

**PREPARATION OF RAW AND TREATED FLAX STRAW SORBENT FOR OIL SPILL
CLEANUP**

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Saskatoon

By

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ABSTRACT

Oil spill incidents occur around the globe and recovering spilled oil from water or soil has become an important subject. One of the significant methods of oil spill cleanup is known as sorption. Most sorbents are made from synthetic materials. Replacing them with a natural and bio friendly material is a sustainable practice. Flax is grown in Canada and specifically in Saskatchewan. In this study, the possibility of developing a natural sorbent from a by-product of linseed oil production is investigated.

Two flax based sorption materials were chemically analyzed: as-received flax straw and processed flax fibers. Various sections of the straw and fiber were observed using scanning electron microscopy (SEM) to view the structure of the plant. The flax straw was cut into small particles of different lengths in order to study the effect of particle size on light and heavy oil uptake. The effect of sorbent density on oil sorption was also determined as well as the effect of shive and fiber. One of the main hinderance to utilizing natural sorbents for oil sorption in aqueous situation is their tendency to adsorb water. To illustrate the behavior of the flax straw in aqueous situations, two experiments were performed on the samples: water uptake and the oil/water selectivity. In order to address the adsorption of water, a chemical acetylation treatment and a proposed novel method for coating sorbents with linseed oil was accessed. Both acetylated and oil coated samples were compared with raw straw to investigate changes in surface morphology, chemical structure, thermal properties, oil sorption and water uptake.

The result of chemical analysis showed the cellulose content of flax fiber was higher than flax straw while its hemicellulose and lignin contents were higher. Based on SEM observations, the major portion of the flax straw stem consisted of a hollow inner tube surrounded by xylem and phloem vascular tubes. The vascular tube area is also known as shives and was considerably porous. Hence, shives may be a promising location for depositing oil in oil sorption projects. Also, it was observed the flax and shives were covered with plant wax, and this wax was mostly removed by the acetylation treatment. In the linseed oil coated samples, the plant wax was covered with a thin layer as well as fiber and shive particles. Fourier-transform infrared (FTIR) spectroscopy revealed changes in the intensity of bands related to -OH groups and acetyl groups which is an indication of a successful acetylation treatment. FTIR results of coated samples showed blockage of hydroxyl functional groups and appearance of C-H functional groups related to the linseed oil

backbone. The success of acetylation was also validated by thermal gravimetric analysis (TGA). The acetylated samples were observed to have a lower thermal stability compared to raw samples due to a decrease in the number of hydrogen bonds. The TGA results of coated samples were similar to those of raw samples as the coating agent was physically bonded to the sample surface and hence it did not change the structure of the coated sample. In terms of oil sorption capacity, the raw sample is capable of adsorbing 13.6 g/g and 11.2 g/g for heavy and light oil, respectively. The amount of water uptake was 6.9 g/g after 5 min. This number increased to 8.2 g/g after 45 min of soaking within the artificial sea water. Despite the high oil uptake capacity in a dry condition, in aqueous situation raw flax straw only adsorbed 5.6 g/g of heavy oil and 4.6 g/g of light oil. Similarly, the amount of water uptake was more than oil, at 7.6 g/g and 8.5 g/g from the mixture of water and heavy and light oil, respectively. The oil sorption of acetylated samples increased by 6.6 % and 9.8 % for heavy and light oil, respectively compared to raw flax straw. This may be due to the partial elimination of surface wax on the fibers and shives during acetylation which resulted in more regions being accessible within the sorbent particles. Acetylation treatment of flax straw also improved oil/water selectivity. While the amount of water uptake reduced by almost 44 % from the mixture of heavy oil and water, the oil uptake capacity improved by 9 %. For linseed oil coated samples, a considerable improvement of 32 % was observed in water adsorption compared to raw samples during the artificial sea water uptake experiments. Moreover, a drop of 81 % in water uptake and an increase of 38 % for light oil sorption was observed in oil/water selectivity tests for the linseed oil coated samples compared to the raw samples. As a final study, the possibility of reusability and disposal of the oily sorbent within a landfill was examined. It was observed that the linseed oil coated samples maintained 89 % of the oil sorption capacity after four sorption/desorption cycles for light oil and 92 % for heavy oil. It was determined the sorbents can be deposited in a landfill after one cycle of centrifuging based on the code of federal regulations (CFR).

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DEDICATION

I dedicate this work to Mina, for her love, patience and supports and to my parents for their sacrifices throughout life. I wouldn't have been here without them.

TABLE OF CONTENTS

PERMISSION TO USE.....	i
ABSTRACT.....	ii
ACKNOWLEDGMENTS	iv
DEDICATION.....	v
TABLE OF CONTENTS.....	vi
LIST OF TABLES.....	x
LIST OF FIGURES	xi
LIST OF ABBREVIATIONS.....	xv
CHAPTER 1: INTRODUCTION.....	1
1.1 Overview	1
1.2 Research objectives	2
1.3 Thesis organization.....	3
CHAPTER 2: LITRETURE REVIEW	4
2.1 The sorption mechanism.....	4
2.2 Conventional oil sorbents	4
2.3 Flax plant	5
2.3.1 Stem structure of the flax plant.....	5
2.3.2 Chemical composition of the flax plant.....	6
2.4 Oil sorption mechanism of natural fibers	7
2.5 Various types of natural oil sorbents	9
2.5.1 Cotton fibers	9
2.5.2 Kapok fibers.....	10
2.5.3 Cattail fibers.....	10
2.5.4 Flax fibers	11
2.6 Effective parameter on the sorption capacity of natural fibers.....	12
2.6.1 Hydrophobicity and oleophilicity	12
2.6.2 Particle size	13
2.6.3 Contact time.....	13

2.6.4	Surface morphology.....	14
2.6.5	Surface functionality groups.....	14
2.6.6	Surface wax.....	15
2.6.7	Sorbent density	15
2.7	Chemical treatment to enhance the sorption property	16
2.7.1	Sol-gel.....	16
2.7.2	Acetylation.....	17
2.8	Sorption characteristics of natural sorbent	18
2.8.1	Oil uptake.....	19
2.8.2	Oil/water selectivity	20
2.8.3	Water uptake	20
2.8.4	Reusability	21
2.8.5	Oil retention	21
2.9	Structural characterization.....	22
2.9.1	FTIR.....	22
2.9.2	TGA	22
2.9.3	SEM	23
2.9.4	Summary.....	24
CHAPTER 3: MATERIALS AND EXPERIMENTAL PROCEDURE		26
3.1	Materials	26
3.2	Chemical analysis of flax straw and flax fiber	27
3.3	Sample preparation.....	28
3.3.1	Purification and drying of the straw	28
3.3.2	Cutting	28
3.3.3	Sieving	29
3.3.4	Raw and treated sample preparation.....	32
3.4	Experimental procedure.....	34
3.4.1	Effect of particle size on oil sorption.....	34
3.4.2	Effect of density on oil sorption	34
3.4.3	Effect of flax fiber and shive on oil sorption.....	36
3.5	Characterization of untreated and treated samples	37

3.5.1	Oil sorption experiment	37
3.5.2	Kinetic water uptake	38
3.5.3	Oil and water selectivity	39
3.5.4	Fourier-transform infrared spectroscopy	41
3.5.5	Scanning electron microscope	41
3.5.6	Thermogravimetric analysis	42
3.5.7	Statistical analysis	43
3.6	Reusability and disposal of the sorbent	43
3.6.1	Waste disposal regulation	44
3.6.2	Oil retention	45
3.6.3	Reusability	45
CHAPTER 4: RESULTS AND DISCUSSION		46
4.1	Characterization of flax straw and flax fiber	46
4.1.1	Chemical composition of the flax fiber and flax straw	46
4.1.2	Flax straw structure	47
4.2	Material preparation	50
4.2.1	Drying of the flax straw	50
4.2.2	Cutting operation	51
4.2.3	Sieving	52
4.3	Microstructure of untreated and treated samples	55
4.3.1	SEM	55
4.3.2	FTIR	57
4.3.3	Thermal gravimetric analysis	59
4.4	Result of initial experiments	61
4.4.1	Oil sorption capacity of fiber and shive	61
4.4.2	Effect of particle size on oil sorption	62
4.4.3	Effect of packing density on oil sorption	63
4.5	Characterization of untreated and treated samples	64
4.5.1	Oil sorption experiment	64
4.5.2	Water uptake	66
4.5.3	Oil and water selectivity	67

4.6 Reusability and disposal of the sorbent	71
4.6.1 Oil retention	71
4.6.2 Reusability	72
4.6.3 PFL test result	74
CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK.....	75
5.1 Conclusions	75
5.2 Recommendations for future work	76
LIST OF REFERENCES	77
APPENDIX A	86
APPENDIX B	87
APPENDIX C	88
APPENDIX D	89

LIST OF TABLES

Table 4.1. Chemical composition of flax based on wet and dry basis.....	64
Table A.1. ANOVA and LSD test result for oil sorption of untreated flax straw with respect to heavy oil and light oil	86
Table B.1. ANOVA and LSD test result for light oil sorption of untreated samples with changing in samples packing density (PD)	87
Table C.1. ANOVA and LSD test result for light oil sorption with varying the sorbent treatment (raw, linseed oil coated and acetylated)	88

LIST OF FIGURES

Figure 2.1. Cross-section of flax stem (a), schematic of the arrangement of stem components (b).....	6
Figure 2.2. A cross-section of a bundle of flax fiber consisting of individual fibers	6
Figure 2.3. Schematic arrangement of a single fiber constitutions.....	8
Figure 2.4. Schematic steps for creating hydrophobic kapok with sol-gel method.....	17
Figure 2.5. Schematic of acetylation treatment on celulosic material	17
Figure 2.6. SEM image of untreated coir fiber (a) and acetylated treated coir fiber (b)	24
Figure 2.7. SEM photo of untreated flax fiber (a) and treated flax fiber (b)	24
Figure 3.1. Sample batch of flax straw (a) and flax fiber (b).....	27
Figure 3.2. Digital image of the multi-blade scissors	29
Figure 3.3. Retsch knife milling machine (a), fixed/rotary blades and 8 mm sieve (b), feeding the stock from the top (c).....	30
Figure 3.4. Cutting procedure diagram	30
Figure 3.5. The different positionof hammer, fully open at (a), compacting the head (b)	31
Figure 3.6. Individual packages for each cut sample containing the sample fiber to shive Ratio.....	31
Figure 3.7. Schematic of sample preparation methods	32
Figure 3.8. The raw samples immersed in acid (a) and acetylation setup (b).....	33
Figure 3.9. The PTFE washer attached to the strainer (a), The Gourmia GJ750 juice extractor (b), and the v-shape strainer and the bending locations (c)	34
Figure 3.10. Schematic steps of investigating the effective parameter on oil sorption	35
Figure 3.11. The mesh bottles used for study the effect of density on the oil sorption.....	36
Figure 3.12. The baskets containing flax fiber (left) and flax shive (right) (a), manually	

separated flax shives (b).....	36
Figure 3.13. Schematic for the summarized methods for treated and untreated samples.....	37
Figure 3.14. Sorbent at the start of experiment in the test cell (a), sorbent immersed in test cell using spatula (b)	38
Figure 3.15. Water uptake experiment setup, sorbent on magnetic stirrer (a), basket used in the experiment (b)	39
Figure 3.16. Sorbent in mixture of oil and water on magnetic stirrer (a), basket used in the experiment (b), separatory funnel (c)	40
Figure 3.17. Digital image of the Bio-RAD FTS-40 FT-IR set-up	41
Figure 3.18. Digital image of the SEM model JEOL JSM-6010 LV	42
Figure 3.19 TA Instruments Q50000IR TGA system (a) aluminum pan (b) ground samples (c).....	43
Figure 3.20 PFL test setup (a), the PFL filter (b).....	44
Figure 4.1. SEM image of the cross-section of the flax stem.....	48
Figure 4.2. SEM photo of skinless part of the stem (a), peeled off skin (b), bundle of fibers and wax attached to part of it (c)	49
Figure 4.3. Moisture reduction during oven-drying process.....	50
Figure 4.4. Pulverized flax stem using multiblade scissors (a), cut flax straw using knife milling machine (b).....	52
Figure 4.5 Digital images of particle captured by various sieve sizes during sieving.....	53
Figure 4.6 Particle capture by sieve size 1.19 mm	53
Figure 4.7 Ground and sieved batch of flax straw (a) and flax fiber (b)	54
Figure 4.8. The 4-gram samples made with the knife milling machine using three sieves sizes.....	55

Figure 4.9. SEM comparison between raw (a) and acetylated flax fiber (b)	56
Figure 4.10. Bundle of fibers coated with linseed oil (a) and coating of individual fibers (b)56	
Figure 4.11. Untreated flax shive (a) and acetylated flax shive (b).....	57
Figure 4.12. Coated shive with linseed oil at 400x (a) and 200x magnification (b).....	57
Figure 4.13. Absorption values with respect to wave length using FTIR for raw and acetylated flax straw samples.....	58
Figure 4.14. Absorption values with respect to wavelength using FTIR for raw and linseed oil coated flax straw samples	59
Figure 4.15. TGA result of raw and acetylated straw samples	60
Figure 4.16. TGA result of raw and linseed oil coated sample.....	61
Figure 4.17. Four grams of flax fibers (left) and four grams of flax shives (right)	62
Figure 4.18. Heavy and light oil sorption values of the sieved raw straw samples	62
Figure 4.19. Light oil sorption results of packing density of flax straw due to sample compaction.....	64
Figure 4.20. The oil sorption result of raw, linseed oil coated (LC) and acetylated (AC) sample	65
Figure 4.21. Water uptake of raw, linseed oil coated (LC) and acetylated (AC) flax straw samples as a function of time.....	66
Figure 4.22. Oil and water selectivity experiment at 15 min on raw (a), acetylated (b) and linseed oil coated (c) flax straw samples.	68
Figure 4.23. The sorption of raw, linseed oil coated (LC) and acetylated (AC) flax straw from the mixture of water and light oil.....	68
Figure 4.24. The sorption of raw, linseed oil coated (LC) and acetylated (AC) flax straw from the mixture of water and heavy oil	69

Figure 4.25. Comparison between buoyancy of raw (a) and linseed oil coated (LC) sample(b).....	70
Figure 4.26. Light and heavy oil to water selectivity for raw, linseed oil coated (LC) and acetylated (AC) flax straw samples	71
Figure 4.27. Heavy and light oil retention of raw and linseed oil coated flax straw samples (LC).....	72
Figure 4.28. Comparison between the reusability of raw and linseed oil coated flax straw samples (LC) for light oil.....	73
Figure 4.29. Comparison between the reusability of raw and linseed oil coated flax straw samples (LC) for heavy oil	74

LIST OF ABBREVIATIONS

AC	Acetylation treated sample
ADF	Acid detergent fiber
AF	Adsorption filtration
ANOVA	Analysis of variance
AOAC	Association of Official Analytical Chemists
CO	Cotton
CFR	The code of federal regulation
DMAP	4-dimethylamino pyridine
FTIR	Fourier-transform infrared
LC	Linseed oil coated sample
LSD	Least significant difference
NBS	N-Bromosuccinimide
NDF	Neutral detergent fiber
PA	Penetration absorbency
PFL	Paint filter liquid test
PP	Polypropylene
PS	Polystyrene
PU	Polyurethane
PVC	Polyvinyl chloride
SC	Sorption capacity
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis

CHAPTER 1

INTRODUCTION

1.1 Overview

One of the major sources of pollution in seas and oceans is the accidental oil spills due to release of crude oil or its derivative products during the transportation, storage or production [1]. In April 2010 in the Gulf of Mexico, as a result of an underwater oil rig explosion, 4.5 million barrels of oil was released into the Gulf of Mexico. This was considered one of the largest oil spills throughout the history of oil industry [2]. Numerous marine life was lost due to the pollution and toxicity of the water [3]. Reliance of the modern society on oil and gas is growing and incidents of oil spills appears to be unavoidable. Interested in oil spill cleanup have continue to grow to address these issues using various types of chemical, biological and physical methods. The chemical and biological approaches focus on burning or dispersing the oil, while the physical method removes the oil and separates it from the water without using chemical agents. For example, skimmers and boomers are considered physical methods as they remove the oil from water using various facilities and power. However, these machineries are costly to operate and transport, therefore they are not suitable for every oil spill cleanup project. Using any of these cleanup techniques, a portion of the oil still remains in the sea or ocean for a long time and causes devastating effects on marine life [4]. Another physical technique is called sorption [5-7]. Sorption is defined as a process where one substance (sorbate) attaches to another material (sorbent) [8]. For some oil spills, sorption is considered as one of the most effective methods [9]. By using sorption, the oil characteristics can be changed from liquid to solid or semi-solid to make it more convenient to collect. Being cost effective in terms of price, efficiency in sorption, low water uptake, high oil uptake, excellent reusability with good physical and chemical stability [10-12]. Oil sorbents can be classified into three main categories: minerals, synthetics, and naturals. Mineral products consist of vermiculites, silica, sorbent natural clay, perlite, graphite, zeolites, and diatomite. These materials do not show adequate buoyancy retention and their oil sorption capacities are generally low [13]. Among synthetic products, polystyrene fiber, polyurethane foam, acrylate and olefin resin are the most widely used sorbents in oil spill cleanup due to their high oleophilic and hydrophobic properties as well as high capacity for oil sorption [14]. Recently

disposing of synthetic materials is however becoming a global concern [15]. Therefore substituting synthetic materials with a sustainable plant based sorbent (natural sorbent) is proposed. Natural fibers such as cotton, wool, milkweed and kapok are capable of oil uptake between 30 and 40 g /g (gram of oil per gram of fiber) [16]. In addition, from having a high oil sorption capacity, hydrophobicity is another important consideration for choosing the sorbent especially for marine oil spills. Being hydrophobic suggests less water uptake with a higher oil separation capacity. A sorbent material with less water uptake, increases its buoyancy. The problem of floatability and low hydrophobicity of natural sorbents are two main disadvantages [17]. Researchers have proposed many chemical treatments to address some of these issues. For instance, it has been found that the modification of Kapok fibers using a sol-gel method enhances oil sorption capacity of the kapok fibers [18]. In a similar study, chemically treated sugarcane bagasse showed a significant increase in the hydrophobicity which suggests improvements in sorption of oily-water contamination [19]. Although considerable research has been done on oil sorption of various natural fibers, less attention has been paid to studying the sorption capacity of the entire plant. Fibers are derived from stems or leaves of a certain plant, where the fiber extraction is a costly process. In order to develop an inexpensive natural oil sorbent, biomasses can be a substitute for fibers [20]. Flax straw, the by-product of oil seed extraction of flax, is widely available in Canada and especially in Saskatchewan where it can be consider an oil sorbent [20]. Studies have been conducted on flax fibers for improving their hydrophobicity for use in composite applications [21]. To date, flax has not been studied to the same extent as other natural oil sorbents for its characteristics. To the best of the author's knowledge, no research has been done on increasing the oil sorption capacity of flax straw.

1.2 Research Objectives

The main goal of this research is to develop an oil sorbent using flax straw. To achieve this goal the following objectives are proposed:

- To study the effect of parameter such as contact time, density and particle size on oil sorption capacity of flax straw.
- To study the acetylation chemical treatment on flax straw with the aim of increasing hydrophobicity.

- To propose a method that is inexpensive, bio-friendly and effective for improving the hydrophobicity of flax straw.
- To study the disposal properties of the sorbent after use as well as its reusability.

1.3 Thesis Organization

This thesis consists of five chapters. After the overview and objectives in Chapter 1, a review of scientific works on oil sorption capacity of natural sorbents is provided in Chapter 2. In Chapter 3, the experimental procedures to achieve the objectives are discussed. In the chapter 4, the results of experiments along with related discussions are presented. Finally, conclusions and some suggestions for future work are summarized in Chapter 5.

CHAPTER 2

LITERATURE REVIEW

The literature review chapter begins by describing the sorption and the conventional sorbents used for oil sorption. Next, the structure and chemical composition of the flax plant and how these elements form the stem have been explained. After understanding the stem structure, the sorption mechanism in natural base materials is reviewed, and some examples of oil sorption capacity of natural fibers are provided. Finally, the chapter ends with a calculation method for oil sorption as well as imaging, compositional and structural characterization techniques.

2.1 The sorption mechanism

Sorption is a process where a substance called sorbate is attached to another substance called sorbent. Sorption is a generic term explaining both adsorption and absorption. Adsorption is the bonding of sorbate molecules, ions or atoms to a surface of the sorbent material, while absorption is the entering of these molecules, ions or atoms within the bulk of the sorbent [22].

2.2 Conventional oil sorbents

Oil sorbents are categorized based on the material they have been derived from. Three main categories of oil sorbents exist including inorganic minerals, synthetics, and organic natural materials. Clay, vermiculites, and graphite are some examples of inorganic mineral sorbents. They are eco-friendly and can uptake oil between 4 to 20 times their weight. These sorbents are also inexpensive and readily available, but their tendency to float on water is generally weak [23]. Synthetic sorbents for oil cleanups are polystyrene (PS) fibers, polyvinyl chloride (PVC) fibers, polyurethane (PU) foam and polypropylene fibers (PP). Zhu *et al.* [24] developed a synthetic oil sorbent by electrospinning the mixture of PVC and PS and compared the result of sorption with a commercial nonwoven PP synthetic. It was observed that the PVC/PS sorbent capacity of motor oil was 146 g/g, while the conventional nonwoven PP sorbent adsorbed 19 g/g. The comparison was also made in aqueous situation. It was observed that none of the samples adsorbed much water due to their excellent hydrophobic nature, and the result was almost the same with the experiment in absence of water. With nearly 100 g/g oil uptake, PU foam revealed strong oil uptake properties.

Another advantage of using PU foam is the fact that they are reusable and can be employed a number of times [25]. Being highly oleophilic, hydrophobic, able to float on the surface of the water as well as being reusable, make these synthetic materials ideal as conventional oil sorbents. However, the drawback of not being biodegradable and environmentally friendly, have made synthetic sorbents a growing concern in recent decades [17]. Disadvantages of these two groups give rise to the third group referred to as organic natural materials. Cotton, wool, milkweed and kapok fibers are examples of this group of sorbents. They are plant-based materials that are biodegradable, widely available and inexpensive. However, their capacity to absorb oil is generally lower than synthetics and their buoyancy is usually weak [14]. Nevertheless, in some specific cases, natural oil sorbents revealed higher oil uptake in comparison with commercially used sorbents. For instance, mats, blocks and screens made with kapok fibers were reported to adsorb 1.5 to 2 times more of the same structure made with PP [17]. In this study, flax straw, an unused portion of the flax plant after production of linseed oil has undergone experiments for its oil sorption characteristics. Hence understanding the plant characteristic, its unique structure and chemical composition is of importance.

2.3 Flax plant

Flax plant is a member of the *Linum* family which is cultivated around the world for two main reasons: its seed oil referred to as linseed oil and its fibers used in the woven industries referred to as linen. Like some other natural plants, stems of flax plants consist of bundles of fibers. These fibers are removed and purified with mechanical and chemical approaches as is used in the textile industry. The flax plant type cultivated for its fiber production is different than the plant that is grown for oil. The main difference is the length of their fibers which is shorter in the latter [26]. The by-product of flax seed cultivation is called flax straw which mainly consist of stems because of its tall and tiny structure.

