thickest layer and forms the major part of the cell wall. The mentioned three layers are mostly used to describe the arrangement of the cellulose fiber wall layers. The hollow part in the centre of the fibre structure is called lumen. It is observed that the lumen part is occasionally coated by a watery layer. Although the described 3-ply model is very popular to describe the structure, cellulose fiber originated from different sources has distinct micro-fibril arrangements in addition to molecular composition. Meaning that, there is a variety of cellulose, hemicellulose and lignin distribution within the fiber wall [42]. Removal of lignin from the middle lamella occurs as the wood pulp is chemically processed. As a result, fibers separate from each other and gain flexibility. There are different chemical modifications that deliver higher flexibility to the fibers. For instance, if hemicelluloses are partly removed as well as lignin, a porous structure of fiber wall will be created. Moreover, cellulose fibrils aggregates separate upon processing [43]. It is for these reasons that the resulted fiber structure after removal of lignin, hemicellulose, xylan, and glucomannan appears in different patterns.

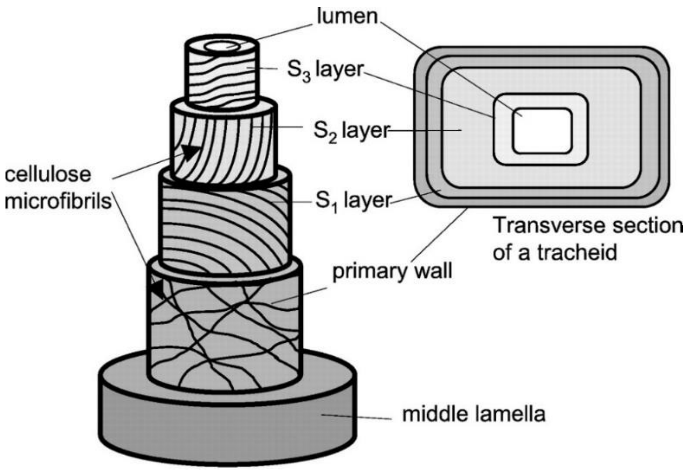


Figure 2.1 Representation of cellulose fibre wall three layer structure [44]

Another way of picturing the structure is called multi-lamellar system in which the swelling degree of the fiber determines the number of lamellae. The lamellas separate upon fiber swelling, and collapse on each other once they are dried [45]. It is stated that fibers become more flexible with the presence of water in their pores [43].

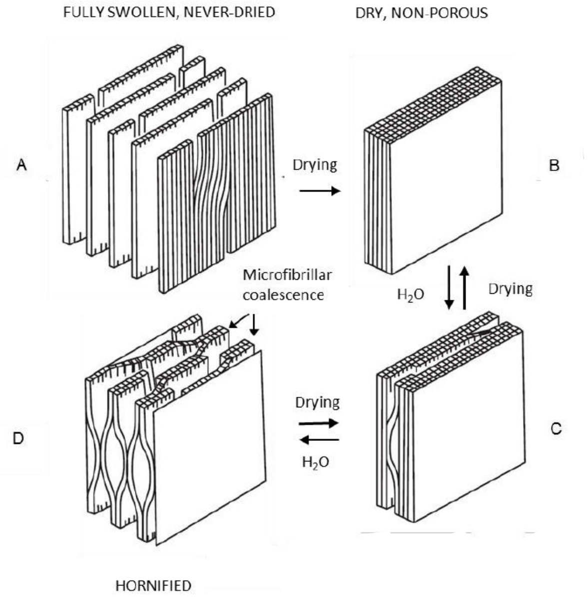


Figure 2.2 Fibre wall fibrillation upon swelling [46]

2.1.3. Specific Surface Area and Pore Size Distribution

The void volume in native cellulose fiber wall before chemical refinery is approximately 0.02 cm^3/g. As a result of wood pulp chemical treatment the voids could expand and increase to 30 times of its initial volume per gram (0.6 cm^3/g) [47]. NMR relaxation method was used to estimate the average pore radius in fiber wall. The average pore size for unbleached softwood kraft pulp fiber is around 65 Å while after bleaching the pulp this number increases to 100 Å [48]. The NMR method is used based on an important assumption that there are two types of water molecules within the fiber structure. The bound water which is affected by the fiber surface and also the free water molecules in the pores with the same properties of the bulk water. Figure 2.3 is a figure of the pore and water inside the pore [45].

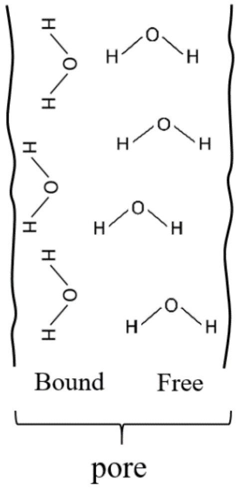


Figure 2.3 Representation of the principle behind NMR method to determine the pore size, there is a fast exchange between the states of bound and free water, regenerated from reference [49]

Hornification is a phenomenon that describes the changes that occur to cellulose fibers upon drying or water removal. It states that pores in the fiber wall collapse as a result of drying; thus, after rewetting it will not recover to the original status. Also, the fibrils join in flat ribbons after drying and packing the wood pulp fiber [50]. The water that absorbed in hydrophilic materials is divided in three different categories where each of them demonstrates a specific thermodynamic behavior. Hence, Differential Scanning Calorimetry (DSC) was used to investigate the changes occur to pore size distribution of fiber wall after drying. The results depict an average pore size of 800 Å at moisture ratios higher than 0.8 g/g which declines to a constant number of 200 Å at moisture ratio less than 0.3 g/g [51].

Pore size is important since it affects the removal and penetration of molecules, water uptake of the fiber, swelling, and flexibility of the fiber [48]. Therefore, it is crucial to have a deep understanding of fiber porous structure in order to predict its behavior. Additionally, the fiber type and the moisture ratio should be taken into consideration when discussing the fiber porous structure.

2.1.4. Chemical Composition of Wood Pulp Fiber

Cellulose is a linear polymer from polysaccharide family, which is made of β-D-glucopyronose units that are attached via β-1.4 glycoside bonds [52]. The repeating unit of cellulose consists of primary and secondary hydroxyl groups as in methylol and hydroxyl respectively.

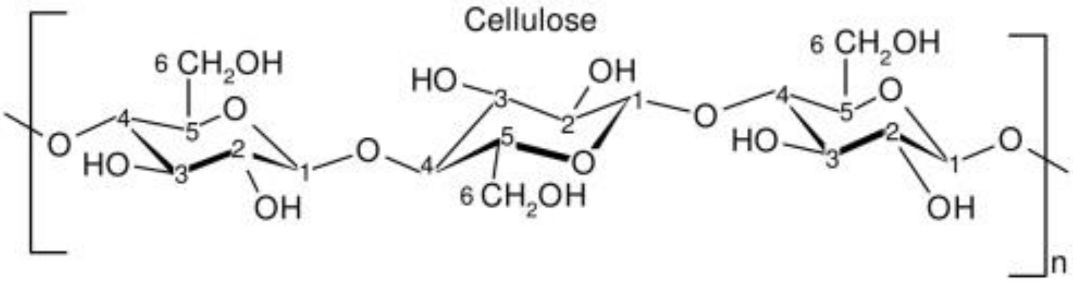


Figure 2.4 Schematic figure of cellulose molecular structure [53]

Primary hydroxyl locates at C6 and secondary hydroxyl at C3 and C4 in the cellulose molecular structure. Hydrogen bonds between cellulose chains and the Van der Waals forces between glucose units has made the semi-crystalline structure of cellulose [54]. Depending on the pH of the pulp suspension, pulp source and the method that through which fibers have been processed, they have different electrically charged surface groups. For instance, carboxyl, sulfonate and phenol groups [55]. The only available charged groups in native wood are carboxyl groups which are mostly originated from 4-O-methyl-D-glucuronic acid that is bound to xylan. However, lignin and pectin materials may contain some carboxyl groups as well [56].

2.1.5. Swelling of fibers

Fibers in an aqueous environment can be explained as cellulosic gels, in which acid groups are attached to the network of cellulose macromolecules. Carboxyl groups are the most common acid group covalently bound to the both surface and bulk of the cellulose fiber. As a result of presence of charged components, the counter ions in the solution remain in the porous fiber rather being available in the surrounding medium. Due to the osmotic effect, water is carried inside the pores of the fiber, hence swelling happens. This phenomenon continues to the point that the difference in osmotic pressure counterbalances the cohesive force inside the network. Important factors that mostly contribute to the degree of swelling are the number of acid groups, the dissociation degree, and the surface charge density of the fiber [56].

2.1.6. The Effect of Modifications on Cellulose Fiber

The influence of fibre modifications that were performed in current research study will be discussed in this section. The resulted chemical groups on the fiber surface and how the fiber wall is affected by those modifications will be briefly reviewed.

2.1.6.1. TEMPO mediated oxidation

TEMPO-mediated oxidation reaction is a highly selective oxidation reaction that is performed on cellulose for two general purposes: introduction of active groups like aldehyde and carboxyl groups [57] and generation of nanocellulose [58]. The reaction mechanism is shown in the Figure 1.4. By addition of NaClO, as co-oxidant, reaction is started in presence of TEMPO and catalytic amounts of NaBr at pH 10-11. The primary hydroxyl groups convert to carboxyl groups via C6 aldehyde groups by consuming NaOH and NaClO [57].