2.3.1 Stem structure of the flax plant

Stems of the flax plant comprise of xylem and phloem cells. They are located longitudinally within the stem, and are responsible for carrying water and nutrition required for the plant growth. Figure 2.1 (a) illustrates the cross-section of a flax stem [27]. Xylem cells form the woody core of the plant and are located between the central hollow tube and phloem cell. The density of this area

decreases toward the middle of the stem. Phloem cells available in the form of hollow tubes are situated at the outer layer of xylem cells. The fibers are available in the form of bundles located alongside the phloem cells within the cortex area. Single fibers within the bundle are attached to each other with wax. Shives are the woody portion of the stem. They consist of phloem and xylem cells, and they have a porous structure (Fig 2.1b) [28].

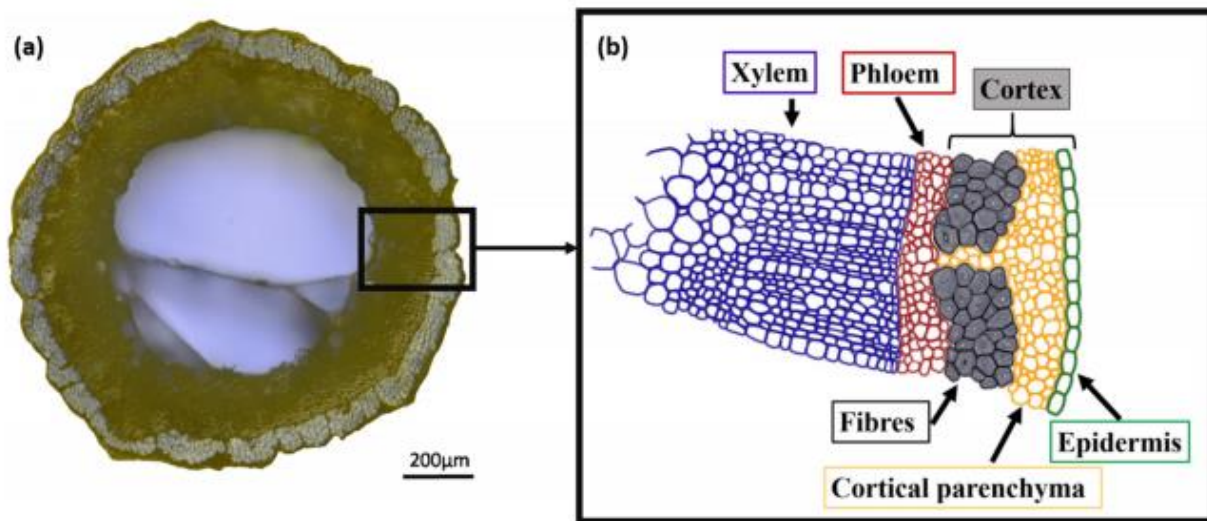


Figure 2.1. Cross-section of a flax stem (a) and schematic of stem components (b) [28].

Each fiber has a hollow lumen in the center which represent approximately 7 % of flax fiber cross-sectional area in a mature plant. In terms of morphology, the average diameter of fiber and lumen diameter is around 19 and 5.0 μm, respectively (Fig 2.2) [29].

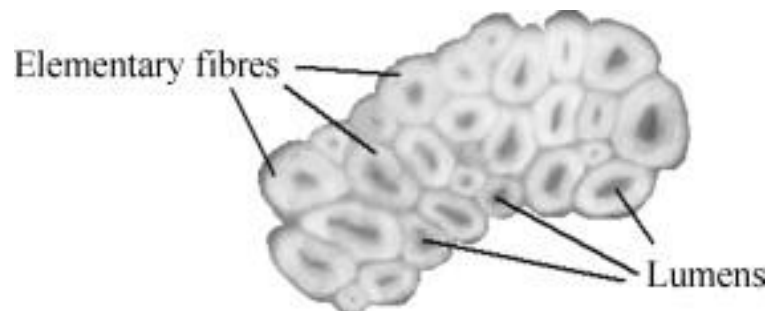


Figure 2.2. A cross-sectional view of a bundle of flax fibers consisting of individual fibers [29].

2.3.2 Chemical composition of the flax plant

In general, organic compounds comprise of carbon, hydrogen, nitrogen, sulphur and oxygen. These

elements are available mainly in the form of cellulose, hemicellulose, lignin, wax, ash and water within the plant [20]. As reported by Mazza *et al.* [30] the chemical composition of flax straw, consists of 53 %, 17 % and 23 % for cellulose, hemicellulose and lignin, respectively. The compositional ratio of these ingredients differs in various parts of the plant. For instance, the amount of cellulose in flax fiber is reported higher than hemicellulose and lignin [31-33], and the amount of lignin is higher in flax shives compared to flax fiber [34]. The literature has reported various chemical compositions for the flax plant. For instance, Bledzki *et al.* [35] reported the ratio of 72 %, 12 % and 5 % for cellulose, hemicellulose and lignin within the flax fiber, while Ansari *et al.* [33] reported 52 %, 13 % and 2 % correspondingly. The difference could be due to many reasons, such as growing conditions (water, sunlight, soil type) and the variety of plant species. Hence, reporting the chemical composition of the sample is crucial part of such studies and it should be done prior to any experiment on biological materials.

Figure 2.3 represent the schematic of cellulose, hemicellulose and lignin arrangements within a single fiber. Cellulose has a crystal structure and mainly responsible for the strength of the plant cell walls. The cellulose fibrils (slender fiber) are attached to each other and to hemicellulose structure with strong hydrogen bonding [36]. Hemicellulose are amorphous polymers with a molecular weight less than cellulose. They are attached to cellulose using a hydrogen bond. Since they are amorphous, they have a lower mechanical property compare to cellulose. The last component is lignin which is located between the spaces of cellulose and hemicellulose structures [37]. The lignin and hemicellulose are attached to each other using covalent bonding and both act as a glue holding the fibers together [36].

2.4 Oil sorption mechanism of natural fibers

The underlying mechanism of sorption for the oil uptake process is essential. However, the number of literatures explaining the detailed process of oil uptake in cellulosic fibers are limited [39,40]. There are different available sites for oil uptake in the sorbent bulk of natural fibers which are mainly divided into two categories: inter-particle and intra-particle. The term particle here refers to any small piece of pulverized flax straw with either a fibrous or wooden origin. Inter-particle sites are the available spaces on the surface of individual particles either from fiber or shive and the void spaces between various particles. On the other hand, intraparticle sites are those available

in the form of pores or vascular tubes within the bulk of the particles and the hollow lumen of the fibers. These hollow lumens may be a reliable storage for oil. For instance, in kapok fibers, the excellent oil uptake behavior was reported to be due to its hollow lumen shape which is about 80 % to 90 % of its overall volume. The oil mainly attached on the surface of fibers or within the lumens [41].

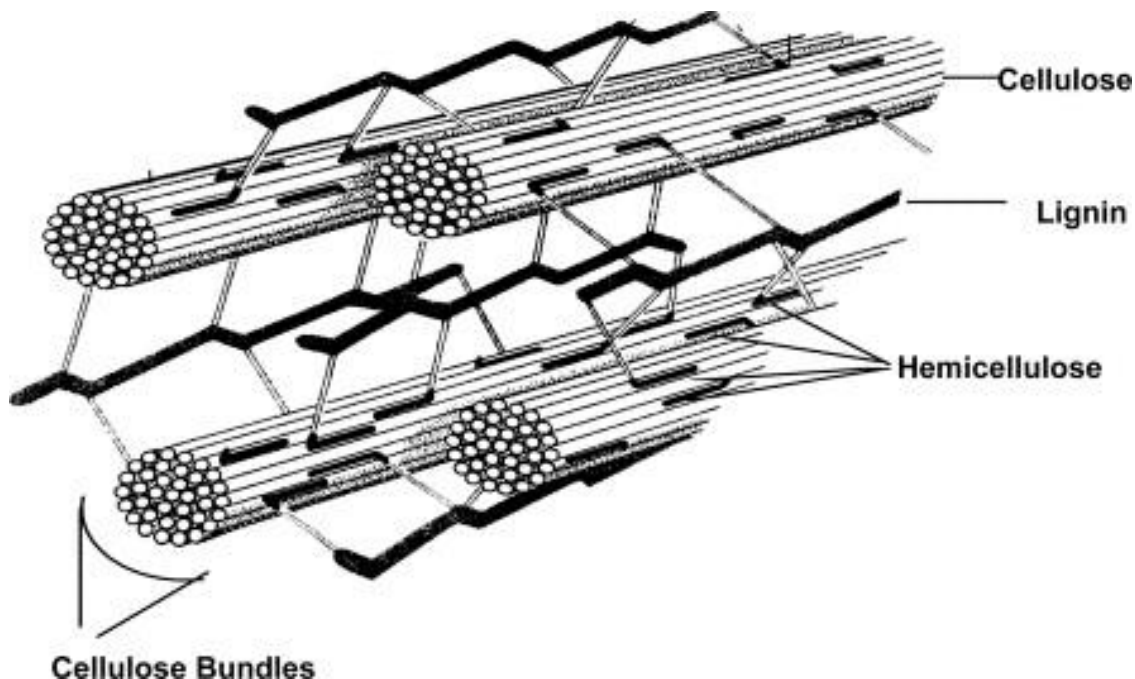


Figure 2.3. Schematic arrangement of fiber constitutions [38].

The oil sorption mechanics mainly consists of three stages. At the early stage of oil sorption, van der waals forces between the surface of natural fibers and oil, adsorb the oil into the intra-particle space and spread on the surface of fibers and shives. The bulk of the oil sorption occurs in intra-particle space in the form of adsorption [20] because of the higher void space in comparison with inter-particle space. In the next stage, the capillary action, which is the tendency of a liquid to flow into narrow pores, drives the oil into the lumens and inter-particle spaces. In the last stage, when the lumen and intra-particle spaces have adsorbed most of the oil, this oil then begins to penetrate into the bulk of the sorbent particles and the absorption process begins [16,42].

In aqueous media, the situation is slightly different. Oil is a non-polar material meaning that it has no electrical poles, and electrons are distributed more symmetrically on its surface. Water, on the

other hand, consists of polar atoms which tend to repel oil or any other non-polar material. The chemical composition of most natural fibers shows a high amount of cellulose material. The cellulose chains have a considerable amount of hydroxyl functional groups on their surface which are polar. Hence, cellulose tends to attract and attach polar molecules of water [43]. However, the wax, available on the surface of most natural fibers can cap these hydroxyl functional groups. The structure of wax is similar to oil as they are both non-polar, and thus natural fibers with higher amount of wax on their surface tends to repel more water and create more space for oil [40].

Besides the basic chemistry of oil sorption of natural fibers, the effect of adsorption and absorption processes on the overall oil sorption phenomenon is an important consideration. A report from the University of Texas on oil uptake of raw cotton suggested that inter-fiber capillary uptake along with adsorption and absorption are involved in oil uptake [39]. In a similar study on oil sorption capacity of corncobs in an aqueous situation, it was found that the sorption mechanism was mainly due to the surface reaction and intra-particle diffusion [42]. In another study, the effectiveness of various biomasses for oil cleanup was investigated. Two different sorption models were adopted which include the sorption capacity (SC) and penetration absorbency (PA). While the SC model can determine the inter-particle oil sorption of natural sorbents, the PA model was applied to estimate the intra-particle uptake of oil within the sorbent particles. In the mentioned study it was found that the governing process in oil sorption of biomass sorbents is adsorption [20].

Overall, in the oil sorption process both absorption and adsorption mechanisms are involved which occurs either by inter-particle or intra-particle spaces. In this research, the effect of each of these factors is not studied, and thus the more general term “sorption” is preferred.

2.5 Various types of natural oil sorbents

Majority of the commercial and conventional oil sorbents are synthetic. However, employing a wide variety of modification techniques in terms of mechanical, chemical or both, scientists developed various reliable oil sorbents using natural plant fiber products. In this section, some of these achievements have been reviewed.

2.5.1 Cotton fibers

Cotton fibers are obtained from the cotton plant. More specifically, they grow from the outer layer

of the seeds which are called seed coats. The final product of purified cotton fiber is referred to as woven cotton which is used in the textile industry. Singh *et al.* [39] studied the oil sorption capacity of raw cotton, and reported the sorption amount of 30.5 g/g for crude oil. Choi *et al.* [44] studied the effect of different processing techniques on the oil sorbent property of cotton (CO) and polypropylene (PP) containing materials. It has been shown that 100 % CO/0 % PP exhibited the best oil sorption with almost 23 g/g followed by a combination of CO/PP of 65 %/35 %, 80 %/20 %, 50 %/50 %, having sorption values of 20.8 g/g, 18.5 g/g and 18.3 g/g, respectively.

2.5.2 Kapok fibers

Kapok fibers are obtained from seeds of the ceiba tree which are mainly grown in the East, Southeast Asia and parts of Africa. When the seeds are harvested, the white, hair-shape fibers are removed. These fibers have been used as stuffing material for pillows due to their light weight and non-allergic characteristics. Also, they are used for making life jackets because of their excellent floatability in water. Although kapok fibers comprise of 64 % cellulose, the waxy cutin available on their surface makes this material a reliable water repellent. The amount of wax on the surface of kapok is reported to be higher in comparison to cotton fiber. Besides being water repellent, this material is also a reliable oil sorbent. For example, a study showed diesel oil sorption by PP was 9.9 g/g compared to 42 g/g for kapok fibers both in loose packing density conditions [45].

2.5.3 Cattail fibers

Another interesting natural sorbent is cattail fibers. Cattail tufts are derived from the flower of the cattail plant which mainly grow beside lakes. Each flower yields up to 300,000 cattail tufts that consist of seeds, a stem and fibers [40]. Like any other natural fibers, they mainly consist of cellulose which is hydrophilic. However, the massive amount of 10.64 % surface wax of cattail fibers makes the material naturally hydrophobic [46]. The water contact angle of cattail fibers is estimated to be 133° which is similar to kapok and cotton fibers which are 139° and 135°, respectively [40]. Another compelling characteristic of cattail tuft is their unique bamboo-shaped structure which provides a large surface area and open spaces between the particles. This structure is responsible for high cattail oil uptake of 14.6 g/g in vegetable oil [47]. Hence, due to its hydrophobic nature and high oil sorption capacity, this sorbent can be a reliable source especially for remediation of oil spilled in water [47].

2.5.4 Flax fibers

Recently, oil sorption applications have been proposed for the flax fibers [32,48]. Oil sorption experiments were performed on flax fibers for different oil types at Leeds University. The oils used in this experiment were Vymox 220, Vymox 100, Vymol 22, crude and diesel oil. The oil sorption capacity of flax fibers in these oil media was reported as 33.6 g/g, 28.3 g/g, 16.0 g/g, 17.5 g/g and 15.6 g/g of sorbent, respectively [32]. It was revealed that flax fibers are also excellent oil sorbents for oil in water situations. The oil sorption of flax fibers in different concentrations of oil in water mixtures using Vymox 100 oil and artificial seawater were investigated. The mixtures studied were 10 g, 25 g and 50 g of oil in 500 mL of artificial seawater. Oil sorption in these different concentrations were 6.6 g/g, 18.2 g/g and 27.9 g/g of sorbent respectively. Another significant characteristic of flax fibers examined in the mentioned study was the reusability of this natural fiber. After performing multiple cycles of sorption-desorption, it was shown that most of the adsorbed oil was recovered. Therefore, the flax fiber could potentially be used more than once [32].

Flax fibers are not the only part of the plant that have undergone oil sorption experiments. For instance, agriculture residue in the form of the remaining plant subsequent to linseed oil production (after removing the seeds) is considered a by-product left in the field to rot or burn. This by-product mainly consisting of stems is called flax straw. In a study at Helsinki University, different types of flax straw in terms of the harvest time were examined for their oil uptake capacity. The highest oil uptake was about 2.7 g/g for fall harvested flax with the particle length of less than 1mm [10]. In a recent study at the University of Calgary, flax straw was calculated as 3 g/g for non-detergent motor oil (SAE 30) [20]. The considerable difference between the reported amounts in these studies were mainly due to two reasons. Firstly, the initial study was performed on pure flax fiber while the second study, was conducted on flax straw containing some wooden impurities of the stem along with fibers. Secondly, the sorption examination method in these studies was performed differently. The first study (Leeds University) used a method according to ASTM F716-09 and ASTM F726-17 standards with slight modifications, while in the other two studies (Helsinki University and University of Calgary), adsorption filtration (AF) [10] method and paint filter liquid test [20] were followed respectively.

2.6 Effective parameter on the sorption capacity of natural fibers

In this study, the process of oil sorption begins with expanding the sorbate media on the surface of sorbent particles and continues by storing the media within intra-particle void spaces and finishes with the diffusion of the media into the bulk of sorbent. Some of the parameters that affect these processes, such as hydrophobicity, particle size, contact time, surface morphology, surface functionality, sorbent density is explained in the following section.

2.6.1 Hydrophobicity and oleophilicity

Hydrophobicity is defined as the tendency of a particular material to repel water, while oleophilicity refers to the desire of a material to attract oil [49]. An excellent natural sorbent should be both oleophilic and hydrophobic, for marine applications. Since the accessible space is limited within the sorbent matrix, less water uptake would provide more available space for oil uptake. Being hydrophilic is one of the main disadvantages of natural fibers in oil sorption applications especially in aqueous situations [45]. However, in some cases, a considerable amount of wax on the surface of these fibers contributes to their elevated hydrophobicity. In the study on wetting of natural fibers, it was observed that cattail, cotton and kapok, revealed a strong water repellency. This characteristic was examined by observing and calculating the contact angle between the water droplet and the fiber [40]. Being hydrophobic and oleophilic depends on several factors including the chemical component of the plant (e.g., amount of cellulose, hemicellulose and lignin), surface property (e.g., amount of waxiness and roughness of the surface), porosity structure and the physical shape of the fiber-like hollow lumen. In a study performed on flax fibers, flax shives (woody stem fragments) and cotton, the composition of cellulose and hemicellulose were about 52 % and 13 %, respectively for flax fiber, 32 % and 24 %, respectively for flax shives and 89.9 % and 0.22 %, respectively for bleached cotton fibers [33]. The amount of cellulose and hemicellulose in the flax straw which consists of both flax fiber and flax shives was assumed to be in the range of 32-52 % and 13-24 %, respectively, which is lower than that of cotton. Furthermore, the amount of wax on flax fibers, flax shives and cotton were reported as 1.9 %, 4.6 % and 0.42 %, respectively. Therefore, flax straw may be considered a better hydrophobic material in comparison with cotton fibers. Research on the hydrophobicity of flax fiber is limited, and to the best of authors knowledge, there has not been any published research on this property for flax

straw.

2.6.2 Particle size

Another parameter that affects the oil sorption capacity of natural-based sorbents is their particle length and diameter. In several studies, the influence of this physical characteristic on oil sorption has been examined. For example, in a study on sugarcane bagasse, the crushed samples were sieved into different particle sizes using sieve numbers 8, 10, 18, 20, 30 and 60. Oil sorption of crude oil for each particle size was calculated separately. It was observed that decreasing the particle size to 0.2 mm resulted in increasing the oil sorption from 3.5 g/g of sorbent to 6 g/g in the dry system [50]. In the same study, a similar observation was found for the mixture of oil in water system. It was argued that smaller particle sizes provided more surface area and available sites for uptake of oil. However, for a particle size smaller than 0.2 mm, the oil sorption declined. The main reason for this was suggested to be the lower amount of vacant space between the small particles as they fill these spaces more easily. This resulted in decreasing the available vacant sites in intra-particle spaces and plugging the open pores of the particles at the same time [50]. In a related study performed on barley straw, a similar result was observed. Different sizes of barley straw were collected using different sieve sizes. It was observed that the ideal particle size for various oil types was in the range of 250-500 μm . However, for particle dimensions greater and smaller than this size, the amount of oil sorption reduced. For the particle above this size, the lower oil sorption capacity was reported to be due to the lower surface area. For particles less than 250 μm , the reduction occurred due to pores and capillary blockage between the small individual fibers [51].

2.6.3 Contact time

Contact time refers to the duration that sorbates and sorbents are in contact with each other. It is the time when the sorbent soaks into the sorbate or the sorbate passes through the sorbent [52]. In a study performed on sugarcane bagasse, the oil sorption was calculated at five-minute intervals. It was found that the maximum oil sorption occurred at 15 min for both crude oil and oil in water situations. After 15 min, the amount of oil sorption remained the same due to saturation [50]. In a similar study on milkweed, cotton and PP, it was demonstrated that the maximum oil sorption was achieved approximately 5 min after the beginning of the experiment where saturation occurred at this point [14]. These studies claimed the amount of adsorbed oil remained the same after the

saturation time. In contrast, another study carried out on barley straw observed the oil sorption capacity began to decrease 15 min after starting the oil sorption experiment. This study was performed in an aqueous situation and claimed decreases in the amount of oil was mainly due to the water uptake of barely straw fibers after 15 min [51]. Therefore, based on past studies, it is clear that there is an ideal contact time to reach the maximum sorption capacity for flax straw which should be investigated. To date, the effect of the contact time on the oil sorption capacity of flax straw has not been reported.

2.6.4 Surface morphology

Surface morphology describes the quality of a surface and it is essential in the oil sorption process, as it has shown to have an effect on the sorption property [14,44]. In a study conducted on wool fibers, it was shown that the exceptional sorption capacity of this natural fiber was mainly due to the high amount of wax and uneven scaly surface [53]. In another study performed on the cattail fiber, the high degree of oil sorption was related to the irregular surface shape of cattail particles which provided enormous available spaces for retaining oil [40]. In an investigation performed on flax fibers, the oil sorption mechanism for flax fiber was shown to be similar to cotton owing to the irregular surface morphologies of these fibers [32]. While some natural materials such as wool, cattail and flax fiber have an uneven surface that contributes to their oil sorption capability, other fibers have smoother and more even surfaces. For instance, single cotton fibers, have been observed to mostly trap oil in twisted areas on the fiber surface rather than along the smooth parts of the fiber. However, this non-uniform distribution of oil on the surface of the fibers has a low impact on the overall oil uptake capability of cotton fiber [44]. A work conducted on milkweed fibers, observed different findings. Although milkweed fibers have circular and even surfaces, the oil sorption capacity was still high because of the availability of the lumens and the interaction of wax and oil on the surface of the sorbent [14].

2.6.5 Surface functionality groups

Functional groups are groups of atoms or molecules that are linked to each other and are responsible for chemical property and characteristics of a material. By monitoring the presence and changes of functional groups on the surface of the materials, some of the chemical and physical properties can be understood [54]. One of the important properties in oil sorption studies,

especially in the presence of water, is hydrophobicity properties of sorbents. This property is essential as less amount of adsorbed water will provide more available vacant space for oil to be adsorbed [51]. Cellulose has mainly hydroxyl groups on its surface, and these hydroxyl groups are hydrophilic. The second main component in natural fibers is hemicellulose. Hemicellulose has hydroxyl and acetyl functional groups on its surface. In contrast with hydroxyl functional groups, the acetyl groups are hydrophobic which tend to repel water. Although hydrophobic functional groups are available on the surface of hemicellulose, the dominant groups are hydrophilic hydroxyl groups, therefore the overall characteristic of hemicellulose is hydrophilic [55]. Lignin, the third most available compound in natural fibers, is shown to have little or no effect on water uptake of natural fibers [56]. Therefore, the primary issue of using natural fibers as an oil sorbent is related to the presence of hydroxyl groups on their surfaces. Various types of chemical treatments have been performed on different natural fibers to modify the availability of functional groups. For instance, the acetylation treatment involves removing the hydroxyl groups and replacing them with acetyl groups to make the sorbent more hydrophobic [57].