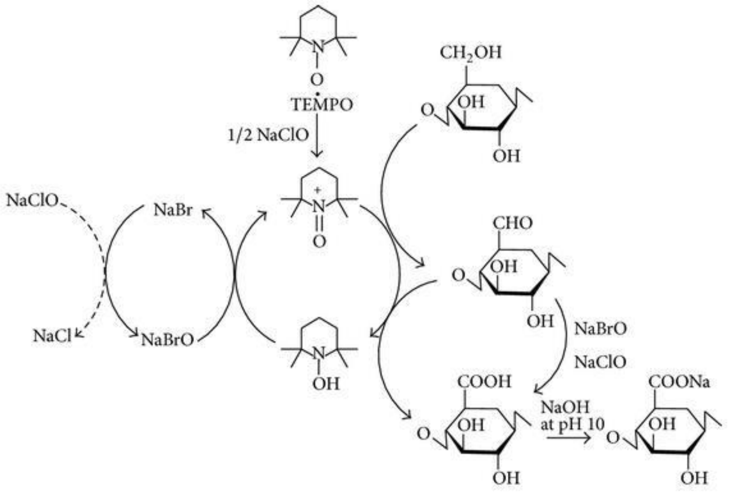


Figure 2.5 Schematic figure of the cellulose oxidation reaction by TEMPO/NaClO/NaBr [59]

The formation of inter-fibril hydrogen bonds is prevented by introduction of aldehyde and carboxyl groups. Hence, fibrils become separated from each other as a result of TEMPO-mediated oxidation[58]. Moreover, TEMPO-mediated oxidation results in formation of fine particles and fibrillation of long fibers; thus affects the whole surface area. By increasing the time of reaction, more short fragments are formed [60]. In current work, TEMPO-mediated oxidation has been utilized to increase the surface chemical activity and also the porosity in the fiber wall.

2.1.6.2. Carboxymethyl cellulose modification

Carboxymethyl cellulose (CMC) is a cellulose derivative that is used in several applications such as food industry and detergent production. In laundering application, CMC prevents the dirt to redeposit on the cotton substrate. There is no evidence of adsorption of CMC on cellulosic surfaces in absence of electrolyte. However, studies show a record of CMC adsorption on the cellulose fiber that is possibly irreversible by electrolytes. The topo-chemical modification of cellulose fiber with CMC was investigated by Laine *et al.* in 2000. It has been found that CMC with low degree of substitution adsorbs better on cellulose fibre. Furthermore, temperature has a significant effect on the adsorption. It is suggested in the literature [61] that the reason behind the irreversible adsorption is the potential co-crystallisation of CMC and cellulose fibers at high temperature [62]. The unsubstituted segments of the CMC chain, form hydrogen bond with the cellulose fiber surface. However, the repulsion between negative charge of CMC and cellulose leads the CMC chain to have a very expanded conformation on the cellulose surface. It is expected that an extra amount of water after CMC attachment is trapped in this layer. Increased temperature in the process causes a bigger part of segment attached to the fiber, hence the extra layer is compressed [29].

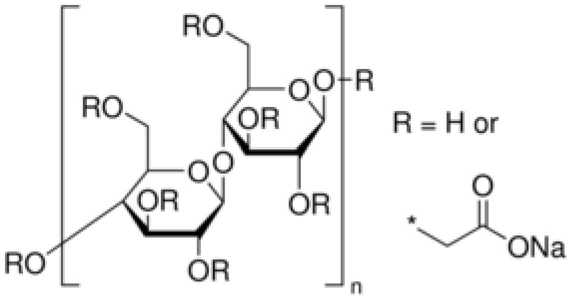


Figure 2.6 Schematic figure of carboxymethyl cellulose sodium salt molecular structure [63]

2.1.7. Cellulosic Substrates as Adsorbents

Use of cellulosic substrate for waste water treatment purposes has been widely reported in literature. There are numerous studies on removing heavy metal ions from waste water by modifying the cellulosic substrate. Also, few studies have covered the removal of pollutant organic compounds from waste water [64]. The BET surface area, and pore volume and diameter of different cellulosic adsorbent have been compared in literature. Low number of active sites on the fiber leads to a very low adsorption capacity of cellulose compared to common materials that are used in waste water treatment such as active carbon [64]. It is through variety of methods of modification that researchers have been able to develop the cellulose based adsorbent with high adsorption capacity. The modification methods are divided in two main categories: grafting of monomers and direct chemical modification [54]. In the grafting method, the resulted material is a branched copolymer in which the side chains are covalently attached to the main backbone. Monomer grafting on cellulose can be performed in heterogeneous medium in which a water soluble initiator is needed. Also, it can be conducted as in homogeneous grafting where a water soluble derivative of cellulose is used or cellulose is dissolved in a proper solvent. In a homogeneous medium, the number of grafts per cellulose chain is higher [65]. The most popular functional groups that have been used for monomer grafting on cellulose have been discussed in literature and is summarized in the Figure 2.7 [66].

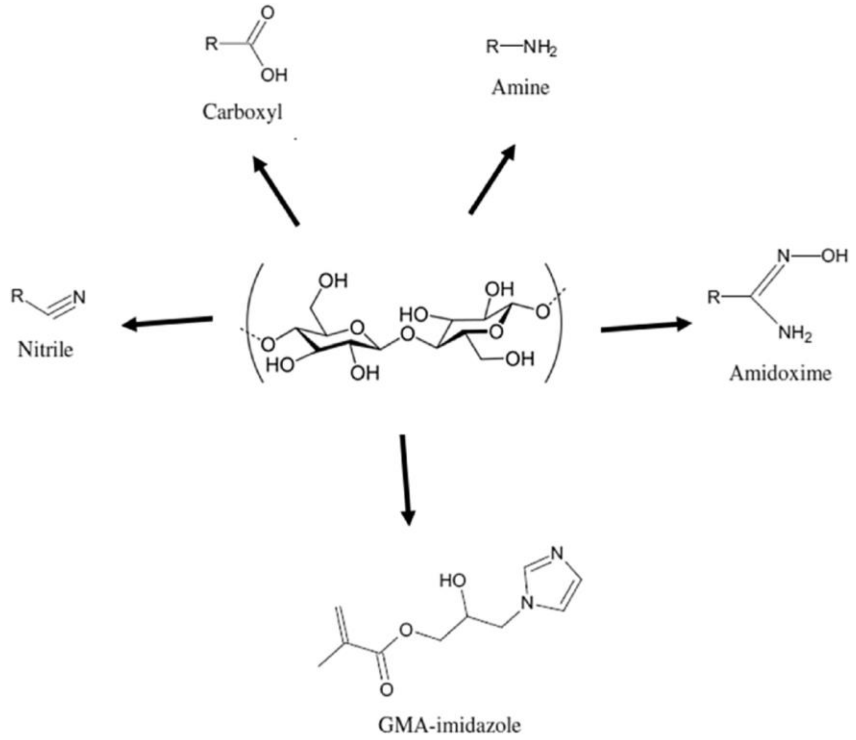


Figure 2.7 Functional groups on grafted cellulose with good adsorption properties [66]

Mainly, the routes for direct chemical modification are through alkali treatment, halogenations, etherification, esterification, and oxidation. Each of the methods has a different effect on surface area, pore volume, and surface activity. Therefore, based on the target compound in waste-water the modification is tailored [54].

2.1.8. Adsorption of Organic Compounds on Cellulose Fibre

Alila *et al.* have studied cellulosic substrate as absorbent for capturing organic molecules from waste water. Adsorption of a wide range of organic molecules has been investigated in their study [64]. It is stated that the primary physical forces affecting the adsorption process are as follows: hydrophobicity, Van der Waals, steric interaction, polarity, dipole induced dipole interaction, and hydrogen bonds. The pollutants are accumulated on the surface of adsorbent by the mentioned forces in physical adsorption [54]. It was found that chemically modifying cellulose surface increases the sorption capacity. For instance, adsorption of cationic surfactants and grafting hydrocarbon chains have been utilized to modify the cellulosic surface. The modified cellulosic compound was able to capture the target organic compound. Results are explained by the fact that accumulation of surfactant hydrophobic tails creates a hydrophobic domain in which, the organic compounds will trap [64, 67, 68]. Research has been done to investigate the adsorption driving force of the pollutant. In a study on adsorption of polycyclic aromatic hydrocarbons it was found that adsorption of these compounds is strongly correlated with their octanol-water partition coefficient [69]. Adversely, this finding is argued by Alila *et al.* who claimed the adsorption capacity is independent of the organic compound hydrophobicity characteristic. They explained that studying hydrophobicity is not enough to predict the adsorption behavior. They also measured the thermodynamic parameters for adsorption of Nitrobenzene on modified cellulose substrate. At all the tested temperatures, the sorption process was known to be spontaneous. Moreover, the negative amount for enthalpy changes showed that it was an exothermic process and also, it is driven by polar Van der Waals interactions [64]. A variety of different sorption mechanisms were found to be involved in cellulose-based absorbents. Surface physical adsorption, micro precipitation, ion-exchange, complexation, and adsorption-complexation onto pores and surface have been shown to drive the sorption [54].

The final application in the reviewed studies involves the common aspect of waste-water treatment. However, current research work is aiming for the usage of cellulose fibers as carriers for agriculturally beneficial compounds. Meaning that, this research work is investigating the possibilities of temporary adsorption of agrochemicals for further release.

2.1.9. Models for Experimental Adsorption Data

The phenomenon that occurs when a substance retains, releases, or moves from an aquatic environment to a solid substrate at a given pH and temperature can be described by adsorption isotherm curve. It is based on thermodynamic presumptions and combined with physiochemical parameters, an adsorption isotherm yields an understanding of the adsorption mechanism. Several equilibrium isotherm models have been developed over the years [70]. Three of them are introduced in the following sections and will be used to explain the further results.