2.6.6 Surface wax

An important surface property of the natural sorbents is the amount of wax on their surfaces. In an oil sorption study on flax fiber samples with different moisture content and various wax amounts, a relationship between the amount of wax on the surface and oil sorption property was determined. It was observed that among two adsorption filters made from flax fibers with different wax concentrations, the one containing wax in an amount of 1.6 % dry basis adsorbed 36 % more engine oil in comparison with the sample with 0.5 % wax concentration [10]. In a similar study, the wax content of natural fibers was observed to be 0.60 %, 0.80 %, 10.64 % and 2.26 % for cotton, kapok, cattail and flax fibers, respectively. In the same study, it was claimed that a more considerable amount of wax content would suggest a more oleophilic property [58].

2.6.7 Sorbent density

Another parameter that effects the oil sorption capacity of natural sorbents is the sorbent packing density. The term “bulk density” should be differentiated with “packing density” which can be manipulated by either increasing or decreasing the weight of samples in a test cell with a fixed volume. The conventional approach for creating various samples with different packing densities

is by placing a known quantity of fiber in a fixed volume test cell, and calculating the packing density [12,45]. The bulk density is defined as the weight of loose sorbent per unit volume. In a study performed on oil sorption capacity of oak, cattail, corn and soybean with bulk densities of 348 kg/m^3 , 89 kg/m^3 , 168 kg/m^3 and 191 kg/m^3 , respectively, it was found that the sorbent with lower bulk density tended to adsorb more oil [59]. In a study carried out on kapok fibers, $1.75 \times 10^{-4} \text{ m}^3$ stainless steel mesh was employed, and kapok samples with different packing densities were prepared. After performing the oil sorption experiments, it was found that the kapok samples with $2 \times 10^4 \text{ g/m}^3$ packing density yielded the highest oil sorption uptake with almost 35 g of diesel oil per g of sorbent. This amount decreased to around 10 g/g of sorbent by increasing the packing density to $9 \times 10^4 \text{ g/m}^3$ [45]. In another study on oil sorption capacity of kapok fibers, various packing densities were also tested. It was observed that by increasing the packing density from 0.02 g/mL to 0.08 g/mL, the amount of adsorbed diesel oil decreased from 36.7 g to 10.8 g oil per gram of sorbent [12]. Although in several experiments the effect of packing density has been studied, in the majority of the literatures this factor has not been considered. In such studies, a certain amount of sorbent loosely is spread over the sorbate, and the oil sorption in a loose sorbent system is calculated [32,47,51,60]. In this study, the different packing density of flax straw along with the loose samples have been investigated.

2.7 Chemical treatment to enhance the sorption property

One major issue of using cellulosic-based sorbents is their tendency to adsorb water and moisture. This becomes a problem especially in an aqueous condition, where both oil and water exist. Uptaking more water suggests less available space for oil within the sorbent, and therefore less oil can be adsorbed. Consequently, one possibility to enhance oil sorption properties is to increase hydrophobicity through surface modification using different chemical or physical techniques such as sol-gel and acetylation.

2.7.1 Sol-gel

To produce superhydrophobic kapok fibers, a method termed sol-gel can be applied [18]. In this method, the fibers were treated with various chemicals with the aim of removing the surface wax in an effort to expose the hydrophilic hydroxyl groups on the surface of fibers (Fig. 2.4). These free functional groups were then introduced with silica nanoparticles throughout another chemical

treatment. Silica nanoparticles bonded with functional groups on the surface of fibers creating a hydrophobic coating. Based on FTIR results, it was reported that the -OH hydroxyl groups from the surface of kapok fibers were eliminated and replaced by hydrophobic silica nanoparticles. Experiments were performed for different oil in water mixtures. The result of oil sorption experiments in aqueous situations showed a 22 % increase in oil sorption for soybean oil, 42 % increase for diesel oil and 32 % increase for gasoline [18].

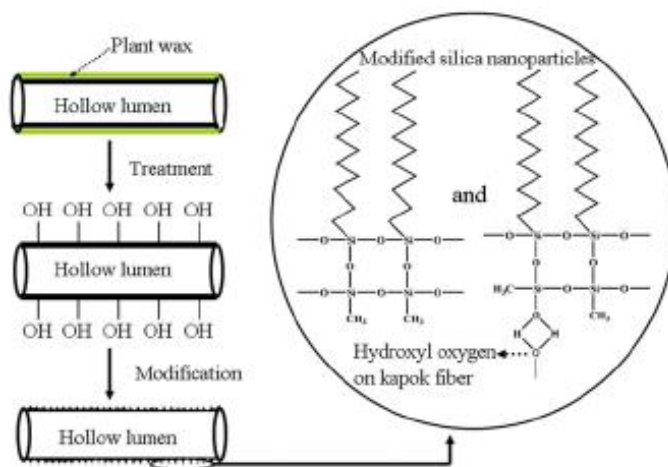


Figure 2.4. Schematic steps for creating hydrophobic kapok with sol-gel method [18].

2.7.2 Acetylation

A second proposed chemical treatment for surface modifications of natural fibers is a technique called acetylation. Acetylation is a process where the hydrophilic hydroxyl groups available on the surface of the natural fibers are removed and replaced by acetyl groups ($\text{CH}_3\text{COO}-$) making the material hydrophobic (Fig 2.5) [57].

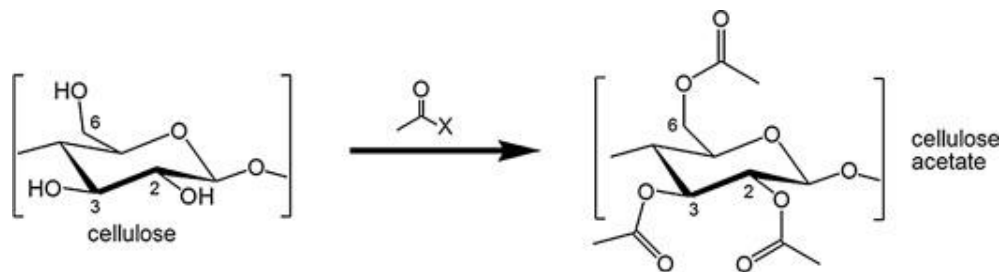


Figure 2.5. Schematic of acetylation treatment on celulosic material[61].

In the literature, various acetylation techniques have been proposed [20,50,62]. Among them, is the common catalyst used for the chemical treatment, N-Bromosuccinimide (NBS) [50]. NBS is a practical yet inexpensive chemical that is proven to be a proper catalyst for the acetylation process [63]. Prior to the use of NBS, 4-dimethylamino pyridine (DMAP) had been used which is expensive and not commercially available [64]. Besides being a catalyzer, the concentration, temperature and time play an important role in the chemical treatment. In a study on oil sorption behavior of raw and acetylated sugarcane bagasse, the different parameters on acetylation were investigated to determine the optimum results. In this study, a certain amount of sugarcane bagasse was placed in a flask containing 300 mL acetic anhydride with 1 % NBS and without NBS. The flask containing the mixture of fiber, acetic anhydride and NBS was then placed in an oil bath. The experiment was repeated for various temperatures ranging from 25°C to 130°C for different durations ranging from 30 min to 67 h. After the process, acetylated sugarcane bagasse was removed from the flask, washed with acetone and ethanol and oven-dried for 16 h at 60°C. It was found that performing this treatment at 130°C for one hour yielded the highest oil sorption result of 20.2 g/g for acetylated sugarcane bagasse with 1 % NBS compared to 6.8 g/g for acetylated sugarcane bagasse without NBS [60].

Acetylation treatment has also been performed on flax fiber to improve its properties in composite production [21,35]. One of the main issues of using natural fibers in composites is their tendency to absorb moisture. Moisture absorption decreases the composite strength in the long term. Bledzk *et al.* [35] introduced raw flax fibers to different acid concentrations for acetylation treatment. Acetylated flax fibers exhibited up to 50 % decrease in their moisture adsorption [35]. To the best of authors knowledge, there has not been any research done on acetylation of flax straw for use as an oil/water sorption material.

2.8 Sorption characteristics of natural sorbent

Sorption characteristics of a sorbent is not only limited to the amount of oil it can absorb, but water uptake, reusability and retention properties should be taken into consideration. In the literature, scattered studies have reported these properties as a result of availability of various measuring methods. The following are a summary of some conventional approaches and results obtained.

2.8.1 Oil uptake

One of the most common methods of calculating the oil uptake is to spread a certain amount of sorbent over the surface of a sorbate and calculate the amount of adsorbed oil per gram of sorbent. Yunhua Cui *et al.* [47] spread 0.5 g of cattail fiber over 100 mL of oil. After 1 min, the fiber assembly was removed from the beaker and suspended in filter gauze for 15 min. Next, the fiber assembly was re-weighted, and the amount of adsorbed oil was calculated. The sorption capacity was calculated by dividing the mass of adsorbed oil to mass of dry fiber assembly. In another experiment, Shengbin Cao *et al.* [40] wrapped 1 g of the sorbent with yarn and placed the assembly in an oil sample for 15 min. The assembly was then removed from the oil bath and placed on a stainless steel mesh and allowed to drip for 15 min. The sorption capacity was calculated based on the mass of assembly before the experiment and after dripping stopped. Tijani *et al.* [20], followed a slightly different method to calculate the amount of liquid within the solid sample. For the oil sorption experiment, 5 g of sorbent was thoroughly mixed with 50 mL of oil in a beaker. The mixture was then passing through a stainless-steel mesh No. 60 and No.80 to separate the sorbent from the oil. The sorbent was then left on the stainless-steel mesh for one hour, while the oil was collected in a beaker underneath the stainless-steel filter. The sorption capacity was then calculated based on the weight difference of the sample before and after the experiment.

Regarding the mentioned methods, three important points need to be highlighted. Firstly, the possibility of experimental errors in the oil sorption tests are high due to the oil that adheres to any test containers, mesh or pad. One of the approaches to minimize such errors would be to increase the amount of sorbent used in the experiment. In this way, the amount of sorbent is high enough to minimize the probable errors. The final result would not vary significantly with other studies since the oil sorption is reported based on gram of adsorbed oil per gram of sorbent. Secondly, using any fabric to fabricate or construct the sorbent will affect the sorption results as the fabric is also capable of oil sorption. Therefore, to shape a sorbent a metal wire is proposed as it has low effect on oil sorption. Finally, the mesh size is an important consideration when it is used as a filter in the oil sorption experiments. Oil is a viscous material with a high cohesion between its molecules. During the use of the small mesh size, the oil becomes trapped within the mesh openings, plugging them. By increasing the size of mesh, part of the loose sorbent passes through the mesh and results in inaccurate data. Thus, matching the sorbent particle size with mesh size is

essential. In this study, the above points are considered to accurately perform the sorption experiments accordingly.

2.8.2 Oil/water selectivity

Another important parameter in oil sorption is the sorbent ability to uptake oil in the aqueous environment. To simulate the oil spill in seawater under practical conditions, most of the literature uses artificial sea water which is a mixture of distilled water and commercially available mineral salt [51,53]. However, different approaches throughout the literature for the water uptake experiments have been followed. For example, Hussein *et al.* [51] mixed 40 g of oil with 500 mL of artificial seawater. After spreading 1 g of sorbent over the oil surface, the system was placed in a shaker for 15 min at 105 cycle/min. Next, the sorbent was suspended for 5 min to allow the excess oil and water to drain. The amount of adsorbed oil and water was then calculated. After introducing a small amount of ether to help extract the oil, the wet samples were compressed to extract the oil, water and ether. After evaporation of the ether, the mixture of oil and water was separated using a centrifuge. The oil and water selectivity were calculated by measuring the amount of water and oil within the centrifugal tube. Behnood *et al.* [50] followed a similar procedure for oil/water selectivity but used a static system. For instance, 50 g of oil was mixed with 100 mL of artificial seawater. After a specific sorption time, ranging from zero to 60 min, the sorbent was removed from the mixture and hung within a net over the beaker for 5 min to drip the excessive oil. The oil uptake was calculated by weighting the remaining oil in the beaker. It is worth mentioning that since the density of oil is less than water, the oil will float on the surface of the water. Stirring the system continuously during the oil/water selectivity experiment seems essential for increasing the accuracy of the result as it allows the sorbent to be in contact with both oil and water at same time.

2.8.3 Water uptake

The water uptake test can be used to determine the degree of hydrophobicity. Pries *et al.* [65] studied the relation of acetylation degree with water uptake. He found that the water uptake of acetylated wood dropped from around 85 % to 70 % percent. Loong *et al.* [21] also studied the effect of acetylation of flax fibers. It was revealed that by increasing the degree of acetylation, the water uptake decreased from 23 g/g to 10 g/g after 5 h of the test. In this study, two treatments will

be performed on raw flax straw, and this test will compare the hydrophobicity of the samples.

2.8.4 Reusability

Reusability of a sorbent is an important consideration for industrial oil spill cleanups due to both economic demands and severe ecological sustainability purposes [66]. Reusability is calculated by subjecting the sorbent into multiple sorption-desorption cycles. Tijani *et al.* [50] performed reusability experiments on oat straw. After performing one oil sorption experiment on an oat straw sample, the sample was compressed using a piece of cloth in order to drain the adsorbed oil out of the sorbent. This cycle of sorption/desorption was repeated six times. The result illustrated a gradual decline in sorption capacity from 6.4 g/g to 5.2 g/g. Ansari *et al.* [32], followed a more precise method for calculating the reusability of flax fibers. After performing the oil sorption test within an oil/ water mixture, the samples were removed and dried at room temperature under a fume hood for 24 h and 48 h. After evaporating the water from the samples, the sorbent was squeezed between two rollers at a pressure of 10^5 kgf/m. The sorption-desorption cycle was repeated three times and the results showed a reduction in the oil uptake of 20.53 g/g, 13.93 g/g and 11.80 g/g for the first, second and third cycles, respectively.

One important consideration in reusability tests is to define the amount of force required for compressing the oily sorbent. The different force applied will vary the amount of oil retained in the sorbent which can affect the oil sorption capacity in the next cycle. Therefore, it is important to clearly define this force.

2.8.5 Oil retention

Retention is the ability of a sorbent to maintain the sorbate within its bulk for a certain amount of time. It is an important factor after oil sorption practices since the sorbent is subjected to further handling and delivering for recycling or to landfills. Yunhua Cui *et al.* [47] calculated the oil retention rate of a cattail assembly. After performing the oil sorption experiment, the cattail assembly was suspended for 24 h to allow the oil to drain out of the sample. The weight of sample after 24 h was determined for its oil retention capability. The oil retention capacity for the cattail fiber assembly was obtained over 95 % for both engine and vegetable oil. Shengbin Cao *et al.* [40] followed a similar method where the assembly of kapok fibers was left on a stainless steel mesh

for 24 h after the oil sorption experiment, and the calculated oil retention rate was 90 % for this assembly.

2.9 Structural characterization

In addition to the sorption characteristics of natural fibers, surface morphology and chemical composition require analysis. Understanding these properties will help researchers acquire in-depth knowledge of the sorption process and mechanisms. Furthermore, it is helpful to compare and monitor the changes of sorbent structure, chemical composition, surface morphology and topography after any chemical treatment.

2.9.1 FTIR

Fourier-transform infrared (FTIR) spectroscopy is a technique to determine characteristics of specific types of bonds, and therefore can be used to identify whether a specific functional group is present in the material [67]. In this method, infrared radiation is emitted to the sample. By calculating the amount of light that is either adsorb or emitted from the sample, and by using the Fourier-transform to translate these data to wavelengths, the chemical composition of an organic or inorganic compound can be determined [68]. Moreover, by comparing the FTIR result for different chemically treated samples, monitoring changes in the functional groups is possible. Sun *et al.* [60] used FTIR to determine the degree of acetylation of sugarcane bagasse. It was observed that the stretching band at a wavelength of 3436 cm^{-1} (as the indicator of -OH hydroxyl group) decreased.

2.9.2 TGA

Thermogravimetric analysis (TGA) is a method to determine the thermal stability and decomposition temperature of a compound. In this technique, the percentage of mass loss is obtained as the sample is heated to elevated temperature under an inert atmosphere at a constant rate [69]. Some studies have been conducted on thermal stability analysis of natural fibers to evaluate the effect of the acetylation treatment. For instance, Nwankwere *et al.* [70] compared the TGA result of raw and acetylated rice husks. The test temperature range was 30-600 °C. It was found that the thermal stability of acetylated samples decreased above 170°C due to hydrogen bonds being disintegrated. Teli *et al.* [62] performed TGA tests on acetylated banana fibers to

investigate the effect of acetylation. The test temperatures ranged from 30-550 °C. The weight loss of the samples at 250°C was 7.39 % and 10.59 % for raw and acetylated samples, respectively. At 350°C, weight loss was 35.67 % and 65.18 % for the raw and acetylated samples, respectively. It was found that the thermal stability of acetylated banana fiber was lower than raw fiber due to the acetylation treatment.

2.9.3 SEM

Scanning electron microscopy (SEM) is a technique where the surface of the specimen is bombarded with a focused beam of electrons to create a surface image. Briefly, a heated filament generates the electrons and these electrons are directed to the specimens using a magnet. The reflected electrons or x-rays from the sample are collected using a detector to form an image. Two main results obtained from SEM which are important for understanding the behavior of natural sorbents are: topography and morphology. Calado *et al.* [71] studied the effect of an acetylation treatment on the surface of coir fibers. Comparing the SEM images of treated and untreated coir fibers, it was found that the outer layer of the untreated fibers mainly consist of uneven distributions of organic matter (Fig 2.6a). This material was removed by the use of a chemical acetylation treatment (Fig 2.6b). By removing the outer layer, the rougher and ordered structure of coir fiber was revealed.

In a similar study, the SEM photos of flax fibers before and after the acetylation treatments were compared. It was observed that the surface of raw flax fiber was rough mainly due to the high amount of wax on the surface (Fig. 2.7a). This layer of wax disappeared in the acetylated samples. The exposed surface of fiber was smoother but small amounts of wax remained on the surface. Another observation was the “bamboo” shape nodes on each fiber that had been developed during the growth (Fig 2.7b) which are not visible in the untreated samples [21].

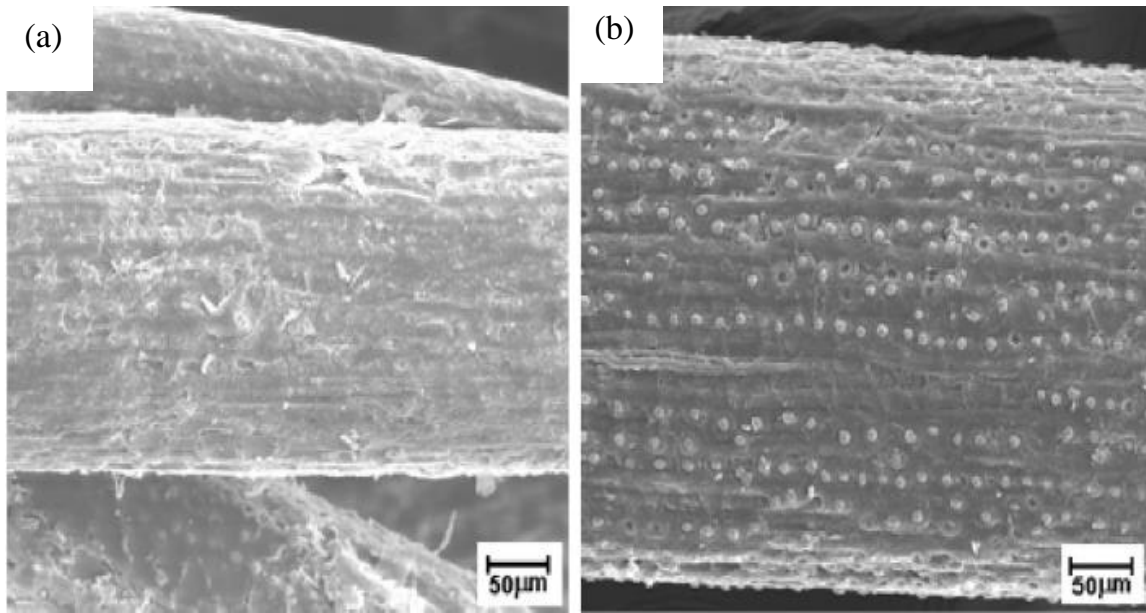


Figure 2.6. SEM image of untreated coir fiber (a) and acetylated treated coir fiber (b) [71].

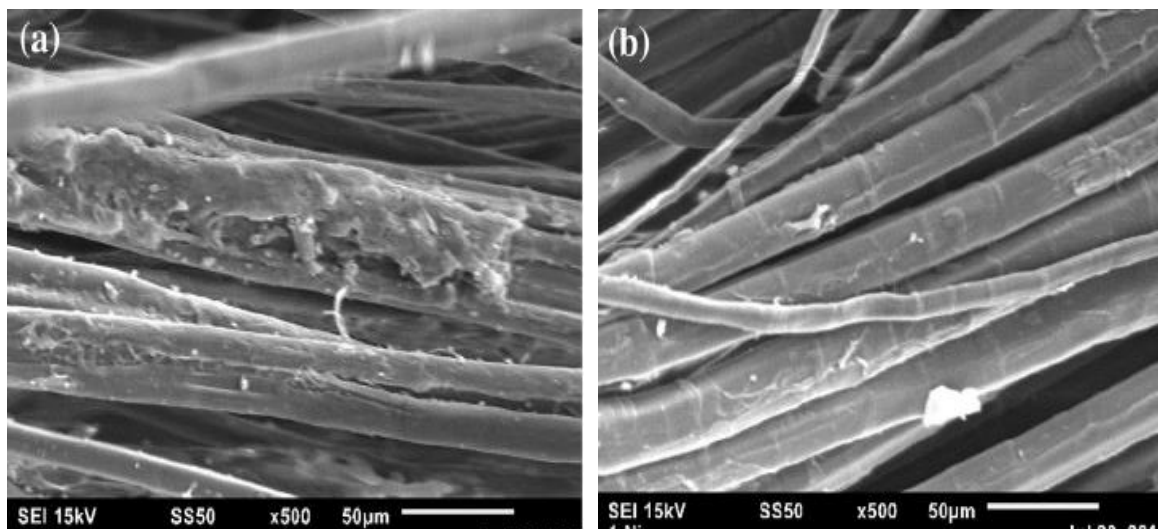


Figure 2.7. SEM photo of untreated flax fiber (a) and acetylated treated flax fiber (b) [21].

2.9.4 Summary

The literature review showed that natural fibers have a potential to be employed as an oil sorbent. Also, the oil sorption mechanisms of natural fiber have been studied as well as the effective parameter on their sorption capacity. Among the natural fiber, flax fibers revealed a promising oil sorption capacity of up to 33 g/g when only oil was present as a sorbate. This amount can be

compared with the synthetic and commercially available oil sorbents. However, the process of fiber extraction from the plant stem is costly. Hence, in the current study, the possibility of sorbent preparation using the whole stem, which is a by-product of linseed oil production and widely available in Canada, is examined. Another issue of employing a plant-based material as an oil sorbent is their tendency to adsorb water in an aqueous situation. This occurs due to high hydrophilicity of cellulose and hemicellulose, the main ingredient of plant base materials. To address this issue various chemical treatments have been applied and examined on natural fibers using acetylation and sol-gel methods. A few studies have been done on acetylation of flax fiber in order to decrease its hydrophilicity. However, no studies have been conducted for decreasing the hydrophobicity of flax straw using chemical treatments. This research gap was the main motivation to study the flax straw for its oil sorption and to find any possible method to enhance this property.

CHAPTER 3

MATERIALS AND EXPERIMENTAL METHODS

The materials, sample preparation, experimental procedure and testing and characterization techniques are explained in this chapter to achieve the objectives of this study. The experimental methods are either novel or have been modified from works of other researchers.