2.1.9.1. Langmuir isotherm model

A fundamental model based on the assumption that there is a fixed number of identical adsorption sites on the substrate. The adsorption sites are considered to have equal affinity towards the adsorbent molecules. Furthermore, it assumes that no lateral interactions happen between adsorbed molecules on the substrate [71]. The adsorption is described to be monolayer so there is a saturation point which beyond that, no additional adsorption will take place [70]. The non-linear form of Langmuir isotherm model is presented in Equation 1.1. C_e represents the concentration at equilibrium (mg/L) and q_e is the corresponding capacity (mg/g). Also, q_m is the theoretical adsorption capacity and K_L is related the Langmuir isotherm constant (L/mg) [72].

$$q_e = q_m k_L \frac{C_e}{1 + k_L C_e}$$

(Equation 2.1)

Separation factor (R_L) has been defined to reflect the adsorption favourability (Equation 1.2). If $0<R_L<1$ it describes a favourable adsorption. For $R_L=0$ and $R_L=1$ the adsorption is irreversible and linear respectively. Plus, if this dimensionless constant is higher than one the adsorption is unfavourable [73].

$$R_L = \frac{1}{1 + k_L C_0}$$

(Equation 2.2)

2.1.9.2. Freundlich isotherm model

Freundlich model describes the non-ideal, reversible, and possibly multilayer adsorption. This empirical model is applied for heterogeneous surfaces in which the stronger sites are covered first with the molecules [70]. In this equation there are two adjustable parameters, K_F (mg/g)(L/g)^n is related to adsorption capacity and *n* represents adsorption intensity [72].

$$q_e = K_F C_e^{1/n}$$

(Equation 2.3)

2.1.9.3. Dubinin-Radushkevich isotherm model

Dubinin-Radushkevich model originally was developed to describe the pore filling mechanism of vapor adsorption on a microporous solids [72]. It is based on the Polanyi potential theory of adsorption. The assumption behind this theory describes the adsorbed layer as a thick film that decreases in density as the distance from the solid surface increases [74].

$$q_e = q_s \exp(-k_{DR}\varepsilon^2)$$

(Equation 2.4)

$$\varepsilon = RT \ln\left[1 + \frac{1}{C_e}\right]$$

(Equation 2.5)

In which, q_s (mg/g) is the adsorption capacity and K_{DR} (mol^2/KJ^2) is the adsorption constant correlated with mean free energy of adsorption. R(J/molK) is the gas constant and T(K) is temperature. The mean free energy of adsorption can be calculated from the equation below [70]. Based on the mean energy equation, the adsorption constant has to be a positive amount.

$$E = \left(\frac{1}{\sqrt{2k_{DR}}}\right)$$

(Equation 2.6)

2.2. Objectives

In current research work, the binding and release properties of agriculturally beneficial materials as a function of fibre surface modification is studied. Wood pulp fibres are modified and their adsorption characteristics of two different organic compounds are studied. Ultimately, cellulose fibres will be utilised in soilless culture in greenhouse farming as a substrate for growing medium. Wood pulp fibres are proposed as an alternative for currently used rockwool in greenhouse agriculture. Studying the adsorption properties of agriculturally important small molecule compounds will help us to have an understanding of wood pulp cellulose fibre as the growing medium.

2.3. Experiments

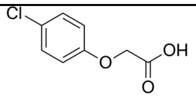
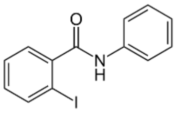
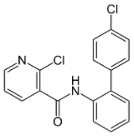
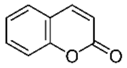
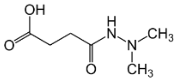
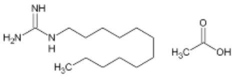
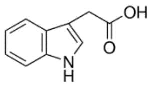
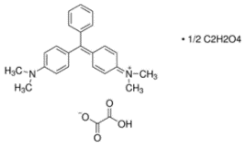
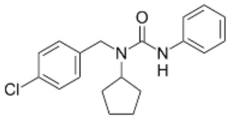
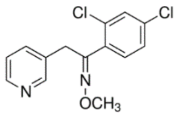
2.3.1. Choice of the Adsorbing Compound

In order to fulfill the objectives of this research project, the agrochemicals or the representative molecules that are used in experiments must be water soluble, capable of being adsorbed through roots of the plant, feasible to identify with common characterization methods like UV/visible light spectroscopy and safe to handle and work with in the laboratory environment. It is preferred that the selected chemicals have a potential affinity towards cellulose fiber surface.

2.3.2. Materials

Softwood Bleached Kraft ECF90, (SBK) and unbleached softwood kraft pulp (UBK) were provided by Canfor pulp products. The fiber length was 2.4-2.6 for both types of pulp. TEMPO, free radical 98% and NaBr were purchased from Sigma Aldrich and used as received. TEMPO was stored in fridge upon arrival. NaClO was purchased in a form of 1.92M solution from Sigma Aldrich and stored in the fridge upon arrival. Carboxymethyl cellulose (CMC) used in this study was Mw 250 kDa with DS 0.9 and was supplied by Sigma Aldrich. Water type 1 (as per ASTM D1193-6, resistivity 18MΩ/cm) were used in all experiments. 4-Chlorophenoxy acetic acid (4-CPA) with molecular weight of 186.59 g/mol purchased from Sigma Aldrich and used as received. Malachite green oxalate salt (MG) was purchased from Sigma Aldrich and used as stored in fridge upon arrival. Also, Table 2.1 presents a list of possible candidates to be used as agrochemicals.

Table 2.1 Possible agrochemicals for use in plant growth medium experiments

Name	**Category**	**Structure**
4-CPA	Auxin, plant growth regulator/herbicid	
Benodanil	Benzanilide fungicide	
Boscalid	Pyridine fungicide	
Coumarin	Natural occurring pesticide	
Daminozide	Plant growth regulator	
Dodine	Aliphatic nitrogen fungicide	
Indole acetic acid	Auxin plant hormone	
Malachite Green	Cationic dye, antibacterial in aquaculture	
Pencycuron	Urea fungicide	
Pyrifenox	Pyridine fungicide	

2.3.3. Fiber Modification

2.3.3.1. Pulp pre-treatment

Pulp samples usually contain a variety of different small particles remaining from the original wood sample, called primary fines. Whereas secondary fines come from the remains of extensive mechanical treatments that have been performed on the wood pulp. Fines are known to have much higher specific surface area than fibers because of their smaller size. Furthermore, they are more swollen compared to the fibers in a similar condition. Hence, the organic solutes dissolved in water has a high tendency to adsorb on the particles [75]. This property of fines fraction in wood pulp may lead them to adsorb water-dissolved organic molecules which can be misleading in this research study. Furthermore, there are metal ions adsorbed on the fibers which likely cover potential sites for organic molecule adsorption. Therefore, before using the fibers in any tests or performing any kind of chemical modification fibers were washed and pretreated. However, in order to investigate the effect of presence of fines fractions in the pulp, first set of experiments have been performed on the unwashed fibers.

The washing stage was done with 3 liters of deionized water while stirring with fibers in the dynamic drainage jar with 76µm pore size screen. Usually the last filtrate contains a very low percentage of fines and fractions as it was noticeable by naked eye. Based on the Laine *et al.* work and their method for removal of adsorbed ions on cellulose fibers, fibers were washed with 0.01 M HCl for 30 minutes. To bring the fibers from their “H-form” to “Na-form” the third stage of washing was performed with 0.001 M $NaHCO_3$ at pH 9 [62].

2.3.3.2. TEMPO mediate oxidation

Pretreated SBK was dispersed in deionized water (25 g of pulp in 4 L water). 60 mg of TEMPO was added to the mixture following by 600 mg of NaBr. The slurry was stirred for 30 minutes to fully dissolve in the suspension. The amount of 0.0175 mol NaClO was added to the slurry to start the reaction under continuous stirring. While the pH was maintained at 10.5 for 60 minutes. After the reaction is completed 50 mL of 95% Ethanol was added to quench the reaction. The fibers were retrieved and washed several times to remove the excess ions to the filtrate conductivity of ~10 µS/cm.

2.3.3.3. CMC modification

20 g of pretreated SBK was added to 400 mL deionized water. Carboxymethyl cellulose sodium salt was dissolved at 10 g/L concentration previously and 100 mL of the solution was added to the pulp suspension. In this method of modification, 50 mg of CMC is used per gram of fiber. 40 mL of $CaCl_2$ solution at 1M concentration was added in as the electrolyte solution. The pH was set to 8 under continuous stirring. The total volume of the suspension was set to 800 mL, making the final concentration of $CaCl_2$ to be 50 mM. the slurry was left in the oil bath at 95°C under slow stirring for 2hours. The fibers were retrieved and washed several times to remove the excess ions to the filtrate conductivity of ~10 µS/cm.

2.3.4. Charge Density Determination

The carboxyl content of fibres was determined following the SCAN-CM65:02 method of conductormetric titration of wood pulp fibres. This method is published in 2002 by Scandinavian pulp, paper and board testing committee. Based on this method, the weak acidic group content of fibres is estimated and is correlated to the carboxyl groups present on cellulose fibre surface. Here the wood pulp fibres are titrated with sodium hydroxide before and after modification.

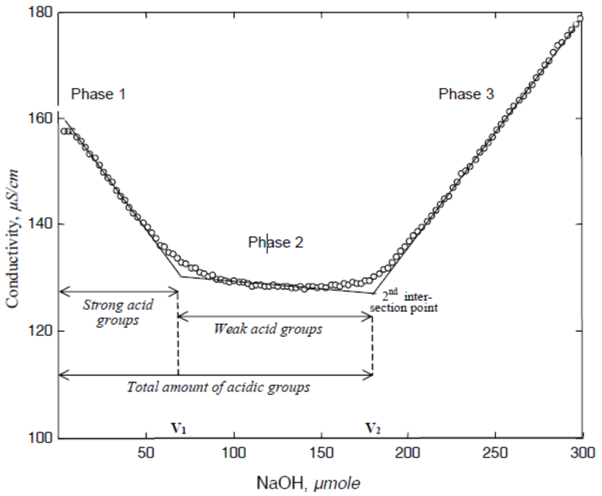


Figure 2.8 An example of titration curve of CTMP fibres obtained from method SCAN-CM65:02. The difference between v_1 and v_2 is used to determine carboxyl content.

2.3.5. Water Retention Value

The maximum capacity of fibers to retain water in their wall is estimated by Water Retention Value (WRV) test [76]. The centrifugation technique following TAPPI useful methods 256 [77] with a small alteration in the testing equipment.

$$\mathrm{WRV\%} = \frac{mass\ of\ centrifuged\ pulp(g) - mass\ of\ dry\ pulp\ (g)}{mass\ of\ dry\ pulp\ (g)} \times 100$$

(Equation 2.7)

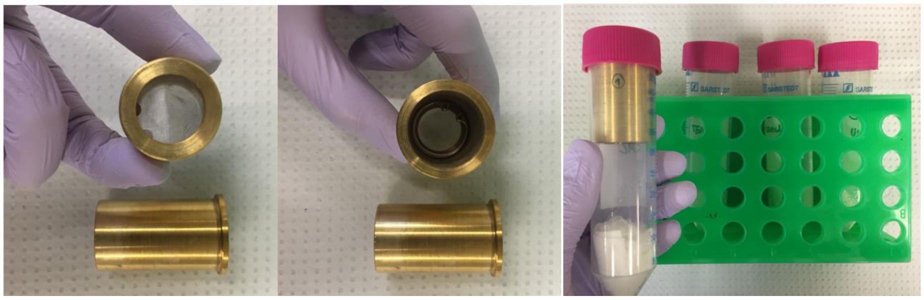


Figure 2.9 Sample holder and centrifuge tubes used for WRV test

Here, a metal sample holder with 200 mesh screen fitted at the bottom (Figure 2.9) is used instead of the glass filtering crucible that is mentioned in the method. The sample holders are redesigned in a way that they are usable with conventional 50 mL centrifuge Falcon tubes. However, the caps that are used to keep the tube and sample holder closed are originally used for centrifuge tubes with built-in membranes. The blotting papers are located at the bottom of the centrifuge tube to collect excess water while centrifuge. The centrifuge was done exactly following the TAPPI method.

2.3.6. Adsorption Test Method

4-Chlorophenoxy acetic acid (4-CPA) was used to make the stock solution with Milipore water at 500 mg/L. It was left overnight for mixing to make sure it is fully dissolved 4-CPA water solubility is 957 mg/L [78].

For all of the adsorption tests, a solution of 5 mM NaCl was used as electrolyte and adsorption medium. The 4-CPA solution in desired concentrations were prepared from the stock solution using the formula $C_1 \cdot v_1 = C_2 \cdot v_2$ in which C_1 and C_2 (mg/L) are the initial concentration of 4-CPA in sample solutions and the stock solution concentration respectively. Also, v_1 is the volume of the sample solution which in all of the adsorption it is equal to 50 mL. The amount of stock solution needed to make the samples is introduced by $v_2(mL)$. The initial concentration of sample solutions is shown as C_0 in calculations and the final concentration of sample is indicated as C_e. The amount of 4-CPA adsorbed per unit weight of fibers at equilibrium is shown with q_e(mg/g) and is calculated as shown in Equation 2.8.

$$q_e = (C_0 - C_e) \cdot \frac{v}{w}$$

(Equation 2.8)

In which, v is the volume of the sample in mL and w is the weight of fiber that is used in $gram$. Samples were prepared in disposable 50 mL plastic beakers prior to being transferred to the centrifuge tubes. From the prepared pulp stored in the fridge at around 10% dry content, 0.25 g of dry fiber is weighed in the beakers (approximately 2.5 g of wet pulp). Each of the sample solutions was prepared separately in a 50 mL graduated cylinder by mixing a volume of v_2 mg/L from the 4-CPA stock solution plus a volume of $[50 - v_2]$ (mL) from 5 mM NaCl solution. Next, the solution was transferred to beaker in which a small stirrer bar was used to mix the fiber suspension. The pH of mixtures was set and for each sample an approximate 15 minutes of equilibrium time is needed. The pH changing rate was tracked accordingly, in some cases longer time was needed for the mixture to reach equilibrium. Sodium Hydroxide and Hydrochloric Acid were used for pH setting.

2.3.6.1. Determination of sample concentration

After 2 hours of mixing fibers with 4-CPA solutions in a tube holder rotary equipment in $23 \pm 2\ ^{\circ}$C, tubes were collected. Centrifugation method was used to separate fibers from the solution for 10-15 minutes at 3000-3500 RPM at $23 \pm 2^{\circ}$C, After fiber separation, 10 mL of the supernatant was collected with disposable 10 mL pipettes. Samples were transferred to separate sample holders for further measurements. A quartz cuvette was used for measuring the light absorption intensity of supernatant between 250-320 nm wavelength in spectrophotometer. The characteristic peak of 4-CPA happens around 277nm and was used to identify 4-CPA in solutions. With its absorption at 278 nm it is considered as an UV-active molecule [79].

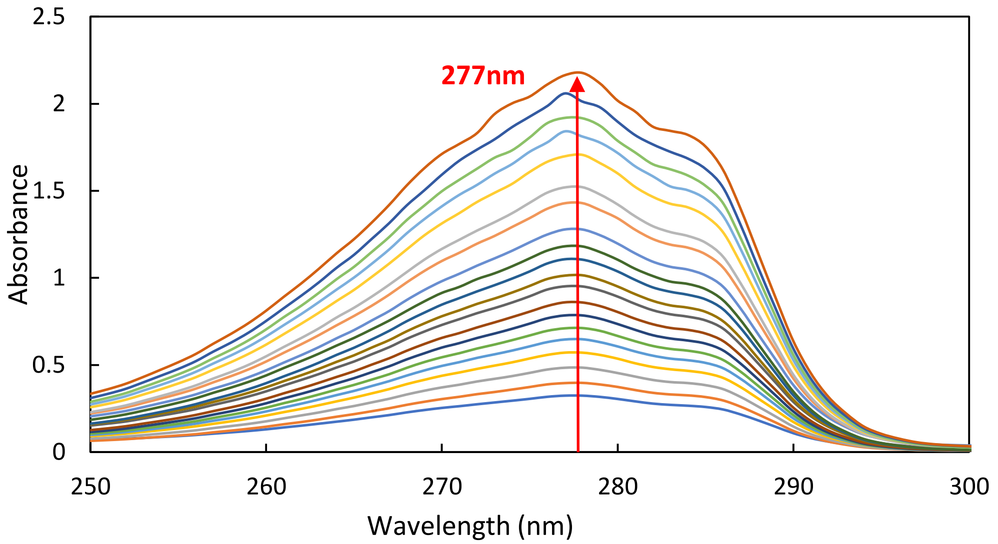


Figure 2.10 Absorbance curve of 4-CPA solution at different concentrations obtained from UV/Visible spectrophotometer, the red arrow shows the characteristic peak of 4-CPA

A calibration curve was plotted based on the known concentrations of 4-CPA and their correlated absorbance intensity. The linear equation shown in the figure was used to calculate the unknown concentration (C_e) of samples after the adsorption test. Also, the molar extinction coefficient was calculated according to the Beer's Law [80], equals to 1176.3 $M^{-1}cm^{-1}$.

$$A = \varepsilon . C$$

(Equation 2.9)

In which, A is absorbance, Ɛ is molar extinction coefficient ($M^{-1}cm^{-}1$) and C is concentration (mg/L).

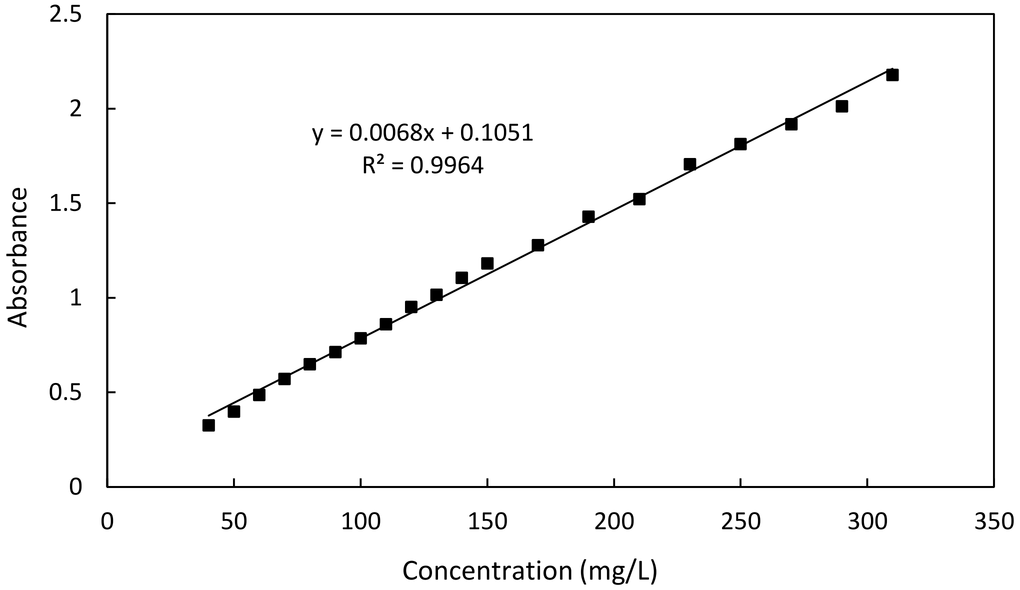


Figure 2.11 Linear calibration curve plotted based on 4-CPA solution with known concentrations

2.3.6.2. Filtration

In order to retrieve the fibers from adsorption tubes after the measurement, 70 µm pore size cell strainer caps were used. In order to confirm the calculated concentrations from centrifuge method, the filtrate was used for UV absorbance measurements.