3.1 Materials

The materials in this study were provided by different suppliers. Flax straw was received from Biolin Research Inc. (Saskatoon, SK, Canada). Biolin is a local research company which has been working on various applications of flax plants for several years. The flax straw was collected from Bethune, Saskatchewan, Canada. The average length of the plant at the time of harvest, as per vendor information, was around 0.55 to 0.60 m. The plant was cut from around 0.10 m above the soil, and the average length of the as-received flax straw was around 0.45 m (Fig.3.1a). The processed flax fiber provided by Biolin is shown in (Fig.3.1b). The bulk density of the flax straw and flax fiber were examined in two situations: lost filled and packed filled. The density was between 25.6 and 97.2 kg/m³ for flax straw and between 15.3 kg/m³ and 76.5 kg/m³.

Two oil types used in this experiment were ordered from Fisher Scientific TM (Ottawa, ON, Canada): heavy oil and light oil. The viscosity and density of heavy oil was 34.5 to 150.0 mm².S⁻¹ and 0.83 g/mL, respectively, while the light oil was 3.0 to 34.4 mm².S⁻¹ (NF) and 0.83 g/mL respectively. For the acetylation process, acetic anhydride and N-Bromosuccinimide (NBS) were both purchased from Fisher Scientific TM with a minimum assay of 97 %. The boiling point of acetic anhydride which is an essential consideration in performing a safe acetylation, was 140 °C. The NBS was received in 100 g bottles with 99 % assay, and the color of the powder was white to light yellow. Sea salt for producing artificial seawater was ordered from the Lake Product Company LLC (Florissant, MO, USA) and received in a 100 g plastic container. As per vendor specification, the product meets standard ASTM D1141-98 (2013) which is standard practice for producing a substitute for ocean water [72]. Boiled linseed oil was ordered from Fisher Scientific TM and it was received in 500 ml packaging.



Figure 3.1. Sample batch of as-received flax straw (a) and processed flax fiber (b).

3.2 Chemical analysis of flax straw and flax fiber

Samples of both flax straw and flax fiber were sent to Feeds Innovation Institute at the University of Saskatchewan for analysis of the chemical composition and moisture content. The amount of cellulose, hemicellulose and lignin was determined using Ankom (Macedon, NY, USA) 200 fiber analyzer. The acid detergent fiber (ADF) and neutral detergent fiber (NDF) was determined using Ankom Method 5 [73] and Ankom Method 6 [74], respectively. The amount of lignin was determined using ANKOM Method 8 [75] and the percentage of cellulose and hemicellulose calculated using equation 3.1 and 3.2, respectively.

$$\text{Cellulose} = \text{ADF} - \text{Lignin} \quad (3.1)$$

$$\text{Hemicellulose} = \text{NDF} - \text{ADF} \quad (3.2)$$

The moisture, fat and ash contents were calculated according to Association of Official

Analytical Chemists (AOAC) standard [76].

3.3 Sample preparation

Raw, linseed oil coated and chemical treated straw were prepared. Initially, raw straw was washed, oven dried, cut and untreated or treated with chemical and physical techniques.

3.3.1 Purification and drying of the straw

Sample preparation consisted of batches of around 150 grams flax straw (as-received) which was weighted to calculate the mass of dry matter using equation 3.3. The straw was then thoroughly washed with distilled water to remove any dirt, mud or foreign particle from the straw. The batch was then left on a strainer in open air for one hour allowing the water to drain out of the straw. The batch was weight again to determine the amount of water adsorbed based on the equation 3.4. Next, the batch was dried in an oven at 65°C for 24 h using a Blue M Constant temperature cabinet to remove any remaining water. The weight of straw was recorded every two h to estimate the moisture content of the sample until it stabilized. After 24 h, the dry weight of the straw was recorded, and moisture content of the dried batch was calculated based on the equation 3.4.

$$W_d = W_t \left(1 - \frac{M_w}{100}\right) \quad (3.3)$$

$$M_{w_i} = 100 \times \left(1 - \frac{W_d}{W_{t_i}}\right) \quad (3.4)$$

Where W_d is weight of dry matter in the sample (g), W_t is total weight of material considering both moisture and dry matter (g), M_w is the wet basis moisture content and subscript “i” is an indicator of time ranging from 0 to 24 h. After drying the straw was cut to size. The best practice for cutting flax straw was determined to be right after oven drying while they still have a low moisture content.

3.3.2 Cutting

Before any treatment on the sample occurred, the untreated straw was cut in small pieces using two approaches as shown in figure 3.4. The first approach was to use a multi-blade scissors which consists of a total of five scissors connected to each other side by side with a 2 mm gap between them (Fig 3.2).



Figure 3.2. Digital image of the multi-blade scissors.

The second and more efficient approach for cutting the flax straw samples was to use a Retsch knife milling (Haan, Germany) (Fig 3.3a). There are two variables in this machine that must be established: the gap between the rotating and fixed blades and the sieve size located underneath the blades (Fig 3.3b). The distance between the rotary and fixed blades was set to 2 mm. The sieves available had square opening shapes with dimension of 4 mm x 4 mm, 6 mm x 6 mm and 8 mm x 8 mm. The machine functions by feeding the straw from the top as shown in (Fig 3.3c). The straw is then pushed into the rotary blade where the blades cut the straw by applying shearing and compression forces. The cut and crushed particles pass through the sieve located at the bottom of the machine and collect into a metal container fastened underneath the machine. Since the best result for cutting will be acquired when the straw has a low moisture content, it is important to use the dry straw that is stored in the desiccator or has just been removed from the oven. An initial oil sorption experiment was performed on the various cut sample to investigate the efficiency of the proposed cutting methods (Fig 3.4).

3.3.3 Sieving

Two methods for sieving were proposed for this experiment. The first method was to utilize a selection of sieves with different size openings, and the second method was to rely only on the sieve from the Retsch knife milling machine. For the first method, six different sieves with sizes 3.36 mm (No. 6), 2.38 mm (No. 8), 1.68 mm (No. 12), 1.19 mm (No. 16), 0.84 mm (No. 20) and 0.59 mm (No. 30) were selected. The progression of the sieve size was square root of two inspired from the ISO standard sieve series for common use [77]. The sieves were placed on top of each other so that the size decreased from top to bottom. For each run, 50 grams of cut samples were

placed on the top sieve and the sieves were mounted into the sieve shaker. While the machine was shaking the sieves in a horizontal plane, the metal hammer located at the top was impacting the sieves in the vertical direction as well (Fig 3.5). The hammer impact helps the particles pass through the top sieves and dropping them into the next sieve. The sieving duration was set to 3 min which was sufficient time for the particles to pass through the different levels of sieves.

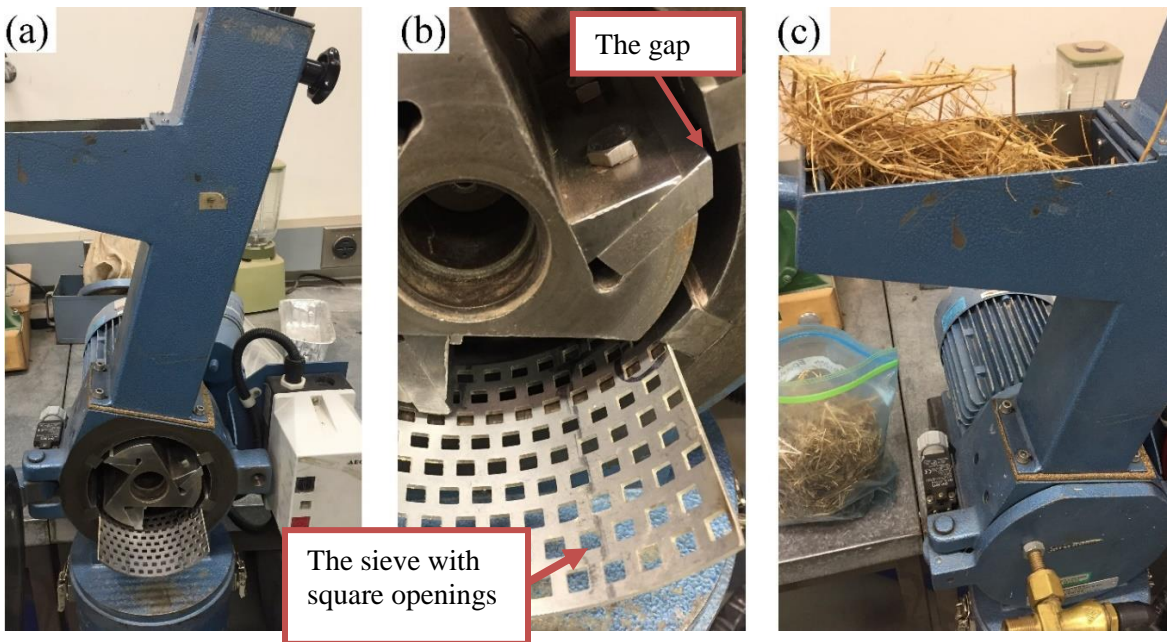


Figure 3.3. Retsch knife milling machine (a), fixed/rotary blades and 8 mm sieve (b), feeding the stock from the top (c).

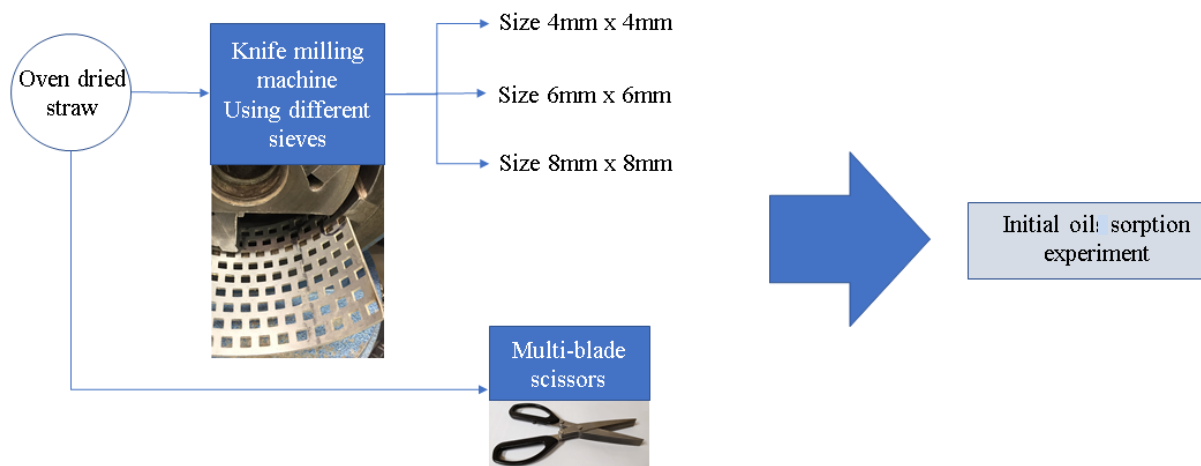


Figure 3.4. Schematic of cutting procedure showing the knife mill versus the scissors.

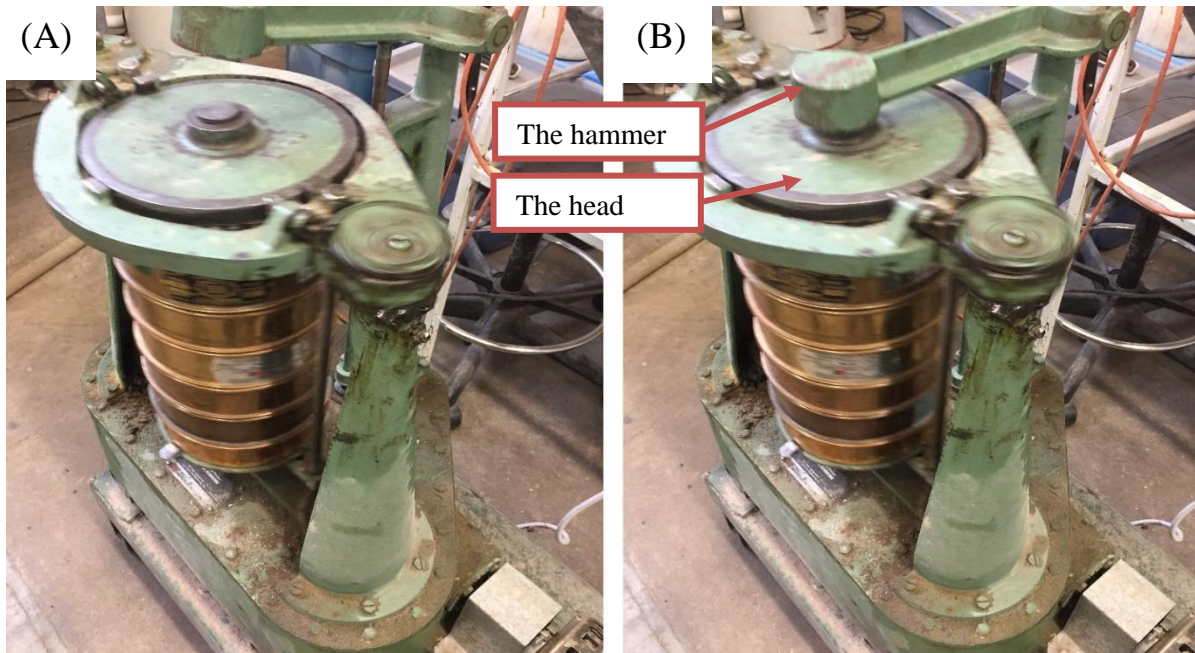


Figure 3.5. The different position of hammer, fully open at (a), compacting the head (b).

As an alternative option to sieving, the sieve mounted onto the knife milling machine was used. Each time around 4 grams of washed and oven dried flax straw was fed into the machine and cut using a sieve size of 6 mm x 6 mm. Each 4-grams was pulverized individually and kept in plastic bags without mixing with other cut samples (Fig 3.6). By following this method, it was ensured that each of the 4-gram samples would represent the same shive to fiber ratio as the straw. The sample made by this method are referred to as 4-gram samples in the remainder of this study.



Figure 3.6. Individual packages for each cut sample containing the sample fiber to shive ratio.

3.3.4 Raw and treated sample preparation

The samples acquired after sieving are considered as untreated samples and are referred to as ‘raw’ samples in the remainder of this study. Two methods of treatment were selected: an acetylation chemical treatment and a novel coating method using linseed oil as shown in figure 3.7.

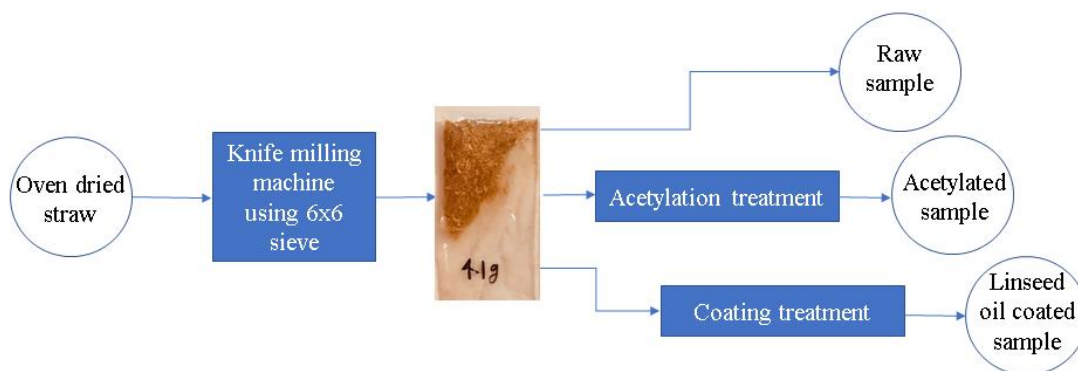


Figure 3.7. Schematic of sample preparation methods for raw, acetylation and linseed oil coating treatment.

For the acetylation process, 300 g of acetic anhydride were mixed with three grams of NBS within a 500 ml round bottom flask. The flask was placed into the oil bath on the hot plate magnetic stirrer. The system was maintained until the temperature of the mixture in the flask and oil bath stabilized at 110°C. About 16 g of raw samples (content of four bags) were placed inside the flask along with a magnetic stirring bar to speed up the reaction rate. A reflux condenser was fitted onto the flask to allow the evaporated acetic anhydride to condense back into the flask. The pressure was atmospheric, and the treatment was performed under the fume hood for safety purposes (Fig 3.8). After one hour, the flask was detached from the condenser and the samples were removed and washed thoroughly with acetone and ethanol. The acetylated samples were initially left under the fume hood for 24 h to evaporate the liquids within the samples followed by oven drying at 60°C for another 24 h to obtain the same moisture content as other samples.

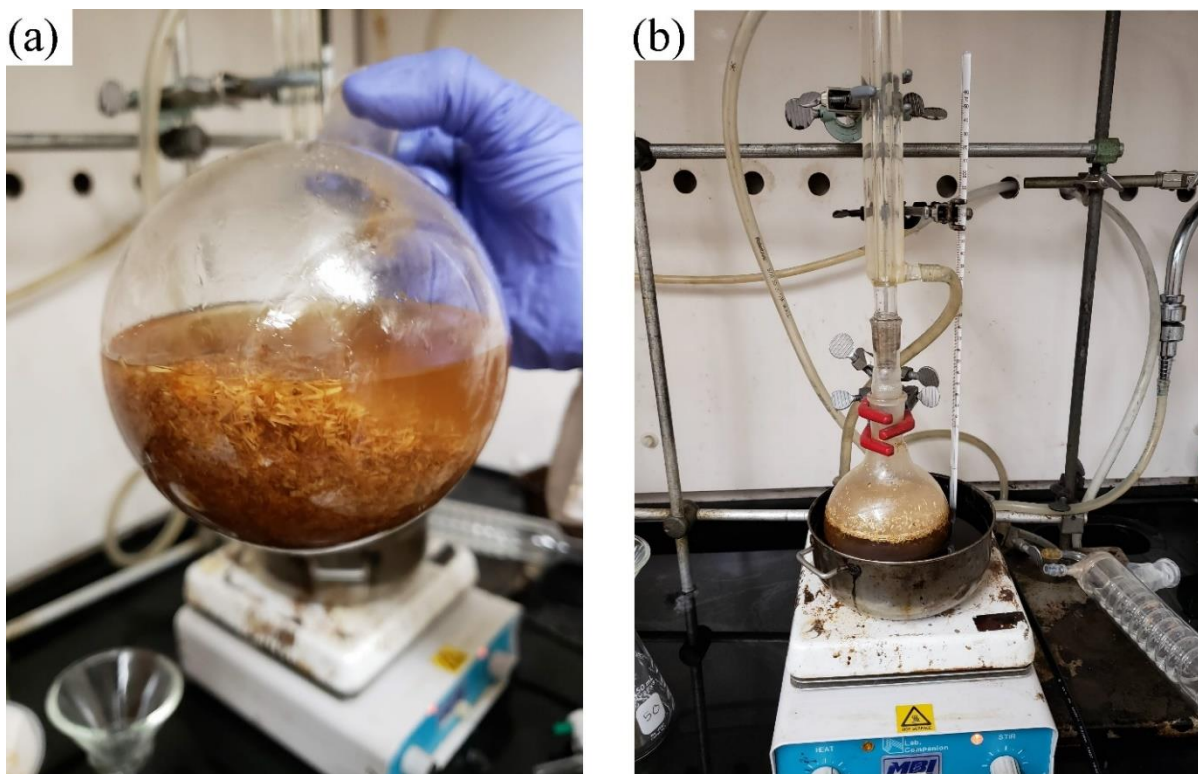


Figure 3.8. The raw samples immersed in acetic anhydride (a) and acetylation setup (b).

The novel coating method used linseed oil as the coating agent. Each time, a batch of 4 g sample was soaked into the linseed oil until all particles were immersed. The wetted samples were immediately removed from the oil and placed inside a centrifuge machine. The centrifuge was a modified juice extractor (Fig 3.9b). The model of the appliance was Gourmia GJ750 with a 850 W motor. For modification, a sealing washer made of polytetrafluoroethylene (PTFE) was attached to the top of the rotating strainer using a two-part adhesive epoxy (Fig 3.9a). This washer acted as an obstacle against the particles moving up toward the edge of the v-shape strainer during high rotational speeds. The oily sample rotated inside the machine for 1 min at a low speed based on vendor specifications equal to 6000 rpm. At this rotational speed and with the particles applying force upward to the washer, there was a possibility of the washer detaching from the strainer at high speed and creating a dangerous situation. Therefore, for safety reasons, the strainer edge was cut and bent onto the washer surface at three points to hold the washer in place (Fig 3.9c). The samples were then removed from the strainer and left at room temperature for 24 h to air dry, and then they were oven dried for another 24 h at 60°C to gain the same moisture content as the other samples.

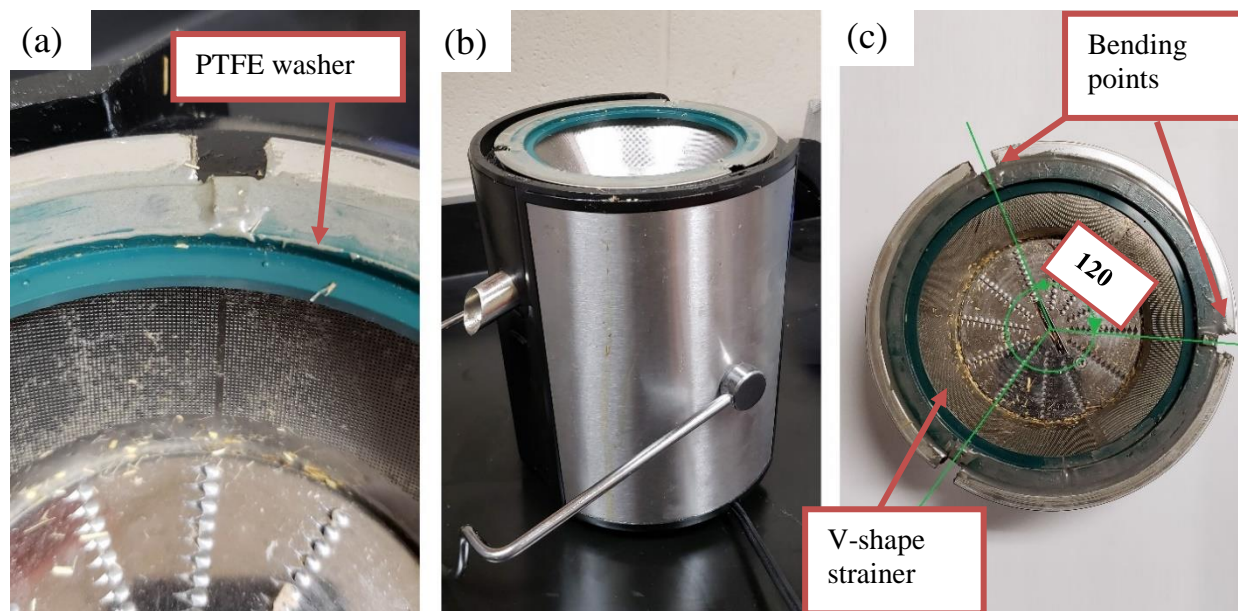


Figure 3.9. The PTFE washer attached to the strainer (a), The Gourmia GJ750 juice extractor (b), and the v-shape strainer and the bending locations (c).

3.4 Experimental procedure

The effect each parameter (particle size, density and shive/fiber ratio) on oil sorption property of raw samples was studied. The initial experiments are summarized in the figure 3.10.

3.4.1 Effect of particle size on oil sorption

In order to study the particle size effect on oil sorption capacity of flax straw, oil sorption experiments were performed on different particle sizes, acquired from the sieving process as explained in section 3.3.3. The procedure for the oil experiment was the same as explained in the section 3.5.1. The experiments were performed using both light and heavy oil to study the effect of oil viscosity.

3.4.2 Effect of density on oil sorption

The bulk of oil sorption takes place in the intra-particle space of the sorbent. By packing more material within a certain volume, it can be argued that the intra-particle spaces would decrease as the flax particles are compacted into each other. Three different samples with different compaction levels (low, medium and high) were produced to examine the effect of sorbent packing density on

the oil sorption capacity. The raw straw was the pulverized samples using the 6 mm x 6 mm sieve. The different sorbent packing densities were achieved by filling 3.5, 5.5 and 7.5 g of cut flax straw into the mesh bottles made of stainless steel mesh size 0.15 mm and plastic centrifuge tubes (Fig 3.11). The bottle height was 80 mm while its internal diameter was 20 mm. The density of the samples was calculated considering the volume of the bottles and weight of the material inside each of the bottles. For oil sorption tests, the sorbent filled bottles were initially weighted and immersed into a beaker containing 300 ml of heavy oil. After 15 min, they were removed from the beaker and held over the beaker for 30 s allowing excess oil to drain. The bottles were then reweighted, and the amount of adsorbed oil was calculated based on the equation 3.5.

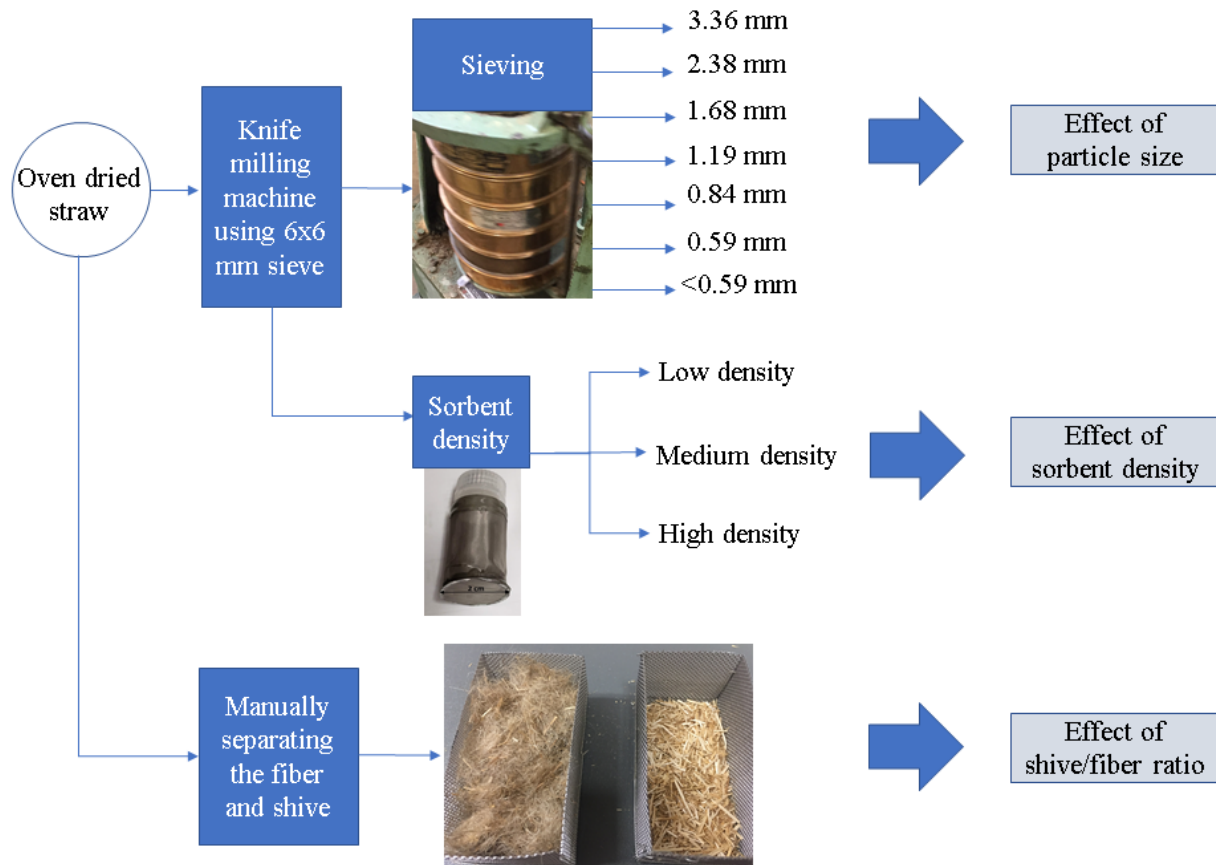


Figure 3.10. Schematic steps of investigating the effective parameter on oil sorption.

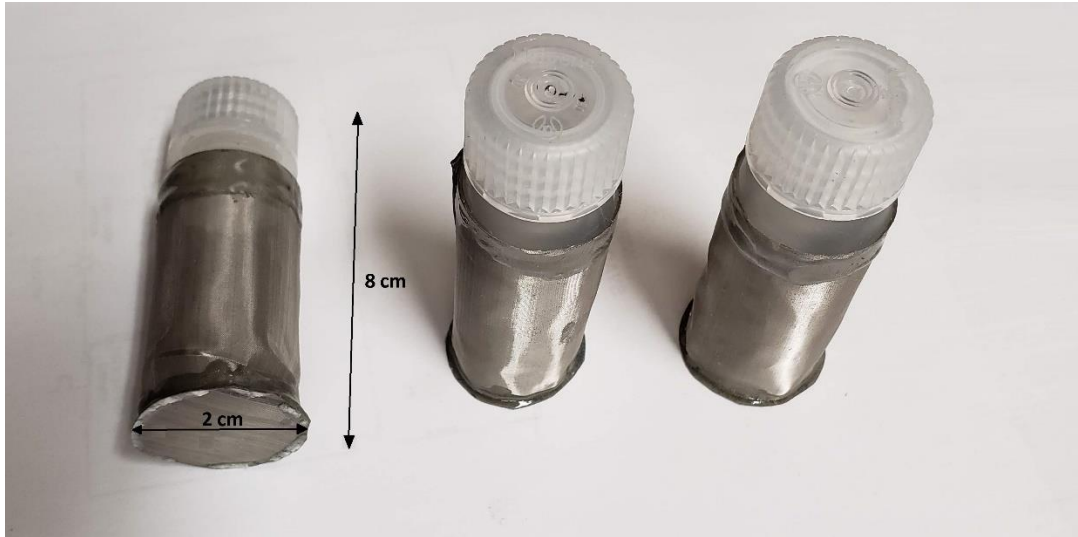


Figure 3.11. The mesh bottles used for studying the effect of density on oil sorption.

3.4.3 Effect of flax fiber and shive on oil sorption

To realize the effect, of oil sorption capacity of pure flax fiber and flax shive, oil sorption experiments explained in the section 3.5.1 were performed on two different samples: pure fiber and pure shive (Fig 3.12 a). The shive samples were made by crushing the stem of flax with a small hammer and manually separating the shives from fiber. This method was inspired by the manual method of separating fiber from straw for textile purposes. The flax fiber samples consisted of 4 grams of as-received pure fiber, and the flax shive sample was 4 grams of shives (Fig 3.12 b).

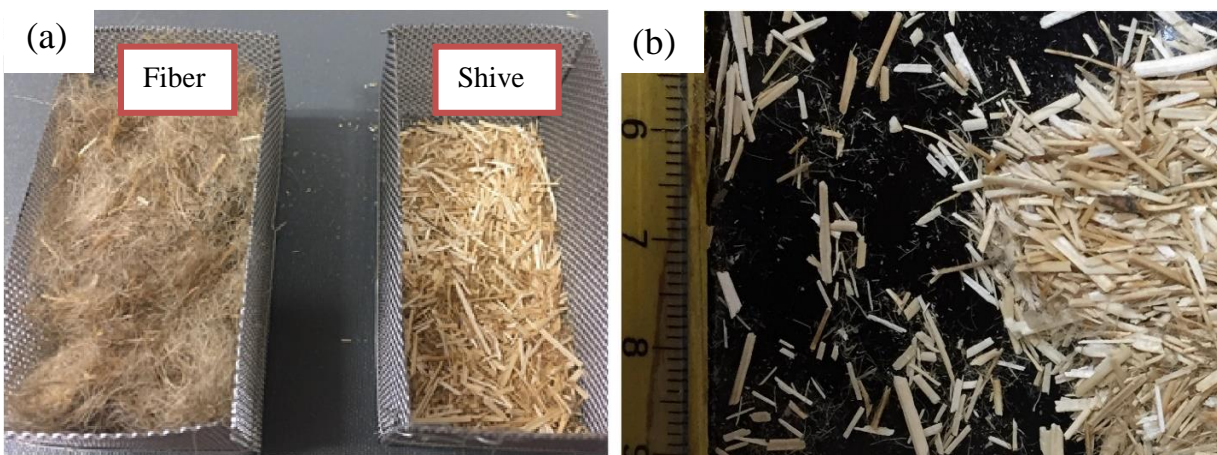


Figure 3.12. The baskets containing flax fiber (left) and flax shive (right) (a) and manually separated flax shives (b).

3.5 Characterization of untreated and treated samples

The effectiveness of two proposed treatments (acetylation and linseed oil coating) on flax straw were investigated, and the result compared with the untreated flax straw. The summarized procedure of sample preparation and the area of comparison are provided in figure 3.13.

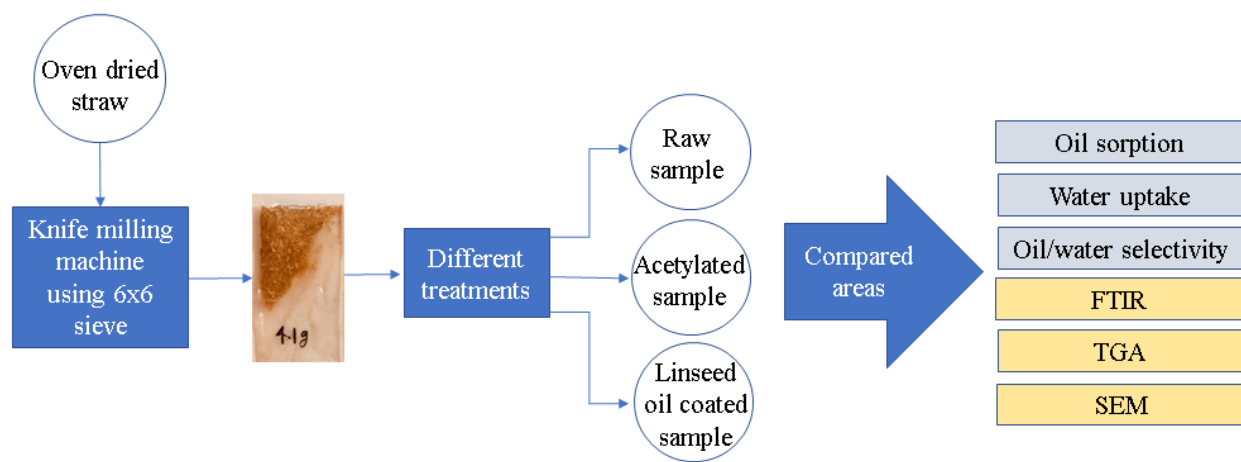


Figure 3.13. Schematic for the summarized methods for treated and untreated samples.

3.5.1 Oil sorption experiment

The oil sorption capacity of raw, acetylated and linseed oil coated samples were compared. The oil sorption experimental method ASTM F726 – 17, was followed as a guideline [78]. Based on this standard for loose sorbents (Type II), the sorbent material should be a minimum weight of 4 grams. Raw and treated flax straw samples obtained from milling or sieving were placed in a cuboid basket made of stainless-steel mesh No.20 (0.841 mm opening). Based on ASTM the loose sorbent should be able to freely float within the test cell in sorbate media, therefore the dimensions of the basket were $50 \times 90 \times 40$ mm (length \times width \times depth) to meet this requirement (Fig 3.12a). The 4-gram sample was placed in the rectangular basket and lowered into the circular trough containing 450 mL of oil (Fig 3.14a). The diameter of the ceramic trough was 140 mm while the height of oil was approximately 30 mm. The shive/oil sample within the basket was slowly mixed using a spatula to ensure all the shive particles were immersed in the oil sorbent (Fig 3.14b). After 15 min of soaking the basket was removed from the oil and held on top of the trough to allow excess oil to drain. After 30 s, the basket containing the oily sample was weighted and the weight

of oily sample was calculated by subtracting the weight of empty basket. The experiments were performed on both heavy and light oil to study the effect of oil viscosity. According to ASTM, each experiment must be repeated three times and the result of each run shall be within 15 % from the mean. The weight of adsorbed oil was the difference in weight of the samples before and after the experiment. Oil sorption capacity of samples was calculated using the equation 3.5.

$$\text{Oil sorption capacity} = \frac{m_w - m_d}{m_d} \quad (3.5)$$

Where, m_w is the weight of the oily sample after 30 s of drainage (g), and m_d is an initial dry weight of the sample (g).

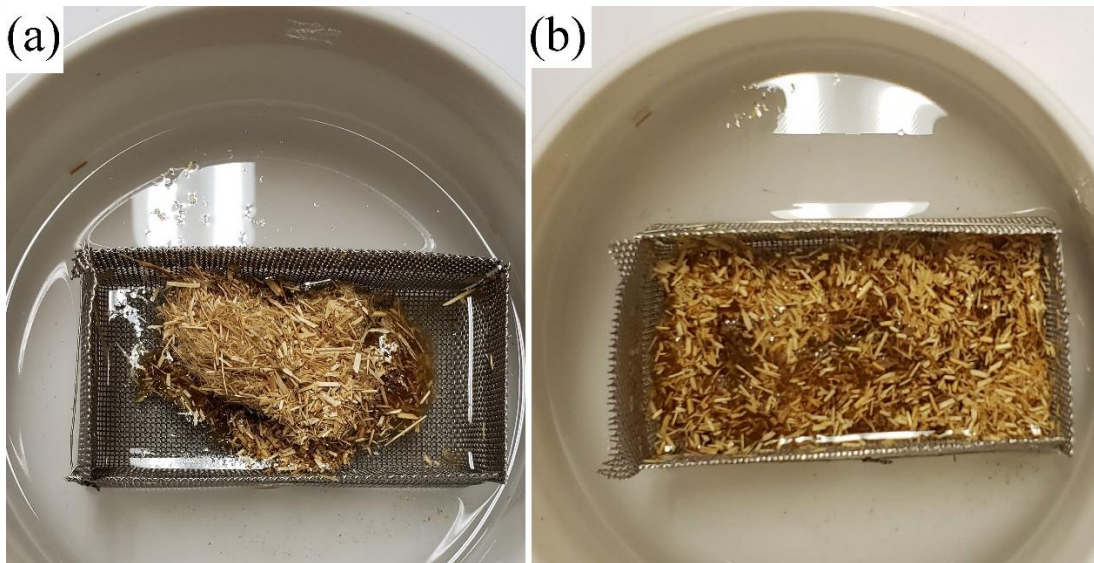


Figure 3.14. Sorbent at the start of experiment in the test cell (a) and sorbent immersed in test cell using spatula (b).

3.5.2 Kinetic water uptake

The hydrophobicity of treated and untreated samples was compared using a water uptake experiment. The 4-gram samples were placed in a 500 mL beaker containing artificial sea water. The artificial sea water was made by mixing 300 ml of distilled water with 12 grams of sea salt thoroughly until the salt dissolved completely. The procedure followed the artificial sea water production provided by the vendor which is based on the standard ASTM D1141 - 98(2013) (standard practice for the preparation of substitute ocean water) [72]. The flax straw/sea water was

mixed thoroughly using a magnetic stirrer with a speed of 500 rpm (Fig 3.15a). The mixture of water and flax straw was poured into a basket and left for 30 s to release excess water (Fig 3.15b). Finally, the basket (containing the wet sample) was weighed and the mass of wet sample was calculated based on the weight of the empty stainless-steel mesh. The percentage of increase in water uptake was calculated using the equation 3.6. The time intervals considered for this experiment was 10 min, and the water uptake recorded and calculated at 5, 15, 25, 35 and 45 min.

$$\text{Increase in water uptake} = 100 \times \left(\frac{m_1 - m_0}{m_0} \right) \quad (3.6)$$

Where m_1 is the weight of the wet sample (g), and m_0 is the weight of the dry sample before the experiment (g).

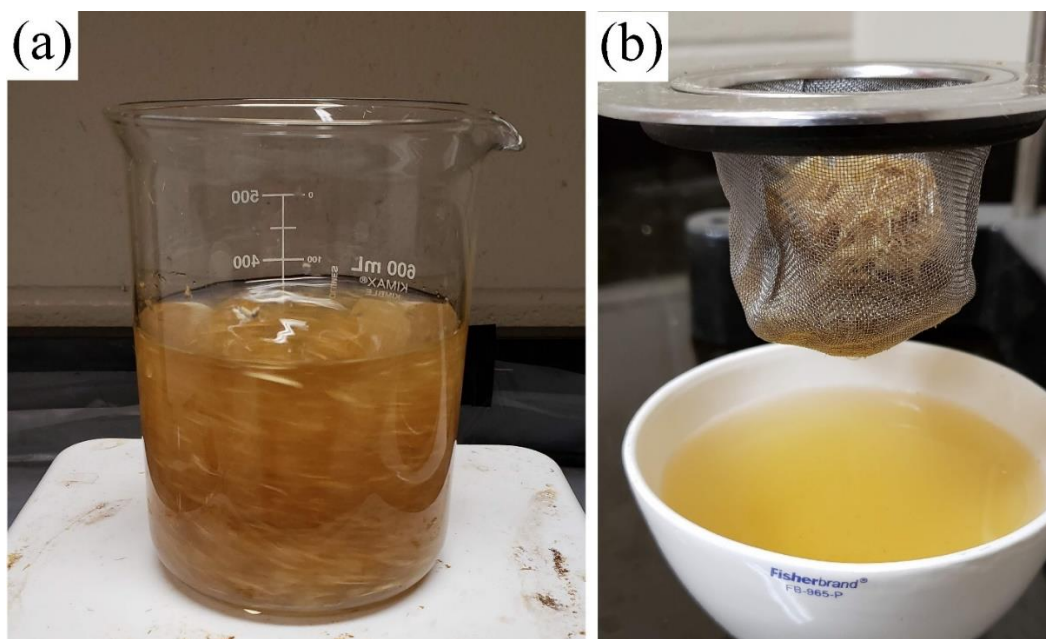


Figure 3.15. Water uptake experiment setup, sorbent positioned on magnetic stirrer (a), metal basket used in the experiment (b).

3.5.3 Oil and water selectivity

The procedure for the oil and water selectivity tests were similar to the oil sorption tests, but in the presence of water. This test simulates situations where an oil spill could occur in oceans. The sorbate media was a mixture of oil (heavy and light) and artificial seawater. Approximately 50 ml of oil was added to 300 g of artificial seawater in a beaker. The beaker was then placed on the

magnetic stirrer and stirred at a speed of 500 rpm for 15 min. The 4-gram sorbent sample was then added to the mixture of oil and water (Fig 3.16a).

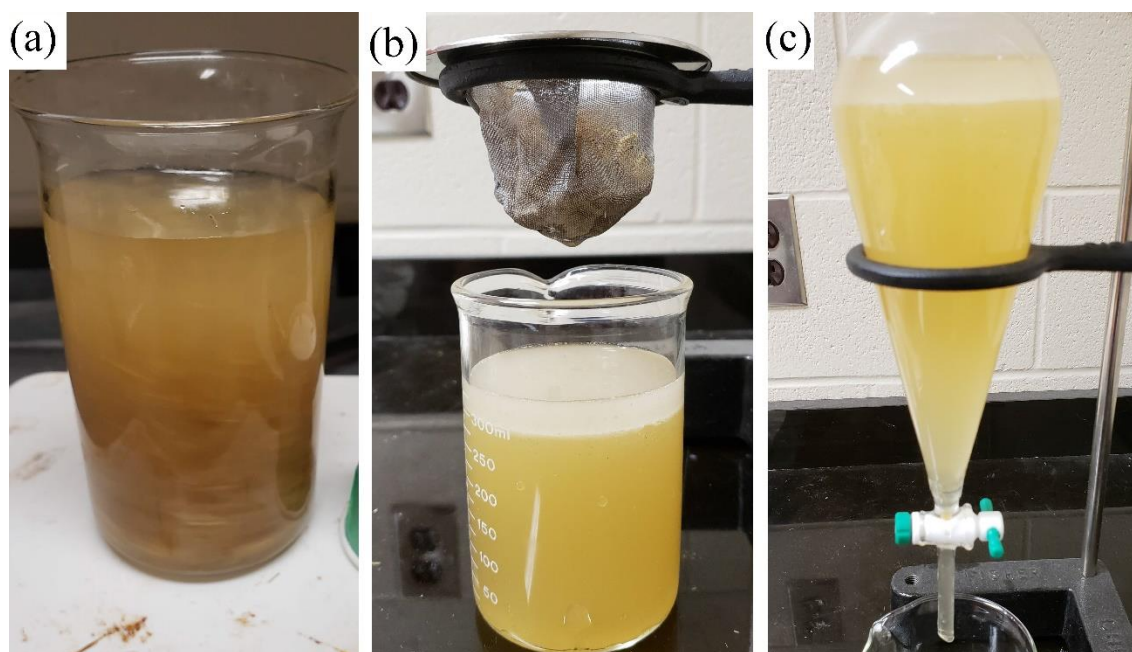


Figure 3.16. Sorbent in mixture of oil and water on magnetic stirrer (a), basket used in the experiment (b) and separatory funnel (c).

After stirring for 15 min, the contents of the beaker was poured into a basket hung over a secondary beaker to separate the sorbate media from the sorbent (Fig 3.16b). The basket was kept over the secondary beaker for 30 s to drain the excessive oil and water within the sorbent. The device used for separating the oil and water was a separatory funnel (Fig 3.16c). The secondary beaker content was poured into the separatory funnel, and the funnel was left static until the oil and water separated leaving the oil to float on top of the water. The water was separated from the oil by opening the valve located underneath the separatory funnel, and the weight of water and oil was recorded. The amount of adsorbed oil (g/g), the amount of adsorb water (g/g) and the oil and water selectivity was calculated by equation 3.7, 3.8 and 3.9 respectively.

$$\Delta o/g = \frac{50-m_o}{m_i} \quad (3.7)$$

$$\Delta w/g = \frac{300-m_w}{m_i} \quad (3.8)$$

$$\text{Oil to water selectivity} = \frac{\Delta o/g}{\Delta w/g} \quad (3.9)$$

Where $\Delta o/g$ is the amount of adsorbed oil per gram of sample (g) and $\Delta w/g$ is the amount of adsorbed water per gram of sample (g). The parameters, m_o and m_w are the weight of remaining oil and water, respectively after the experiment (g) and m_i is the initial weight of sorbent.

It is important to note that the weight gain of first and secondary beaker in this experiment was calculated to determine the experimental error. To minimize this error, the content of both beakers was thoroughly emptied using a spatula. Also, the mass of the remaining oil within the separator funnel was calculated based on the weight of empty funnel.

3.5.4 Fourier-transform infrared spectroscopy

A Bio-RAD (Hercules, CA, USA) FTS-40 IR was used to determine the functional groups of raw and treated samples (Fig 3.17). FTIR required a ground sample mixed with a spectroscopic grade KBr powder. The weight ratio of the sample to the KBr was 1 to 10. After grinding the mixture using a mortar and pestle, 30 mg of the mixture was placed in an aluminum pan and mounted into the machine. The results were normalized and plotted using Microsoft Excel software.