2.3.7. Desorption Test Method of Malachite Green

The collected fibres from adsorption test were used to investigate the reversibility of MG adsorption on fibres. In order to measure the amount of MG released from fibres, a medium of 5 mM NaCl at pH~7 was used. Fibres were rotated in total volume of 50 mL of the solution at 23 ±2 °C for 120 minutes. Centrifuge was used to separate the fibres from supernatant and then the concentration of MG was measured. The reported numbers in results section is the ratio of released MG to the initially adsorbed amount.

2.4. Results and Analysis

2.4.1. Fiber Charge Density

The electrostatic surface charge density of fibers was determined by conductometric titration method. The TEMPO-oxidized fibers have the highest charge density as expected.

Table 2.2 Carboxyl group content on different fibers used in the adsorption study, the standard deviation from average is calculated based on numbers obtained from repeated experiments

Type of pulp	Carboxyl group content (μmol/g)
CMC-modified SBK	67±3
TEMPO-oxidized SBK	180±21
UBK	49±3
Unmodified SBK	57±5

2.4.2. Water Retention Value

As it is shown in the table below, the CMC modified fibers have the highest percentage of water retention. This was expected due to the effect of CMC modification on fibers mentioned before. TEMPO modified fibers also shows a high WRV number, which can be related to the excess pores that are created in the fiber structure. Unmodified SBK and unmodified unbleached pulp have the lowest WRV consequently. Thus, modification has altered the fibre water holding capacity which is correlated with the increased fibre swelling.

Table 2.3 Water Retention Value of different fibers used in adsorption studies and the reported number in literature, the standard deviation from averaged calculated from repetitive measurements of WRV%

Type of pulp	WRV (%)	Average WRV in literature
CMC-modified SBK	198±5	205[29]
TEMPO-oxidized SBK	189±2	150[60]
Unmodified SBK	156±3	136[29]
UBK	152±8	120[81]

2.4.3. Adsorption of 4-CPA on Fibers with no Pre-treatments

Initially, 4-Cholorophenoxy acetic acid (4-CPA) with water solubility of 957 mg/L in water was used to perform adsorption experiments.

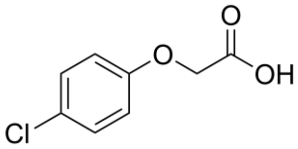


Figure 2.12 4-CPA molecular structure, obtained from the supplier website (Sigma Aldrich)

The first set of experiments was performed on fibers with no pre-treatment. Results from this batch of fibers show that the presence of fines and fractions in the wood pulp affects the consistency of the final adsorbed amount. This test has been repeated multiple times to ensure the accuracy of data and determine the error. Below in Figure 2.13, the adsorption curve for unmodified fibres is presented. A wide range of initial concentration of 4-CPA is covered. For the ill-defined adsorbent surfaces like the un-treated, unmodified wood pulp fibers the results are expected to lack enough accuracy and reproducibility.

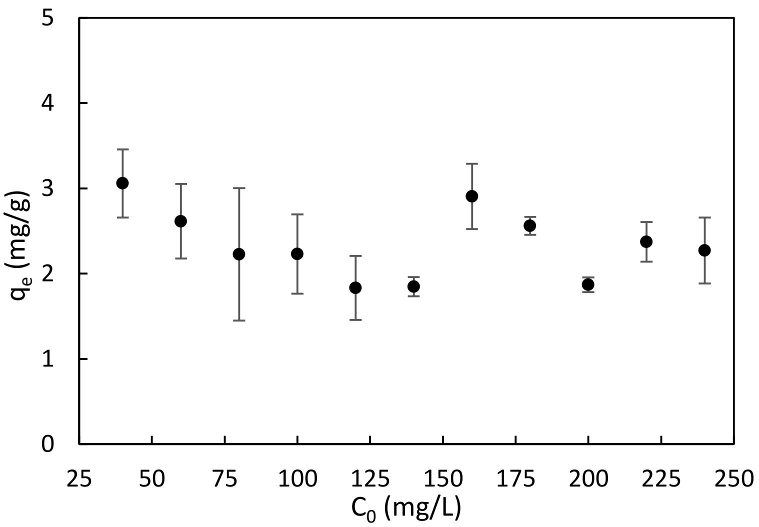


Figure 2.13 Adsorption of 4-CPA on unmodified SBK at pH [3.3- 4.8], experiment performed in 5mM NaCl as electrolyte solution, standard deviation from average generated from multiple measurements of supernatant

The initial pH for the samples were in the range of [3.3- 4.8] due to the acidic properties of 4-CPA by increasing the concentration, the acidity increased.

The following graph in Figure 2.14, shows the adsorption data of 4-CPA on fibers at high pH. Where fibers are at a high swollen state due to their negative charges originated from carboxylic groups on surface and the bulk of the fiber. Furthermore, the pores are expected to be widely open because of the swelling effect. As it is shown in the figure the amount of 4-CPA adsorbed on fibers is close to the unmodified state.

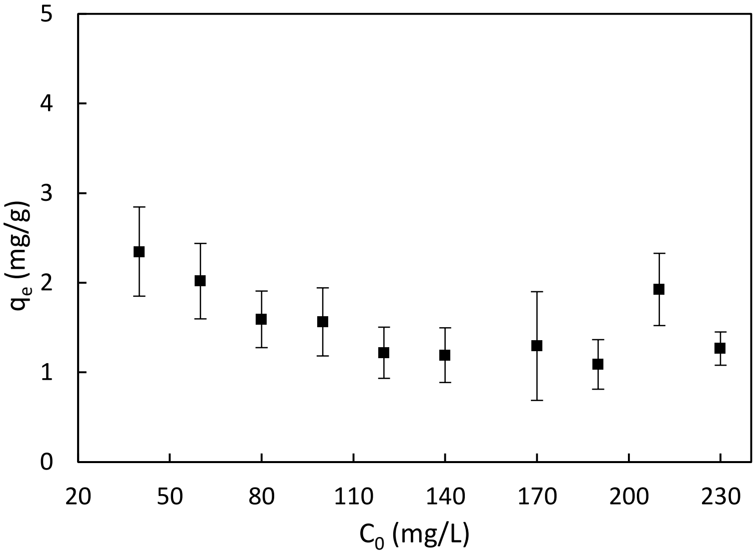


Figure 2.14 4-CPA adsorption on unmodified SBK at pH ~10 in 5mM NaCl solution, standard deviation from average generated from multiple measurements of supernatant

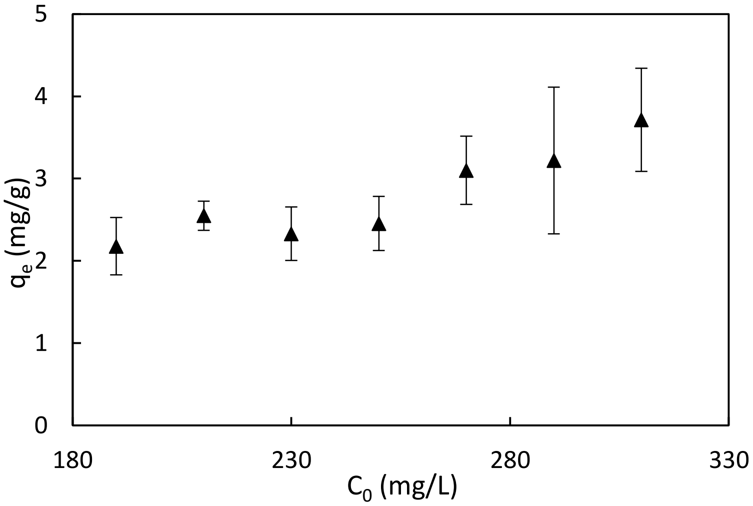


Figure 2.15 4-CPA adsorption on TEMPO-oxidized SBK at pH ~ 10 and 5mM NaCl concentration, standard deviation from average generated from multiple measurements of supernatant

The effect of TEMPO oxidization on the adsorption was investigated. 4-CPA initial concentration of 190-310 mg/L and the initial pH of 10 on TEMPO oxidized fibers with no pre-treatment. The plot in Figure 2.15 shows the data collected for this experiment. The combination of TEMPO oxidation and high pH is expected to result in higher adsorption of 4-CPA. Moreover, a higher range of initial concentration was selected. As it is demonstrated in the Figure 2.15, the general trend is increasing. This indicates that TEMPO oxidation had a positive effect on adsorption. However, the standard deviation from the average increases at high concentrations. Furthermore, after the adsorption, the pH measurements showed a decrease from 10 to ~ 6 which might be the result of an ion exchange in solution which resulted in $[OH]^-$ reduction.

Although most of the experiments with untreated fibers resulted in uncertain series of data points, a few of the trials resulted in an adsorption isotherm that follows the linear Langmuir model for adsorption ($r^2 > 0.94$).

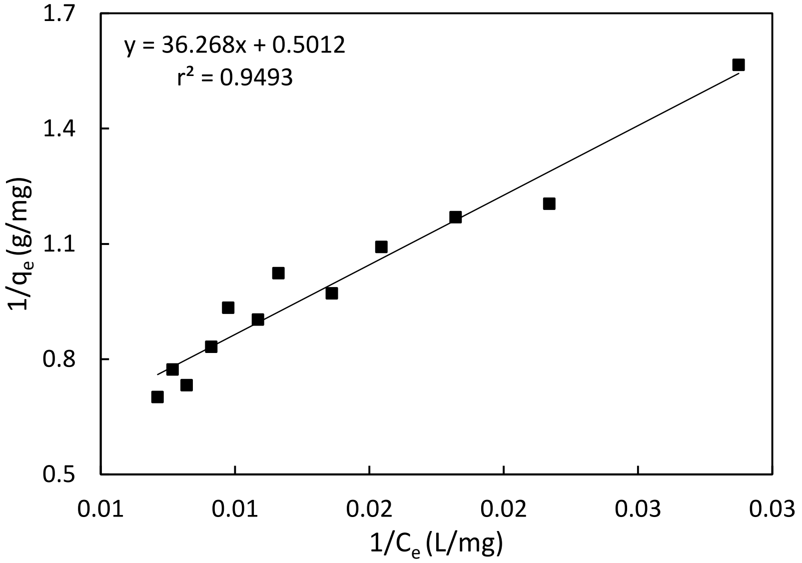


Figure 2.16 Linear Langmuir isotherm model fitted to 4-CPA adsorption data on TEMPO modified SBK at 4.5< pH< 5.8 and 5mM NaCl concentration

From the calculations, the Langmuir constants are q_{mon}=2 mg/g and K_L=0.0138 L/mg. These numbers suggest that the adsorption capacity of TEMPO modified fibers at the mentioned range of pH is 2 milligrams of 4-CPA per gram of fibers. Although this data series from fibers without pre-treatment seems satisfactory, the large deviation from the average remains as an issue. Due to the previously mentioned possible effects of fines fractions, next series of adsorption tests are all done with fibers that have been pretreated with the mentioned method in experimental section prior to any modification.

2.4.4. Adsorption of 4-CPA on Pre-treated Fibers

The second part of the experiment results is related to the pretreated batches of fibers. High concentrations of 4-CPA were used in the following adsorption test to reach the saturation point. The following graph in Figure 2.17 shows the comparison between different pulp fibers at neutral pH in the range of initial concentration same as previous.

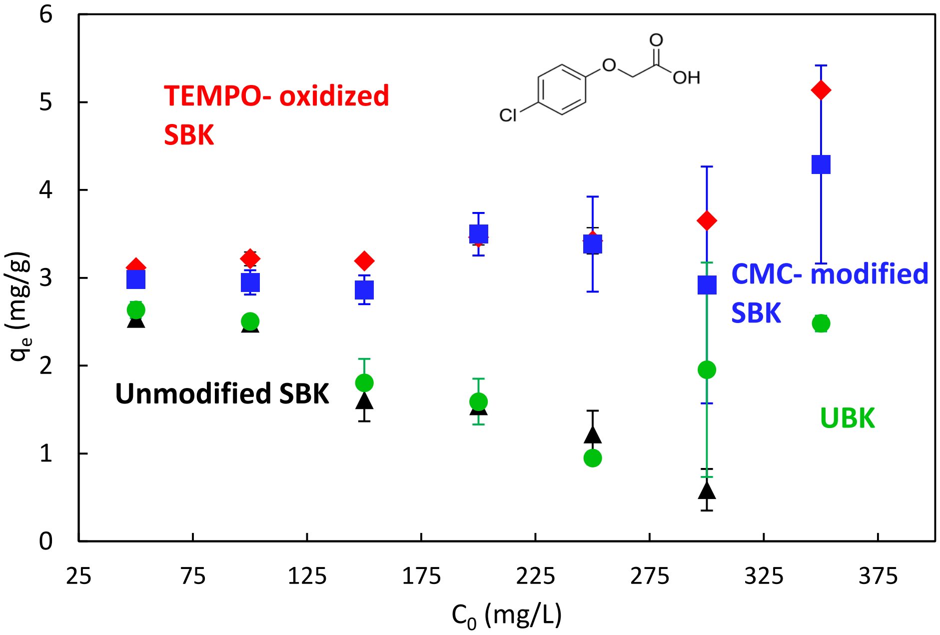


Figure 2.17 4-CPA adsorption on pretreated and modified and unmodified SBK and pretrested and unmodified UBK at pH ~7 and 5mM NaCl concentration, standard deviation from average generated from multiple measurements of supernatant

The first characteristic feature of this adsorption isotherm compared to the not pretreated fibers adsorption results is that the deviation from average is much lower. This means that the standard error that is calculated based on repetitive measurements has been decreased by performing pre-treatment. Fines and fractions that are remained from the initial wood material, and chemical pulping process, and they are under 76 µm were removed by pre-treatment. Their small dimension, high specific surface area, and their high degree of swelling make them a desirable target for adsorption of small molecules. This results show that the presence of fines and fractions in the fibre slurry causes inconsistency in the adsorption data. TEMPO-oxidized and CMC-modified fibers seem to have the highest adsorption capacity among the other fiber types. These results align with the hypothesis about porosity and swelling ratio increment by fiber modification. Also, the WRV numbers confirm that swelling plays an important role (Figure 2.18).

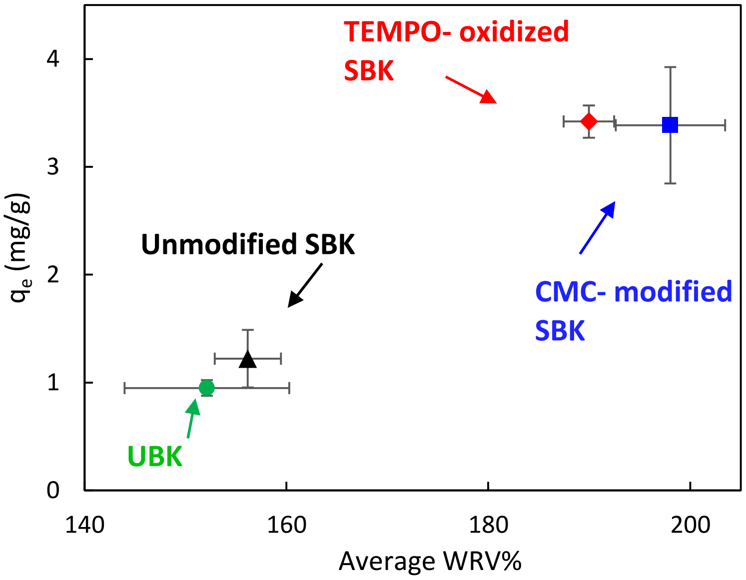


Figure 2.18 4-CPA adsorption at C_0=250 mg/L on pretreated and modified and unmodified SBK and pretrested and unmodified UBK at pH ~7 and 5mM NaCl concentration as a function of average WRV%

Furthermore, Figure 2.17 shows that unmodified SBK have the lowest capacity and unbleached pulp shows a slightly higher numbers compared to bleached pulp. The latter can be in correlation with the presence of several hydrophobic groups on the unbleached pulp and the tendency of 4-CPA molecules to adsorb on them. The effect of modification on pulp fibers is clearly the increment in the adsorbed amount of 4-CPA up to 5 mg/g.

2.4.4.1. The effect of pH on adsorption capacity

Adsorption test was performed for at different pH values for fiber types at a certain concentration (50mg/L). Results of the adsorption test is plotted in Figure 2.19.

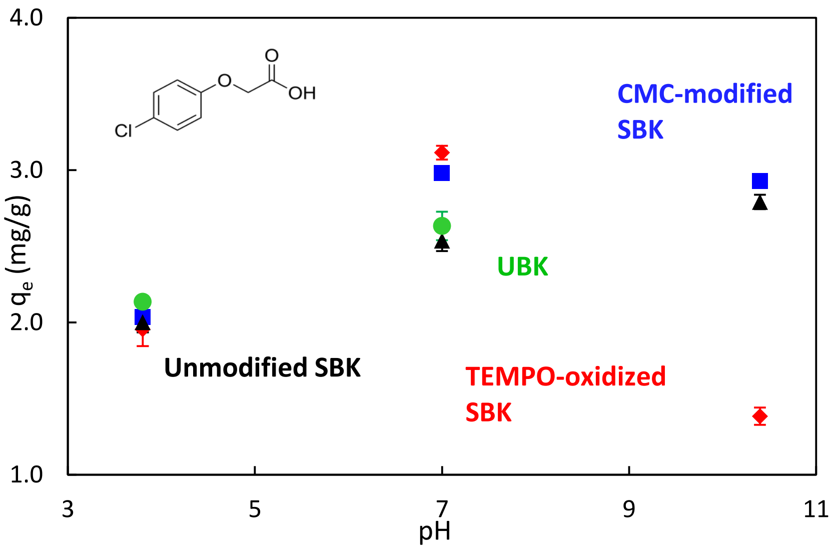


Figure 2.19 Changes in 4-CPA adsorption capacity at different pH values, initial 4-CPA concentration equals to 50mg/L, in 5mM NaCl concentration