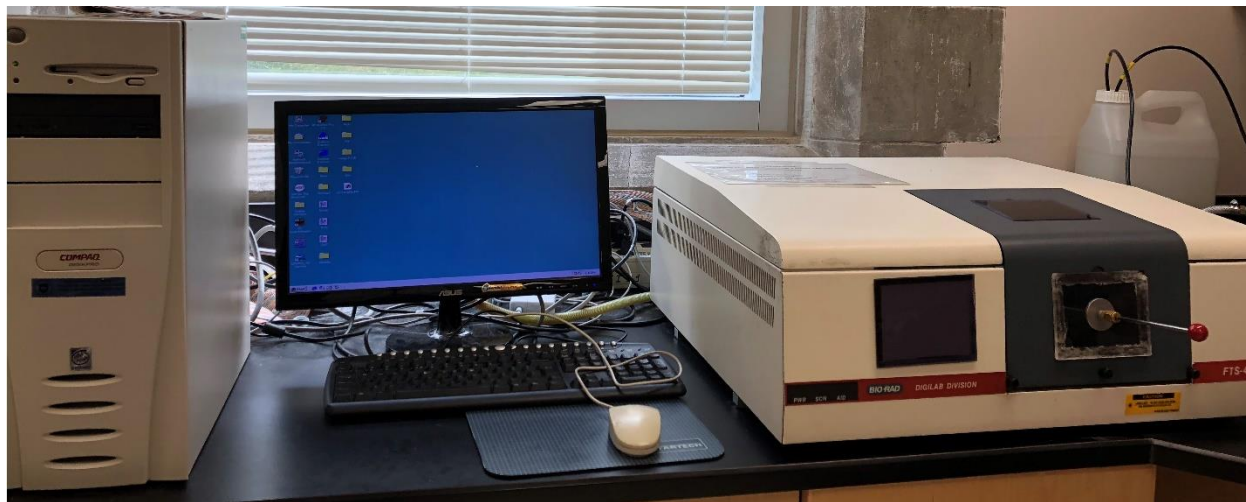


Figure 3.17. Digital image of the Bio-RAD FTS-40 FT-IR set-up.

3.5.5 Scanning electron microscope

Three-dimensional imaging on raw, acetylated and linseed oil coated flax shive samples were

conducted to monitor the surface morphology of the samples. The SEM model was a JEOL (Tokyo, Japan) JSM-6010 LV (Fig 3.18). Since the samples were biological and non-conductive, they were gold coated prior to SEM viewing. A two-sided adhesive carbon tape was used to attach specimens to the metal SEM mount stand. In total, 12 samples were prepared, and images were taken at operating voltages of 10 kV and 15 kV using a range of magnifications from 100x to 1200x.

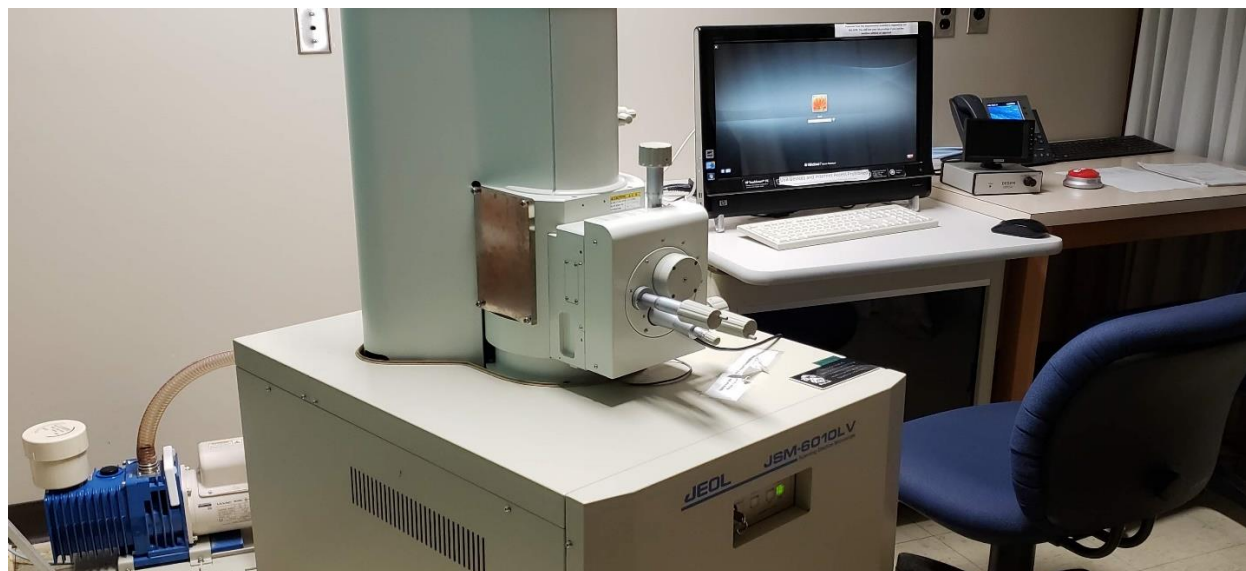


Figure 3.18. Digital image of the SEM model JEOL JSM-6010 LV.

3.5.6 Thermogravimetric analysis

The thermal stability of the samples was determined using the TGA method. The system utilized in this experiment was the TA Instruments (New Castle, DE, USA) Q50000IR TGA system (Fig 3.19a). A small amount of raw and treated samples were ground using mortar and pestle (Fig 3.19c). Then 30 mg of the ground sample was placed in an aluminum pan and mounted into the TGA system (Fig 3.19b). The temperature range for this experiment was from 25°C to 500°C, and the temperature increment rate was set to 5°C per minute under a nitrogen gas atmosphere.

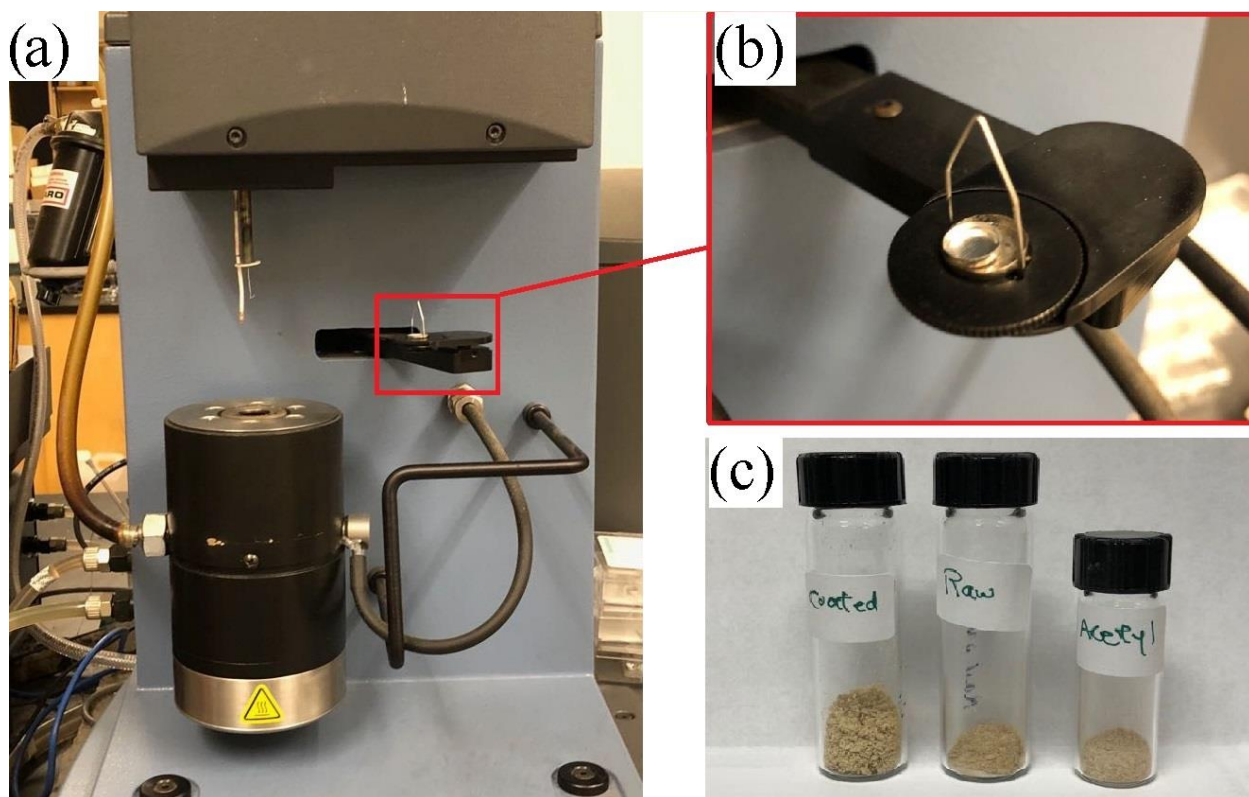


Figure 3.19 TA Instruments Q50000IR TGA system (a) aluminum pan (b) ground samples (c).

3.5.7 Statistical Analysis

Results of the particle size experiment, the density experiment and the oil sorption experiment were statistically analyzed using analysis of variance (ANOVA) and least significant difference (LSD) methods. The aim of performing these analyses was to examine if changes made by manipulating the variables such as particle size, density and treatments influenced the oil sorption capacity of the samples significantly. The level of confidence in these experiments considered to be 95 %.

3.6 Reusability and disposal of the sorbent

After characterization of the sorbents in terms of oil sorption, water uptake and the structure property, the possibility of reusing the sorbent and the disposal requirements were tested. A brief outline of the regulation, the capacity of material to retain oil and the possibility of reusing the sorbent are examined in this section.

3.6.1 Waste disposal regulation

In order to dispose of waste within a landfill in Canada there are some requirements that need to be met. Based on the code of federal regulation (CFR), “the placement of bulk or non-containerized liquid hazardous waste or hazardous waste containing free liquids (whether or not sorbents have been added) in any landfill is prohibited” [79]. Used oil, in certain circumstances explained in the CFR, is considered a hazardous material. Therefore, it cannot be deposit in the landfill if it contains free liquid. To demonstrate the availability of free liquids within the sorbent there is a test method defined as method 9095B, paint filter liquid test (PFL) [80]. The summary of the test method is to place the oily sorbent in the paint filter (mesh number of 60). If any oil passes through the filter after 5 min, it implies the oily sample contains free liquid and cannot be discarded in a landfill. In this experiment, the PFL tests were performed on the oily samples in three different circumstances: oily sample after the oil sorption experiment (section 3.5.1), oily sample after 24 h of retention (section 3.6.2) and oily sample after each desorption cycle (section 3.6.3). The PFL test setup is shown in figure 3.20.

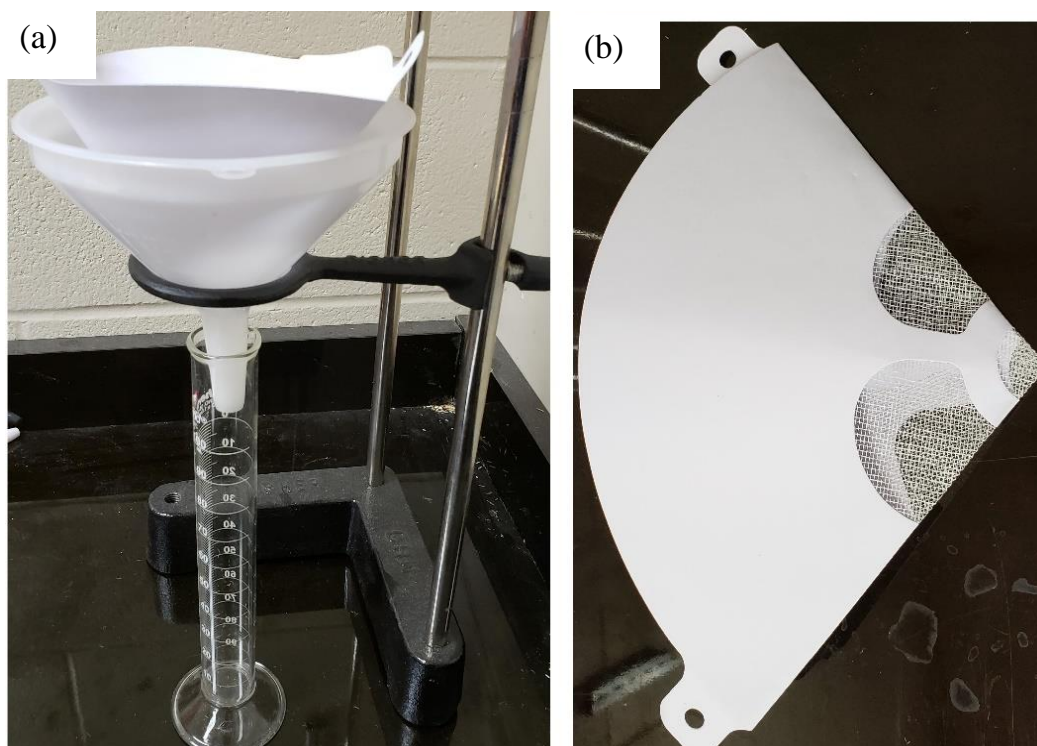


Figure 3.20 PFL test setup (a), the PFL filter (b)

3.6.2 Oil retention

Oil retention is the ability of a sorbent to retain oil within its structure. For calculating this characteristic, the oil sorption test was performed based on the oil sorption experiment procedure (section 3.5.1). After 15 min, the basket containing the oily samples were hung for 24 h. After 24 h, the weight of oily samples was recorded, and the oil retention capacity was calculated using equation 3.10.

$$\text{Oil retention capacity} = \frac{m_w - m_d}{m_d} \quad (3.10)$$

Where m_w is the weight of the oily sample after 24 h (g), and m_d is the initial weight of the sample.

3.6.3 Reusability

For reusability, four cycles of oil sorption and desorption were performed on the samples. For oil sorption, the method in section 3.5.1 was followed, and for desorption, the modified centrifuge machine was employed. The centrifuge was run for 30 second at 6000 rpm for each desorption cycle. The oil sorption after each cycle was calculated using the equation 3.5.

CHAPTER 4

RESULTS AND DISCUSSION

The results of experimental practices are discussed in this chapter which consists of three parts: sample preparation observations, discussions of oil sorption parameters and the effects each treatment had on oil sorption properties.

4.1 Characterization of flax straw and flax fiber

The chemical composition and the structure of the flax straw play an important role in determining the sorption property. Chemical composition helps explain how the amount of cellulose, hemicellulose and lignin are related to the interaction of oil and water with the straw. The structural study, number of voids, pores and lumens are important for discussions related to the storage space for oil or water.

4.1.1 Chemical composition of the flax fiber and flax straw

The result of chemical composition and moisture content was received based on wet and dry basis for flax fiber and flax straw (Table 4.1). Wet basis content is the percentage amount of all material including water and the dry basis composition is the ratio of constituents except for water [27]. The dry basis report can be used to compare the amount of cellulose, hemicellulose and lignin as it is independent from the moisture content.

The first observation in table 4.1 is the difference between the cellulose content in the flax fiber and the straw. The cellulose content in the fiber is around 64 %, while for flax straw it was 53 %. It can be argued that, since the straw consist of shives and fibers, the amount of cellulose within the shives, the woody part of flax straw, is lower than 53 %. Also, the amount of hemicellulose and lignin was higher than that of flax straw. This suggests that the content of hemicellulose and lignin is higher in shive compare with flax fiber which is in consistent with the data found in literature [30,35]. For the flax straw, the majority of material (more than half) consists of cellulose which is hydrophilic.

Table 4.1. Chemical composition of flax based on wet and dry basis.

	Wet basis		Dry basis	
	Flax Fiber	Flax Straw	Flax Fiber	Flax Straw
Moisture (%)	6.60	8.54	-	-
Cellulose (%)	60.43	48.49	64.70	53.02
Hemicellulose (%)	11.90	15.70	12.74	17.17
Lignin (%)	8.65	14.26	9.26	15.59
Crude Fat (EE) (%)	0.64	0.51	0.69	0.56
Ash (%)	1.39	2.85	1.49	3.12

4.1.2 Flax straw structure

The SEM observations of the raw flax straw was carried out. Photos were taken at different magnifications ranging from 85x to 200x. The structure of stem, fibers and shives were examined in terms of the surface morphology, amount of wax and the arrangement of the stem. Figure 4.1 illustrates the cross-section of the stem at 85x and accelerating voltage of 10 kV. Moving from the outer layer to the center of the stem, the skin and bundles of fibers can be observed. Next are the phloem and xylem cells. These cells are responsible for carrying nutrition and water for the plant and consist of a large number of tiny tubes expanding vertically along the stem. This portion of the stem is also called the shive area. Therefore, it can be concluded that the flax shives consist of pores and internal spaces that can be considered as a reliable storage area for the oil, in oil sorption practices.

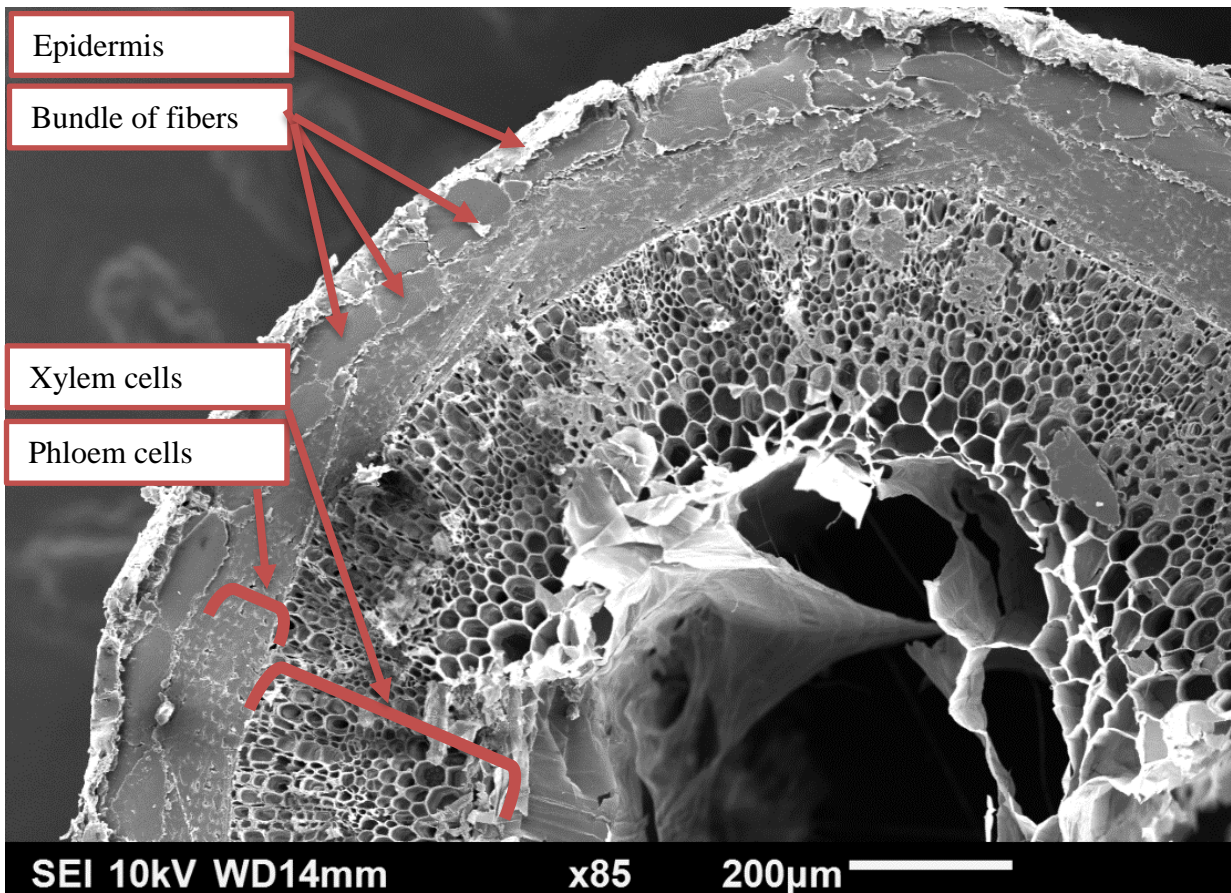


Figure 4.1. SEM image of the cross-section of the flax stem.

In addition to shives, another important part of the flax stem for this study are the flax fibers. To acquire a better understanding of the location and morphology of the fibers, a piece of stem was cut to 3 mm length. The cut piece was then rolled onto adhesive tape in order to remove the outer layer of the stem (epidermis). Figure 4.2(a) shows an image with the skin removed, figure 4.2(b) shows the removed skin which was attached to adhesive tape. At position A of figure 4.2(a) the tissues of phloem cells and the vascular tubes can be observed in the magnified area. These tubes and void spaces can be considered another area for storage of the sorbent. Position B illustrates tiny vents on the walls of the phloem tubes that provide access to the neighboring xylem phloem tissues. The channel at position C was formed from displacement of the bundle of fibers as shown in figure 4.2(c). The fibers in this area were initially connected to each other by wax [81] creating a strong structure similar to a binding/adhesive agent in composites.

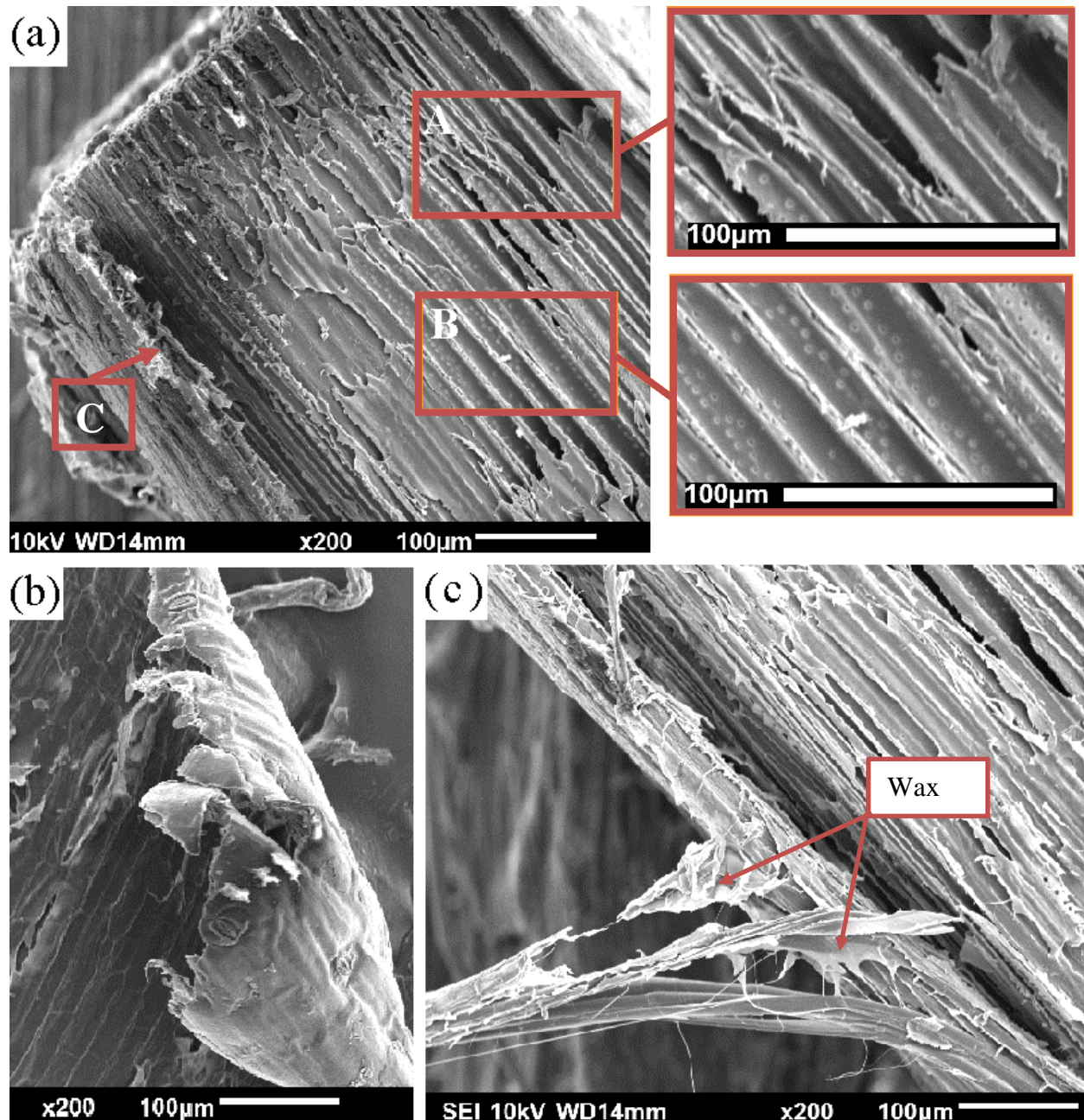


Figure 4.2. SEM photo of skinless part of the stem (a), stem showing removed skin(epidermis)(b), bundle of fibers with attached wax (c).

The waxes available on the surface of the fibers (Fig 4.2c) are water repellent. However, since they partially covered the outer surface of the fibers and shives, water can easily reach the hydroxyl functional groups on the cellulosic substances. This may be a contributing factor to high hydrophilicity of natural fibers although they have a waxy surface. The tiny vents on the walls of the vascular tubes (Fig 4.2a) may be the initial penetration point for water or oil to enter the bulk

of the material. Considering the viscosity of oil, water might be a dominant liquid to enter to these tiny spaces in aqueous situation.

4.2 Material preparation

Sample preparation, observations and initial oil sorption experiments were performed. The aim of initial trials at this stage was to choose the most practical method for sample production. The results of these experiments are discussed in this section.

4.2.1 Drying of the flax straw

The process of washing, oven drying, and pulverizing were performed a number of times throughout this study. However, the tracking of weight change for the samples during washing and oven drying were recorded one time. Since the weight of the dry matter does not change during drying, the change in wet basis moisture content were calculated using equation 3.3. The moisture content results as a function of time are summarized in figure 4.3.

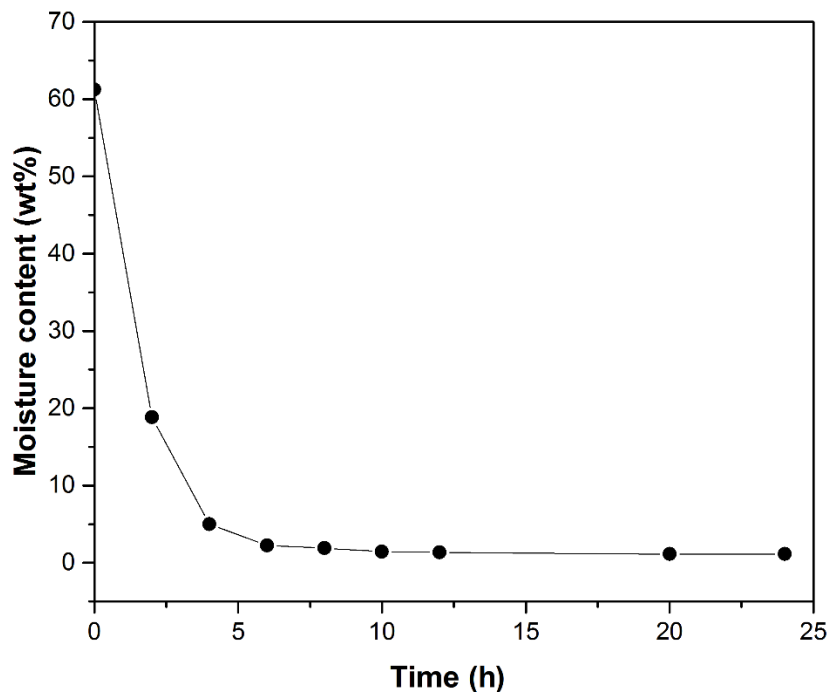


Figure 4.3. Moisture content during the oven-drying process.

The moisture content of the samples after being washed and drained for one hour was 61.2 wt.%. This amount dropped sharply by 43.2 % after 2 h from the start of oven drying. This sharp decline

was due to the fact that the water could not totally diffuse into the bulk of the straw as the washing duration was short. After almost 5 h from the start of drying, the moisture removal began to slow down, and after 10 h became steady at 1.1 wt.% moisture content. This agrees with ASTM WK58359 which is a new practice for drying flax fiber prior to moisture sensitive processing or testing [82]. Procedure “A” of this standard states that the samples containing more than 10 % moisture content shall be partially dried in an oven after 24h at 55°C. Procedure “B”, however, explains that the straw with moisture contents greater than 10 % shall be fully dried after 24 h of drying at 80°C. Therefore, the washed straw at 65°C after 24 h should contain small amounts of moisture.

4.2.2 Cutting operation

The reason for choosing the multi-blade scissors was the fixed distance between its blades which allowed the straw to be cut into cylindrical shapes of the same lengths. After cutting a batch of straw, it was observed that the structure of the stem during the cutting process remained intact and did not fully crush down into the fibers and shive (Fig 4.4a). The hollow lumen of the fibers, the porous structure of the shives, and the intra-particle spaces are the main storage areas for sorbate. Therefore, by breaking and opening the stem structure into small pieces, rather than intact cylindrical shapes, more surface area would be accessible for oil sorption. Instead of using scissors which apply only a shear cutting force, a knife milling machine is a better option as it is capable of providing shear and compaction forces at the same time. The knife milling machine is able to crush and cut the stems into small particles. Particle size reduction with this machine results in straw that was well broken into small particles of fibers and shives which is more desirable for oil sorption purposes (Fig 4.4b).

Another observation during the cutting process was the importance of moisture content on cutting practice. For moisture contents of around 8 wt.%, it was observed that a portion of the fibers locked into each other and did not pass through the sieve of the knife milling machine. It was also observed that the amount of fiber stuck in the machine decreased by reducing the moisture content. The best results for cutting the straw with the knife milling machine was acquired when the straw had a lower moisture content of around 1 wt.%.

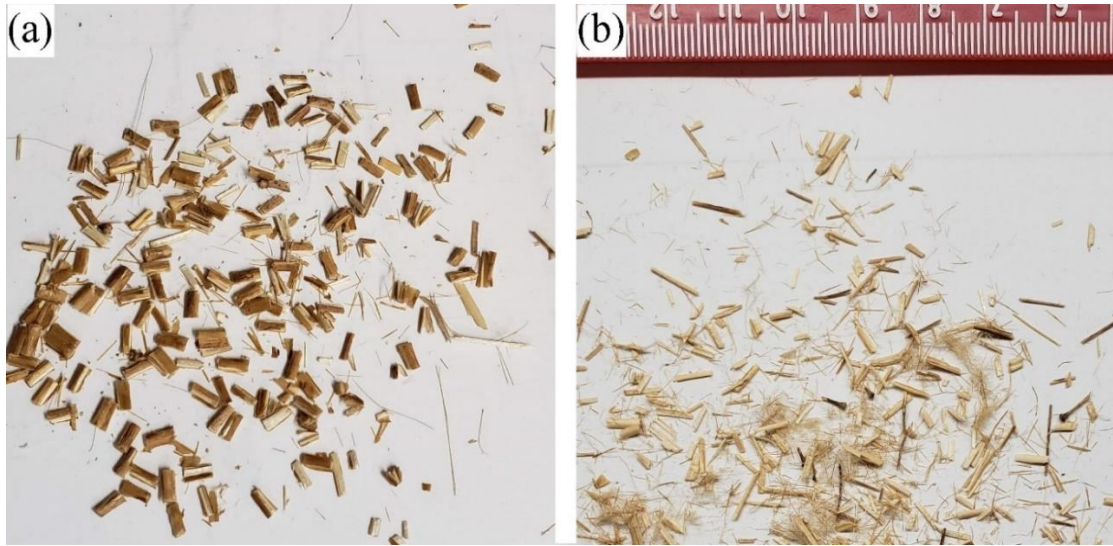


Figure 4.4. Pulverized flax stem using multi-blade scissors (a), cut flax straw using knife milling machine (b).

4.2.3 Sieving

The particles captured by various sieve sizes are shown in figure 4.5. The initial visual observation after the sieving process was the difference between the fiber to shive ratio. The amount of fiber was higher than shive when sieve sizes 3.36 mm, 2.38 mm and 1.68 mm (Fig 4.5 a, b and c) were used. The amount of shives that did not pass through sieve size 0.84 mm was considerably higher than the amount of fibers (Fig 4.5e). The magnification of this sieve is shown in figure 4.5 (i). The availability of fiber and shive was almost the same at sieve size 1.19 mm and 0.59 mm (fig 4.5d and f). Finally, for the particle deposited at the lower pan (fig 4.5 g) the amount of small fibers was higher. This is magnified in figure 4.5 (h).

The main reason for trapping the fibers in the sieves with large openings is the tendency of the fibers with higher lengths to weave into each other while shaking in the sieve shaker. In the woven industry, the length of fibers is a determinant for the quality of yarn as they can weave effectively into each other and create more strength [83]. Smaller size fibers, however, have an application in nonwoven fabrics where weaving is not required [84]. This may be the reason for small size fibers passing through various sieves and being deposited at the lower pan. The shive particles were trapped mostly in the sieve size of 0.84 mm due to particle sizes being slightly larger than the sieve opening. This is shown in figure 4.5(i) where the square shape opening has a dimension of 0.84 mm.

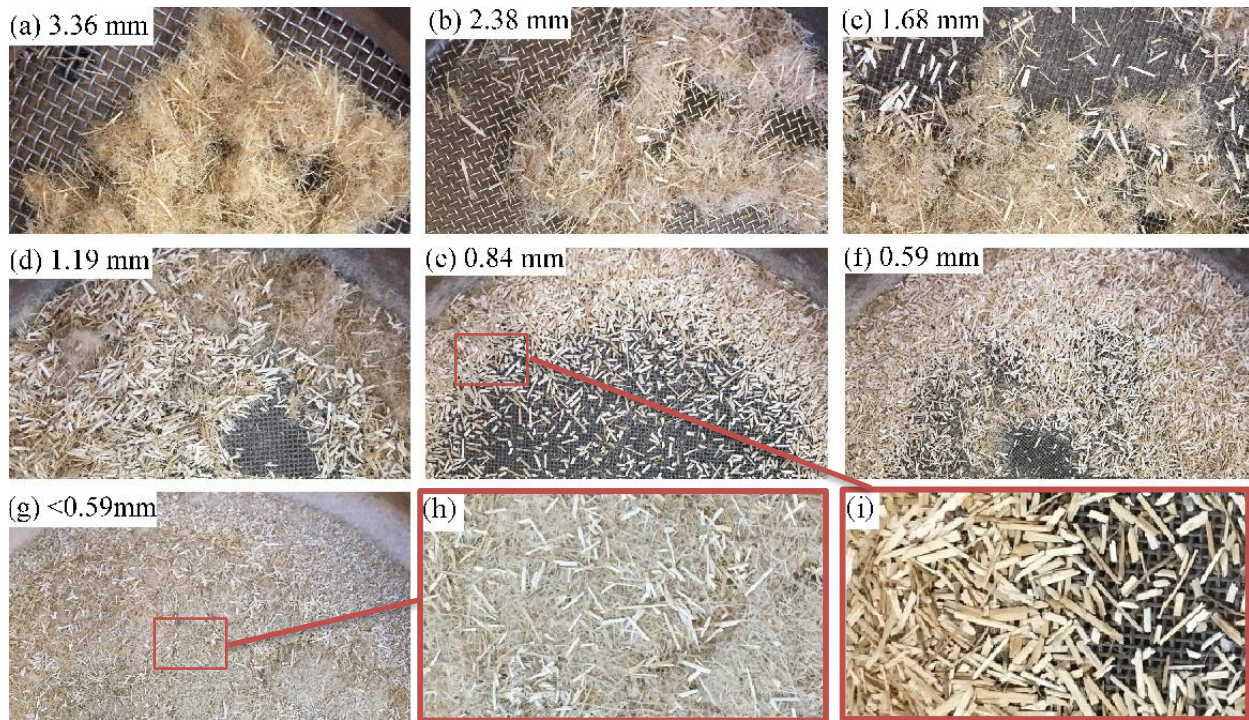


Figure 4.5 Digital images of particle captured by various sieve sizes.

Another important observation was the length of particles captured by each sieve was not consistent with the size of the sieve. For instance, the size of the particles captured by sieve size 1.19 mm, ranged from less than one millimeter to more than ten millimeters (Fig 4.6).



Figure 4.6 Particle capture by sieve size 1.19 mm.

This can be explained by the cylindrical shape of the particles and their high length to cross-sectional diameter ratio. During sieving, the particles, regardless of their lengths tend to slide on top of each other until they became perpendicular and pass through the sieve openings. Other contributing factor to this is the hammer at the top of sieving machine impacting the sieves vertically. This made the particles move up and down and pass through the openings regardless of their length. The issue of inconsistency between length and sieve opening size could be addressed by cutting the straw to sizes smaller than 0.6 mm as this would reduce the length to diameter ratio. On the other hand, flax straw is a fibrous plant and cutting it in very small sizes would result in the formation of a network of fiber/shive particles. These particles would not pass through the sieves easily and would remain on the top sieve during the sieving practice. Figure 4.7 illustrates a batch of flax straw and a batch of flax fiber ground using the knife milling machine with sieve size of 2 mm x 2 mm for the purpose of chemical composition analysis.



Figure 4.7 Ground and sieved batch of flax straw (a) and flax fiber (b).

Another method of sorbent preparation was to directly use the sieve of the knife milling machine. Each sample size consisted of 4 grams and were kept in an individual bag to maintain a constant fiber to shive ratio. Figure 4.8 shows 4-gram samples made by the milling machine using 4 x 4 mm, 6 x 6 mm and 8 x 8 mm size sieves.



Figure 4.8. The 4-gram samples made with the knife milling machine using three sieve sizes.

4.3 Microstructure of untreated and treated samples

4.3.1 SEM

The raw, acetylation treated, and linseed oil coated samples were compared using SEM. Figure 4.9 shows the raw and acetylated samples. The wax covered the fiber surface (Fig 4.9 a) and occupied the intra-fiber spaces had largely been removed by the acetylation treatment (Fig 4.9 b) which resulted in exposure of the fiber and shive surfaces. The surface of flax fiber illustrates a bamboo shape consisting of many nodes which are characteristic of the plant growth. These nodes appear to extend along the length of the fibers creating an uneven surface morphology. Another change in the morphology due to acetylation is the appearance of microfibrils on the surface of the fibers as shown in the magnified portion of Figure 4.9 (b). Fibrillation occurred due to the interaction of the acid with the lignin between the individual fibers. The crack damage was not observed in the non-acetylated samples, therefore it can be concluded that the degree of acetylation was enough to remove the wax and prevent damage to the fiber structure [35].

The linseed oil coated sample is shown in figure 4.10 (a) and (b). The linseed oil formed a layer on the outer surface of the fiber bundle (figure 4.10a). The space between individual fibers within the fiber bundle is not visible as the oil spread over the bundle of fiber and covered any access to the intra-fiber spaces. Figure 4.10 (b) illustrates individual coated fibers at higher magnification. The coating appears to have covered the entire surface of the fibers as depicted by a smoother surface. This novel method of coating provides a very thin layer such that the small particles of wax on the surface of the fibers are still visible as observed in (Fig 4.10 b).

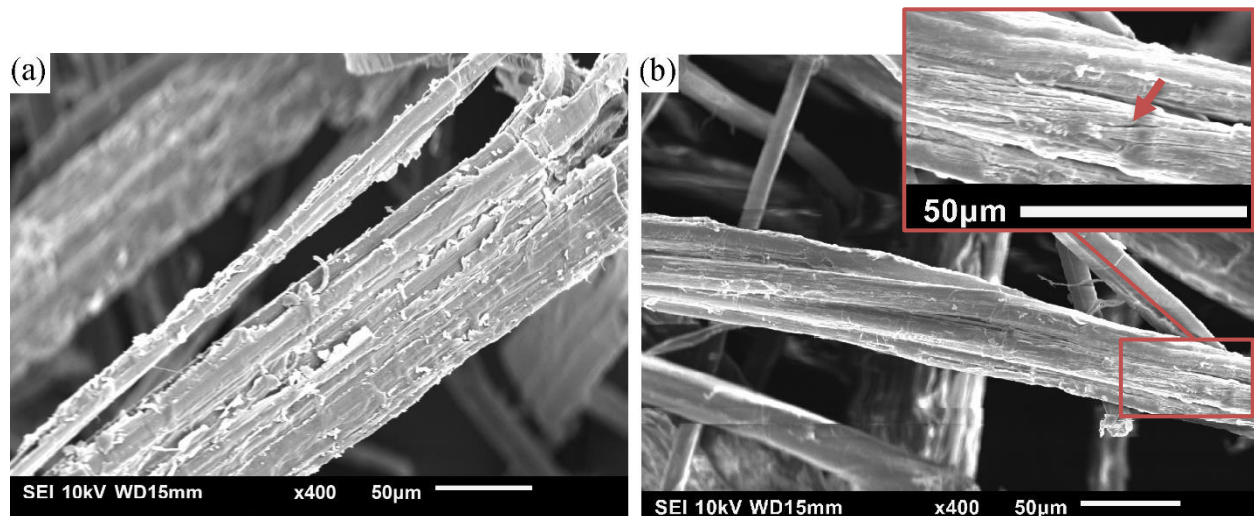


Figure 4.9. SEM comparison between raw (a) and acetylated flax fiber (b).

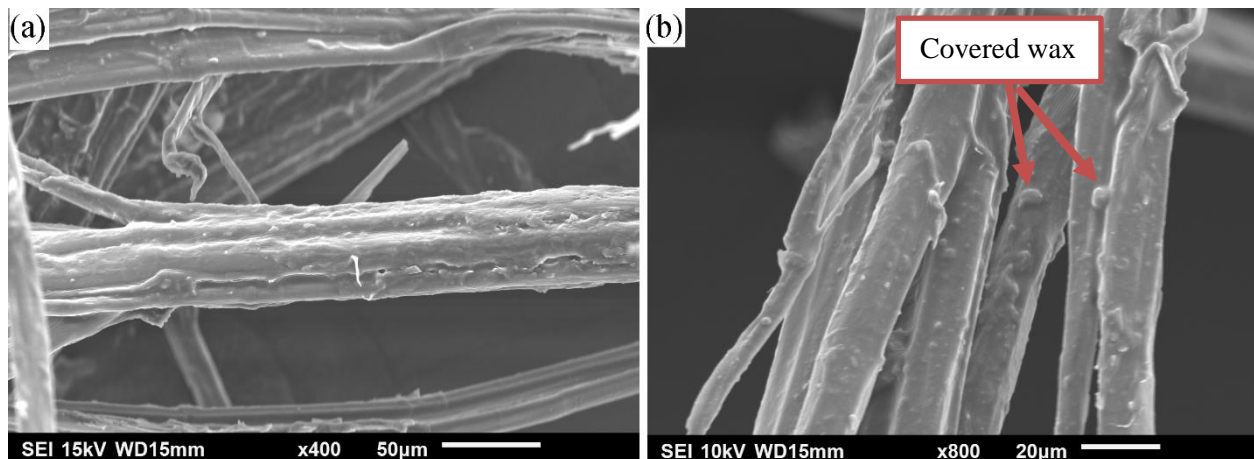


Figure 4.10. Bundle of flax fibers (a) and individual fibers both coated with linseed oil (b).

Figure 4.11 compares the untreated and acetylated flax shive particles. The change in flax shive due to the acetylation was similar to the flax fibers: the disappearance of the wax and exposure of the surface of the shive (Fig.4.11b). The fiber nodes on the surface of the shive particle can be observed in figure 4.11 (b) when the surface wax is removed.

The shive particles coated with a thin layer of linseed oil are shown in (Fig 4.12b). The pre-existing wax on the surface of shives have been covered with a thin layer of coating agent (Fig 4.12a). The vascular tubes within the shive remained empty and their openings were not obstructed with linseed oil (Fig 4.12a).

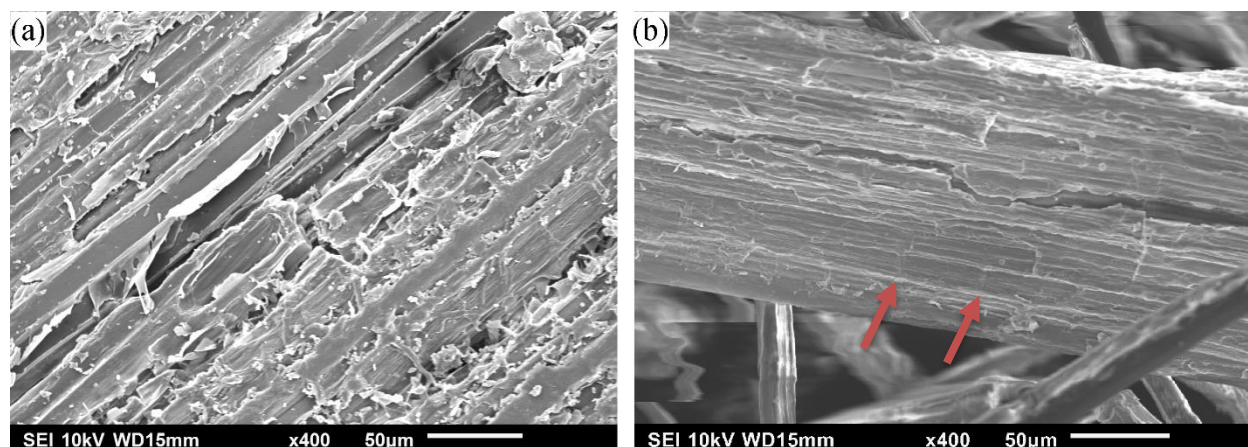


Figure 4.11. Untreated flax shive (a) and acetylated flax shive (b).

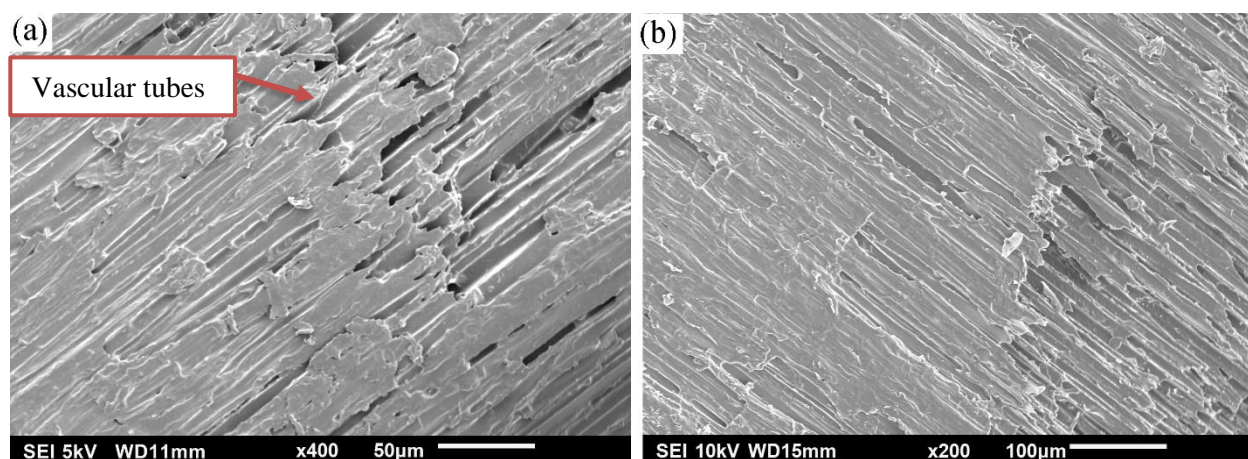


Figure 4.12. Coated shive with linseed oil at 400x (a) and 200x magnification (b).