From what is shown in the graph, pH variations do not affect the adsorption on CMC-SBK and unmodified SBK in a great extent. The difference between lowest and highest amount of adsorption for both unmodified SBK and CMC-modified SBK is ~0.5 mg/g. The reason behind that is the low charge density of unmodified SBK moderates the fibre swelling sensitivity towards pH variations. However, for CMC-modified SBK there is an increase in adsorption when pH changes from 3.5 to ~7. This can be correlated with the higher charge density of CMC-modified SBK compared to the unmodified SBK. TEMPO-oxidized fibers in contrast, show a great degree of sensitivity towards pH changes due to their high charge density. The sharp decrease in adsorption at high pH is attributed to the increased negativity of the surface and also the 4-CPA molecule. Hence the electrostatic repulsion between the adsorbent and the 4-CPA molecules prevent the adsorption. The UBK and unmodified SBK follow a similar trend except for the highest pH point. At this point, measurements show an increase in UBK capacity of 4-CPA adsorption. There is a possibility that UBK fibres release phenolic compounds under pH as high as 10.4. These compounds can interfere with the light absorption of 4-CPA. Due to this difficulty with the analytical chemistry the expected trend is shown with dashed line. It is expected that at high pH where the phenol groups on the surface of UBK are negatively charged, the adsorption of negatively charged 4-CPA declines.

2.4.4.2. The effect of suspension ionic strength

Adsorption experiment was also performed at four different NaCl concentration, i.e different ionic strength. From what is shown in the graph in Figure 2.20, it seems that at the highest NaCl concentration (100 mM) the amount of adsorbed 4-CPA is almost the same for all fiber types. Unmodified fibers do not show much sensitivity towards ion strength changes in the suspension. The trend for TEMPO-oxidized fibers is generally increasing while it is decreasing for CMC-modified fibres.

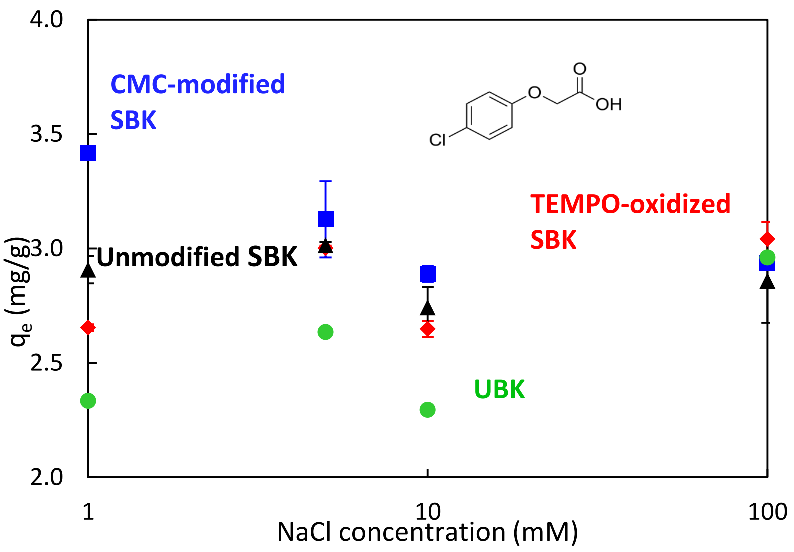


Figure 2.20 Changes in 4-CPA adsorption capacity at various ionic strength at pH~7, 4-CPA C_0=50mg/L for all samples, the x axis is in logarithmic scale

The balancing of pH playing an important role in dictating the adsorption behavior here. The difference in pH between inside and outside of the fiber wall decreases as the ionic strength of the suspension increases [49]. Hence, at 100mM, the pH inside the wall is higher compared to 1mM condition. It is more feasible for 4-CPA to penetrate through the pores in the wall due to the decreased osmotic pressure. However, there is a decrease in adsorption amount when the NaCl concentration increases from 5 to 10 mM, which can be described as follows. There are two factors that are changing by variation in ionic strength in the fiber suspension: fiber swelling and the pH difference between inside and outside of the fiber. High degree of fiber swelling is desirable for 4-CPA adsorption while the pH needs to be balanced in order to let the negatively charged organic molecule enter the pores in the wall. These two factors are opposing each other as the NaCl concentration increases in the suspension. TEMPO-modified fibers are the most negatively charged among other fibers. Hence, they are more sensitive to the pH balance inside and outside the fiber wall. If we look at CMC-modified fibers behavior, there is a decrease in adsorbed 4-CPA amount as the salt concentration rises. As mentioned before, CMC-modified fibers are more responsive towards changes in the swelling of the fiber wall. At higher ionic strength of the medium the difference in osmotic pressure decreases, as well as swelling. It is suggested that because of this reason, the adsorbed amount decreases. The unbleached fiber shows a generally increasing adsorption capacity by increasing the salt concentration. The explanation behind this matter can be the availability of hydrophobic groups on unbleached fibers. As the negative charges on the fiber are more screened by increased ion concentration, the 4-CPA molecules can detect the hydrophobic sites on the fiber better.

2.4.5. Adsorption of Malachite Green

Malachite Green was used for adsorption tests on cellulose fibers to resemble the behavior of a cationic dye. It is also used as antibacterial in aquaculture. Its characteristic absorption peak at 614-616nm was used to determine the concentration in the solution. MG solubility in water is 4×10^4 mg/L [82].

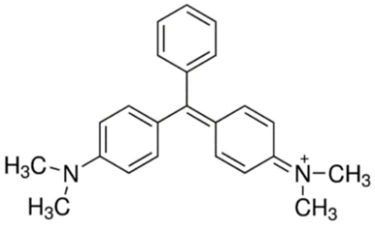


Figure 2.21 Molecular structure of MG cation obtained from the provider website (Sigma Aldrich)

The adsorption isotherm of Malachite Green is plotted in Figure 2.22 at temperature 22±3 °C for four different fibers at pH [6.5-7]. TEMPO-oxidized and CMC-modified fibers show a similar adsorbed amount except for the highest concentration point. The trend for both TEMPO and CMC modified fibers shows a rapid increase. UBK also show a competitive amount of adsorption; however, based on the Dubinin-Radushkevich adsorption model (Table 2.4) the expected plateau will happen at much lower q_e (mg/g) for unbleached fibers. Unmodified SBK show the lowest adsorbed amount per gram of fibre among the samples.

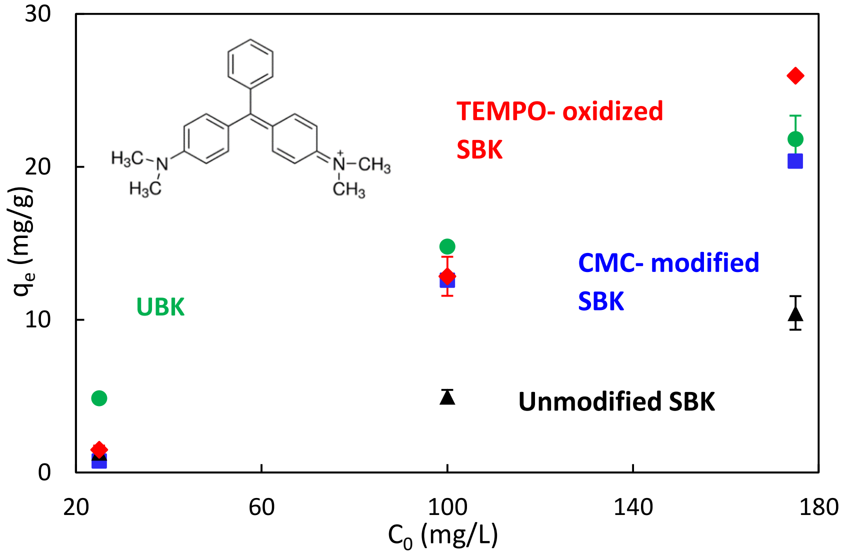


Figure 2.22 Adsorption of Malachite Green on different fibers at pH ~7 and 5mM NaCl concentration based on the initial concentration of the solution, standard deviation was from average generated from multiple measurements of supernatant

Three adsorption models were used to evaluate the adsorption capacity. TEMPO and CMC modified fibers seem to not follow Langmuir adsorption model. Furthermore, although the R^2 for linear form of Freundlich equation appeared to be acceptable for TEMPO and CMC modified fibers, the experimental adsorption data does not confirm the adsorption capacity number resulted from Freundlich equation. Calculations show that the Dubinin-Radushkevich describes the adsorption behavior of MG on cellulose substrate more accurately. This finding aligns with the assumptions based on which Dubinin-Radushkevich adsorption model is defined and it is mentioned in the review section. The adsorption capacity calculated from Langmuir and Dubinin-Radushkevich models are presented in table 2.4. Based on the isotherm curves, the q_s from Dubinin-Radushkevich represent the experimental data more accurately specifically for unmodified fibers. Furthermore, K_{DR} is a positive amount which confirms that Dubinin-Radushkevich equation is correctly used. The parameters of each adsorption model were calculated and presented in Table 2.4.

Table 2.4 The adjustable variables resulted from fitted experimental data to linear form of Langmuir, Freundlich, and Dubinin-Radushkevich adsorption isotherm models standard deviation from average generated from multiple measurements of supernatant and their linear fittings

Model/ Parameters	**Langmuir**		**Freundlich**		**Dubinin- Radushkevich**	
Fiber type	q_m(mg/g)	K_L(L/mg)	n	K_F	q_s(mg/g)	K_{DR} (mol^2/KJ^2)
UBK	19.27±0.31	0.49±0.03	3.09±0.18	5.41±0.03	18.42±0.20	$3\times10^{-7}\pm0$
Unmodified SBK	2.67±0.46	0.02±0.00	1.00±0.01	0.06±0.01	7.84±0.76	$1\times10^{-4}\pm0$
TEMPO-oxidized SBK	_	_	0.35±0.07	0	41.91±4.51	$2\times10^{-4}\pm0$
CMC-modified SBK	_	_	0.39±0.02	0	55.28±14.19	$35\times10^{-5}\pm7\times10^{-5}$

The earlier study on adsorption of MG on neem sawdust resulted in adsorption capacity of 4.35 (mg/g) at $25^{\circ C}$ and 0.2% consistency based on Langmuir adsorption isotherm. The neem sawdust mainly contains cellulose and lignin [83]. The wood pulp fiber used in current study has a better defined surface which could be one of the reasons why the calculated adsorption capacity is higher in our study.

In Figure 2.23, Dubinin-Rdushkevich adsorption isotherm is plotted based on the calculated adjustable variables from the linear fitting of data in Table 2.4. As it is discussed before, unmodified SBK and UBK fibres reach the plateau at much lower q_e compared to CMC-modified and TEMPO-oxidized fibres.

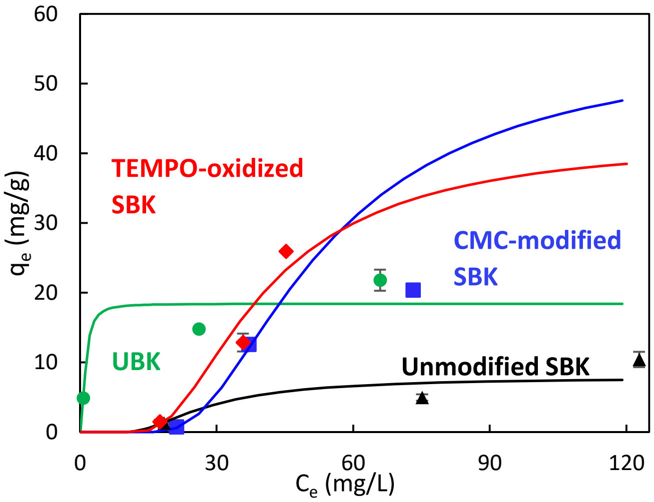


Figure 2.23 Dubinin-Radushkevich adsorption isotherm model for MG plotted based on the calculated values from linear fitting versus the experimental data points

2.4.5.1. Determination of the occupied surface area

Here, an estimation of the corresponding occupied surface area of fibres with the theoretical maximum adsorbed amount of MG molecules is presented. The total surface area of one molecule is approximately 110.85 Å^2 assuming that the molecule is flat and it is in shape of an equilateral triangle. Maximum adsorption was measured for CMC-modified SBK q_e= 55.3 mg/g based on Dubinin- Radushkevich equation.

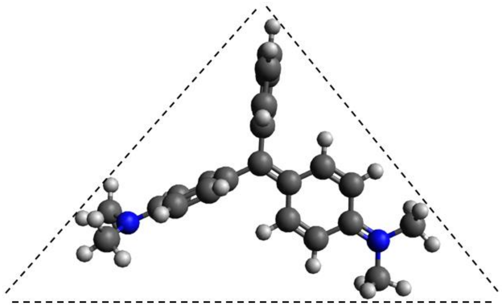


Figure 2.24 3-D molecular structure of MG and the hypothetical equilateral triangle used for estimation of the surface are of one molecule, each side is ~16 Å

The corresponding surface area for 55.3 mg of adsorbed MG per gram of fibre is estimated as follows. *SSA* is the surface are of MG molecule per gram, *Av* is the Avogadro number, SA_M is the estimated surface area of one molecule of MG, and M_{MG} is the molecular weight of MG molecule.

$$SSA(m^2.g^{-1}) = \frac{SA_M(\text{Å}^2) \times Av}{M_{MG}(g.mol^{-1})} \times 10^{-20}$$

(Equation 2.10)

Here, the specific surface area of MG is estimated to be 1829.29 m^2/g. This leaves us with the corresponding surface area for maximum adsorbed amount on CMC-modified fibre to be 101.12 m^2/g. Based on the estimated surface area of the porous fibres, this number gives a reasonable estimation of fibre accessible surface area.

2.4.6. Release Properties of Malachite Green

The reversibility of adsorption of MG molecules was investigated. The results are presented in Table 2.5. The release percentages were calculated based on the maximum adsorbed amount from experimental data. The SBK fibers show the highest and CMC-modified fibers depict the lowest release amount. The modification on bleached fibers have shown to be effective in controlling the release of MG from fibers. The excess layer of water in the CMC-modified fiber wall might be the reason behind the lowest release percentage among other fibers.

Table 2.5 MG desorption percentage from different fibers based on their maximum adsorbed amount

Fiber type	**Max adsorbed amount (mg/g)**	**Desorption percentage**
UBK	21.73±0.18	18.83±0.23
Unmodified SBK	11.95±0.07	31.00±0.83
TEMPO-oxidized SBK	27.48±0.12	17.39±1.35
CMC-modified SBK	22.99±0.73	10.69±0.10

The desorption of MG from neem sawdust has shown to be as high as 46% [83]. The highest percentage of MG desorption here is 31% for SBK fibers. This comparison shows that the performed modifications were also effective in reducing the desorption.

2.5. Implications for Fibre-based Growth Media

The feasibility of using wood pulp fibers as growth media substrate, soaked with agriculturally important chemicals is discussed in this section. This is performed based on the recommended dose of chemicals reported from greenhouse usage.

The effective dosage for every agrochemical is different in the plant growth medium. The general recommended dosage range for plant growth regulator and antimicrobial is presented in table below. The calculated total gram of fiber needed for the growth medium is also presented in table 2.6.

Table 2.6 The estimated total amount of pre-adsorbed fibers with agrochemicals that is needed for a 1liter volume plant growth medium in greenhouse. The average desorption percentage is assumed to be 20% and the recommended dose is reported from literature [84, 85]

	Growth regulator	**Antimicrobial agent**
Recommended average dose	[0.1- 10.0] ppm	[50- 200] ppm
Max. q_e obtained in current work	2.5 mg/g	55 mg/g
Total fiber needed in 1L medium	[0.4- 40] g	[4.5-18.2] g
Fiber consistency in the medium	[0.04- 4] %	[0.45- 1.82] %

The fiber percentage in standard Rockwool products is around 5% [86]. Based on the estimated numbers depicted in Table 6.1, the fiber percentage presented here falls in an acceptable range. It should be noted that for a single 1L growth medium, the agrochemicals need to be applied frequently; hence, based on the required final dose a certain consistency will be chosen. This consistency can be the reported fiber consistency in Table 6.1 multiplied by the number of the agrochemical application times. However, it is recommended that the selected dose is in the middle of the range so it is more feasible to handle the final fiber consistency. For instance, it is more feasible to adjust the optimum air to moisture ratio in fiber consistency of 4-6% rather than 10-12%.

2.6. Conclusions

The adsorption properties of two compounds on four different forms of wood pulp fiber were investigated. 4-Chlorophenoxy acetic acid (4-CPA) is a plant growth regulator and Malachite Green (MG) has an antimicrobial effect.

1. Negatively charged organic compound 4-CPA, adsorbed onto the fibers with a maximum adsorption capacity of approximately 5 mg/g. TEMPO oxidation and CMC modification on bleached fiber resulted in an increased adsorption capacity up to four times compared to the unmodified state.

2. The positive effect of TEMPO oxidation on adsorption is correlated with the increased WRV and subsequently, more fibre swelling. Moreover, another contributing factor can be the increased porosity of the fiber wall as a result of TEMPO oxidation.

3. Similar to TEMPO-oxidization, CMC-modification has also increased the WRV and swelling of the fibers which resulted in higher adsorption capacity.

4. Based on the pH and ionic strength study, the enhancement of adsorption by TEMPO oxidation and CMC modification is originated from different characteristics. TEMPO oxidation increases the surface charge, hence the electrostatic attraction forces. Furthermore, fibrils are separated upon TEMPO oxidation which increases the surface availability for adsorption. Whereas in CMC modification, fiber swelling plays an important role to increase the adsorption capacity.

5. The driving force of the adsorption is the hydrogen bonding between the 4-CPA aromatic ring and the cellulose fiber surface. The negative surface charge of fibres is screened by ions in electrolyte solution.

6. MG, a positively charged organic compound, adsorbed on four different pulp fibre forms. Linear form of Dubinin-Radushkevich model of adsorption isotherm showed more compatibility with the resulted adsorption capacities.

7. The main intermolecular force that drives the adsorption of MG on fibers is the electrostatic attraction between negatively charged fiber surface and positively charged MG molecules. Furthermore, hydrogen bond between the aromatic ring of MG and cellulose -OH surface groups contribute to the adsorption.

8. The performed modifications on fibers, increased the availability of charges to the MG molecules. Furthermore, the increased swelling was an asset for adsorption.

9. The low desorption percentage of MG also supports the effect of swelling as the molecules are trapped in the swelled fiber wall and held by ion bonding between opposite charges and hydrogen bonding between the aromatic ring and the cellulose surface. Furthermore, the desorption analysis shows promising results as the modifications were effective in decreasing the desorbed amount of the MG compound.

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