4.3.2 FTIR

Success of the acetylation treatment can be determined using FTIR. Figure 4.13 compares the FTIR results of raw and acetylated flax straw.

The FTIR spectrum is characterized by adsorption bands at $\sim 3300\text{ cm}^{-1}$ for hydrogen bonds, at $\sim 2900\text{ cm}^{-1}$ for aliphatic C-H bonds, at $\sim 1700\text{ cm}^{-1}$ for carbonyl groups and at $\sim 1230\text{ cm}^{-1}$ for ether bonds. The intensity of the peak at 3000 cm^{-1} to 3500 cm^{-1} is an illustration of the availability of functional groups capable of hydrogen bond formation. The IR result of raw and acetylated samples, showed the band intensity of the peak decreased at around 3300 cm^{-1} , suggesting the number of -OH functional groups reduced in acetylated samples. Also, acetylated groups in the region of 1730 cm^{-1} correspond to acetyl carbonyl groups. The other noticeable and important

change in the peak intensity occurred at around 1227 cm^{-1} which is related to the appearance of -C-O- acetyl groups. The three stretches in the band intensity of the FTIR result are illustration of successful acetylation treatment [85].

The IR spectrum of raw straw and the straw coated with linseed oil are compared in (Fig 4.14). Three major changes in the intensity of the FTIR peaks was observed at $\sim 3300\text{ cm}^{-1}$, $\sim 2900\text{ cm}^{-1}$ and 1730 cm^{-1} . First, the band intensity at $\sim 3300\text{ cm}^{-1}$ decreased considerably which may be attributed to partial blockage of hydroxyl functional groups due to the linseed oil coating. Second, increasing the intensity of signature at $\sim 2900\text{ cm}^{-1}$ was attributed to the high number of aliphatic C-H groups present in the oil backbone. The third remarkable observation was the strong band at 1730 cm^{-1} which is assigned to the high number of carbonyl groups in the oil structure.

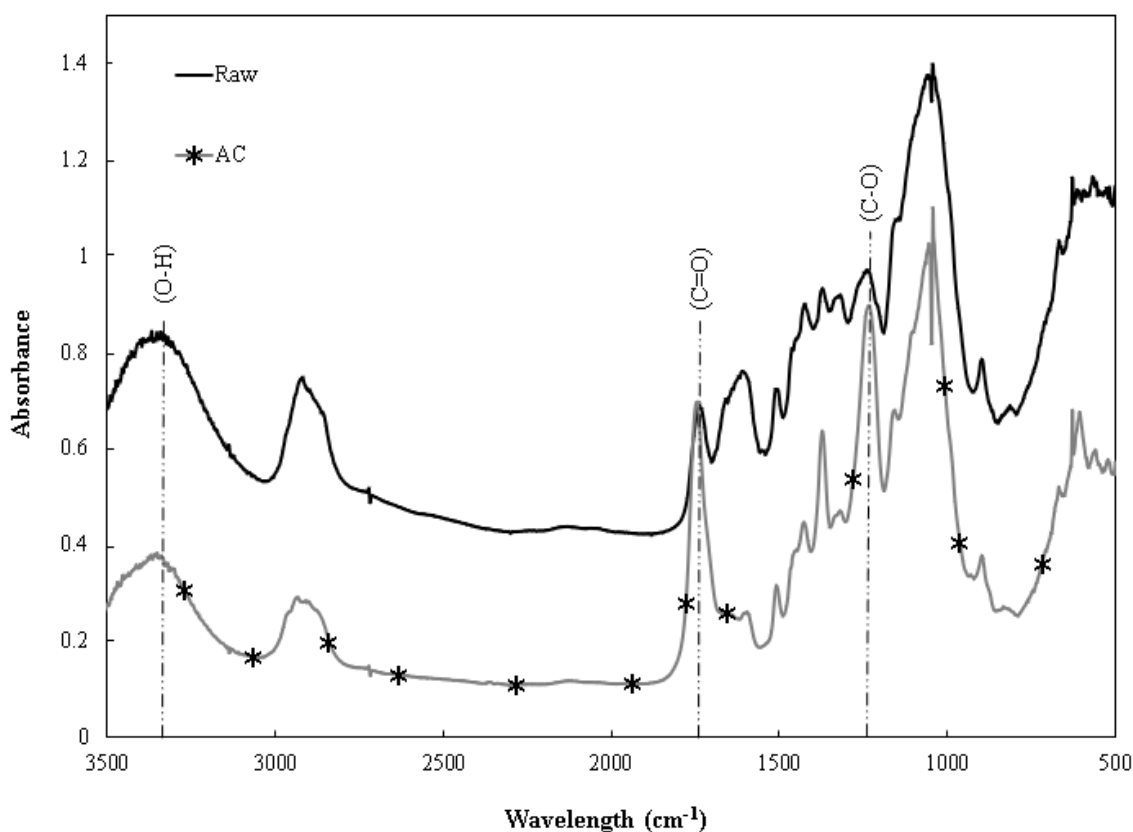


Figure 4.13. Absorption values with respect to wavelength using FTIR for raw and acetylated flax straw samples.

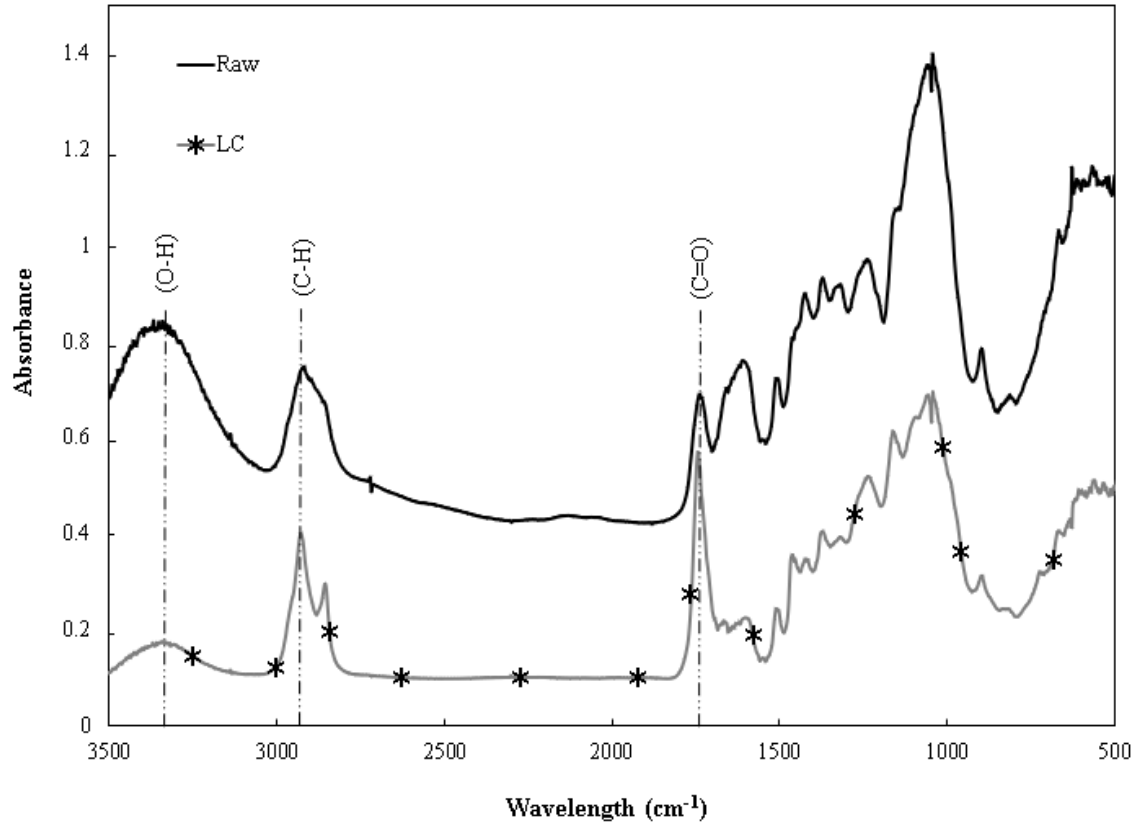


Figure 4.14. Absorption values with respect to wavelength using FTIR for raw and linseed oil coated flax straw samples.

4.3.3 Thermal gravimetric analysis

The TGA result of raw untreated straw were compared to acetylated (AC) and linseed oil coated samples (LC) to study the changes in thermal stability. Figure 4.15 shows the comparison between the TGA results of raw and acetylated flax straw.

Weight loss up to 100 °C was almost 8 % for both samples. The weight loss in this temperature range can be attributed from water desorption in both samples due to drying. The weight loss continued to decrease slightly for acetylated samples while it was almost steady for the raw sample up to 250°C. From 250-375°C the weight of both samples started to decrease sharply to almost 70 % for raw and 75 % for acetylated samples due to the extreme decomposition. The rate of weight loss decreased considerably above 375 °C for both samples. At 475°C, the weight of the remaining residue of raw and acetylated samples dropped by 77 % and 80 % of their initial weights.

Hemicellulose, cellulose and lignin thermal degradation is around 200-260°C, 240-350°C and 250-

500°C, respectively [70]. Since flax straw comprises of about 53 % cellulose, 17 % hemicellulose and 15 % lignin, the weight loss of both samples at the temperature range of 250 to 350 °C can be explained by the high amount of cellulose in the sample which breakdowns within this temperature range. However, the decomposition rate of acetylated sample was slightly higher than raw sample within this range. This can be explained by the reduction of hydrogen bonds in acetylated samples compared to raw samples. In the raw straw, the oxygen atoms of a similar or nearby chain of cellulose molecules create hydrogen bonds with multiple -OH functional groups available on the surface of cellulose [86]. These bonds disintegrated by acetylation treatment as some of the hydrogen bonds were replaced by acetyl groups. The reduction in the number of hydrogen bonds, contributed to a decrease in the thermal stability of acetylated samples compared to raw samples which is an indication of successful acetylation treatment on the samples.

Figure 4.16 is a comparison between the TGA result of raw and linseed oil coated flax straw samples. Since the coating of linseed oil is consider a physical bonding in terms of thermal decomposition, it is expected that the trend for both samples would be similar. Below 100 °C, linseed oil lost less moisture than the raw samples. This can be explained by the water repellent coating of the linseed oil. Above 350 °C, the raw samples decomposed faster than linseed coated samples. This may be due to the presence of linseed oil in the sample.

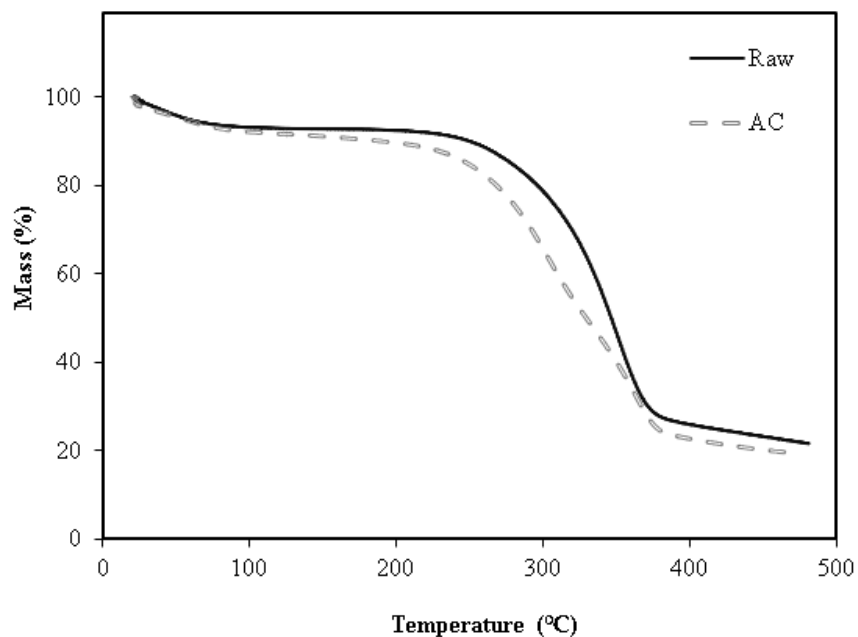


Figure 4.15. TGA result of raw and acetylated flax straw samples.

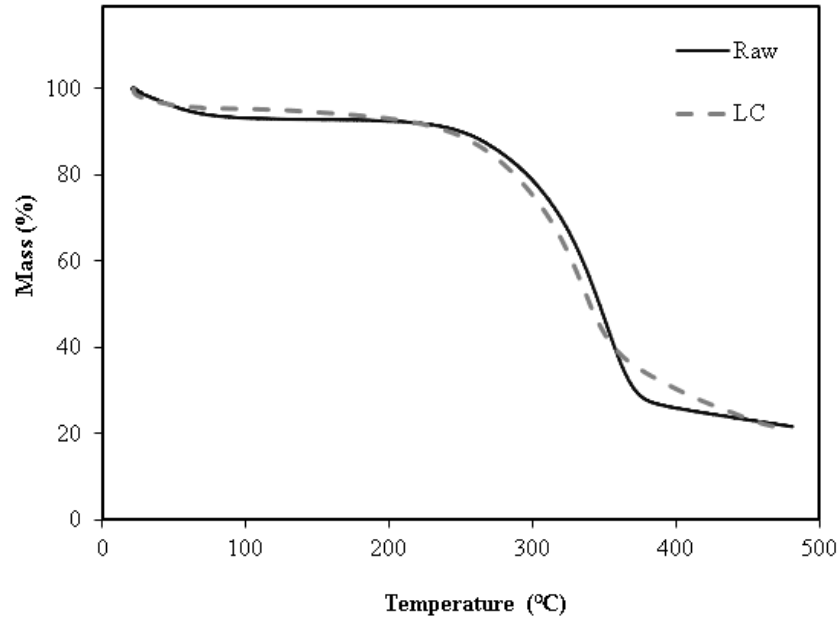


Figure 4.16. TGA result of raw and linseed oil coated flax straw samples.

4.4 Result of initial experiments

4.4.1 Oil sorption capacity of fiber and shive

To compare the sorption capacity of flax fibers and shives, four grams of each were placed in separate baskets and oil sorption experiments were performed in triplicates using heavy oil. A noticeable difference in oil sorption capacity was observed for flax fibers and flax shives. The fibers adsorbed 15.87 g/g and the shives adsorbed 4.50 g/g. The reason for this large difference is the bulk density of the two samples (Fig 4.17). While the bulk density of the fiber sample was $2 \times 10^4 \text{ g/m}^3$, the shive sample was 10^5 g/m^3 . On the other hand, the particle density of flax fibers and flax shives were calculated to be $1.5 \times 10^6 \text{ g/m}^3$ and $1.3 \times 10^6 \text{ g/m}^3$, respectively. Since the particle density of the fibers and shives are similar, it can be concluded that the lower bulk density of the fibers resulted in more void intra-particle spaces. The bulk of oil sorption occurs in intra-particle spaces, and this is appearing to be the contributing factor to the higher oil sorption of flax fibers.



Figure 4.17. Four grams of flax fibers (left) and four grams of flax shives (right).

4.4.2 Effect of particle size on oil sorption

The result of oil sorption experiments for raw pulverized flax straw sieved to various sizes are plotted in figure 4.18.

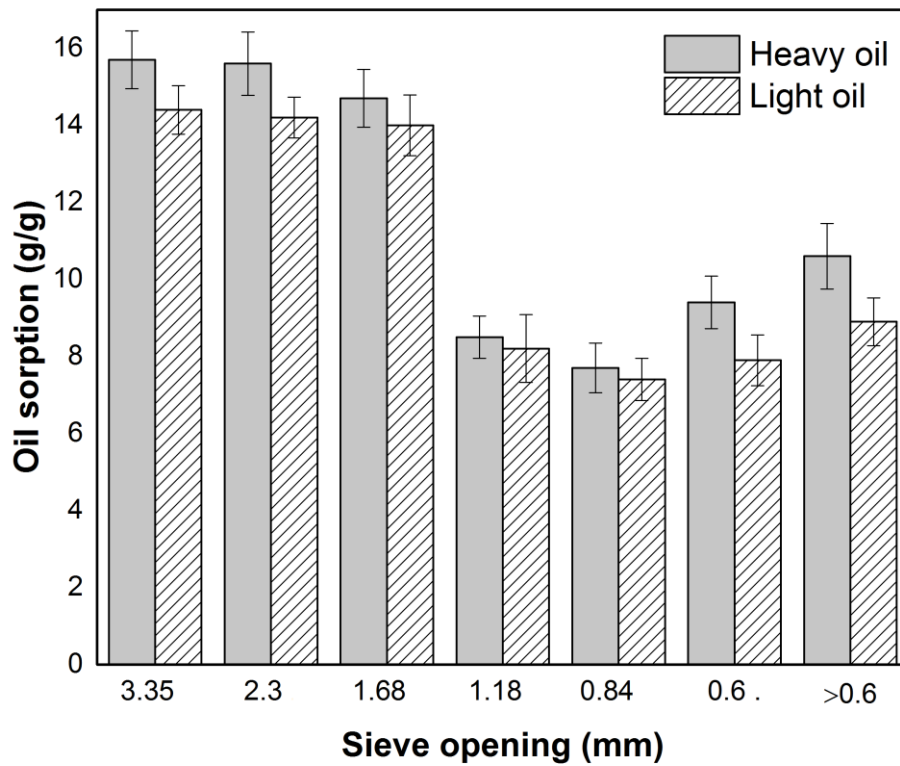


Figure 4.18. Heavy and light oil sorption values of the sieved raw straw samples.

A large difference was observed between the oil sorption of the particles capture by sieve size greater and lower than 1.68. For the sieve sizes of 1.68, 2.3 and 3.35 mm, the amount of adsorbed oil was almost the same for all sizes; 15 g/g for heavy oil and 14 g/g for light oil. The higher amount of oil sorption for these sizes was due to the availability of higher length fibers compared to shive as explained in the section 4.2.3. These high length fibers inter-woven to each other created a sorbent with low bulk density. For size 1.68 mm, the oil sorption in both heavy and light oil was slightly lower than the other two sizes mainly due to the presence of more shive particles in the samples (Fig 4.5c). For particles captured by sieve size 0.841 mm, the oil sorption for both heavy and light oil was the lowest. This can be explained by the high shive to fiber ratio of the samples as shown in Figure 4.5e. With the same reasoning, the slightly higher amount of oil sorption for the particles with sizes less than 0.6 mm was due to the lower amount of shive to fiber ratio (Fig 4.5g).

In addition to the amount of flax fibers and shives in the samples, the increased amount of oil sorption can attribute to smaller particles sizes. Surface area increases by decreasing the particle size. Larger surface areas may have more locations for the oil to be adsorbed. However, decreasing the particle size resulted in increasing the bulk density and decreasing the volume of the samples. Since the majority of the oil adsorbs in spaces between the sorbent particles, the oil sorption capacity has direct relation with the volume of sorbent. This can be seen by comparing the oil sorption results of around 10 g/g for above mentioned sieved samples with around 14 g/g of 4-gram samples. In all sieved samples, the sorption of heavy oil was slightly higher than light oil. However, at 95 % level of confidence the difference between the sorption of light and heavy oil was not significant based on the result of ANOVA and LSD (Appendix A). Higher viscosity oil tends to adhere to the sorbent particles and remain in the bulk of the material.

In conclusion, although sieving has been utilized in many literatures for studying the effect of particle size on oil sorption, it is not proposed for high length particles made by pulverizing fibrous biomasses such as flax straw due to the tendency of fibers to weave into each other.

4.4.3 Effect of packing density on oil sorption

The effect of compaction has been investigated on raw, acetylated and linseed oil coated samples. The packing density of the samples were calculated based on the weight of sorbent and the approximate volume of the bottles (Fig 3.11). The results are plotted in Figure 4.19.

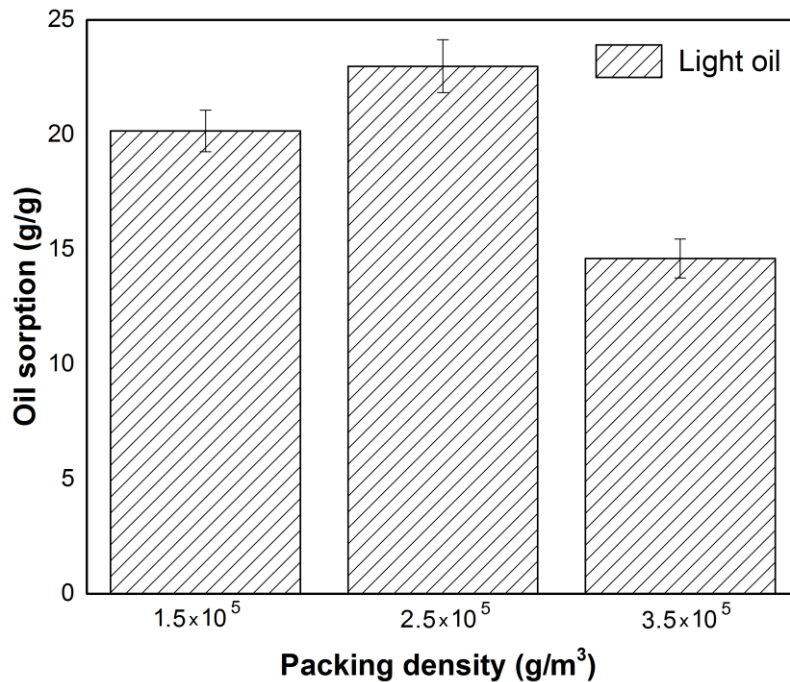


Figure 4.19. Light oil sorption results of packing density of flax straw due to sample compaction.

The samples with packing densities of 1.5×10^5 , 2.5×10^5 and 3.5×10^5 g/m³, had 3.5, 5.5 and 7.5 grams of sorbent material, respectively. The sample with 3.5×10^5 g/m³ packing density had the least oil sorption capacity, while the samples with a packing density of 2.5×10^5 g/m³ had the highest sorption capacity. The sample with 3.5×10^5 g/m³ had the lowest void spaces from being well compacted within the bottle. On the other hand, samples with 1.5×10^5 g/m³ packing density had the highest void spaces but did not adsorb the highest oil content. The distances between the particles may have been too large to be effective for oil sorption. The experiments showed these spaces were ineffective due to a large distance between individual particles. The sample with the packing densities of 2.5×10^5 g/m³ had the highest oil sorption which illustrates an optimum packing density. Based on the result of ANOVA and LSD analysis, there was a significant difference between the oil sorption of the three compacted samples (Appendix B).

4.5 Characterization of untreated and treated samples

4.5.1 Oil sorption experiment

The oil sorption results of raw, linseed oil coated and acetylated samples in a loose condition in both heavy and light oil are plotted in figure 4.20.

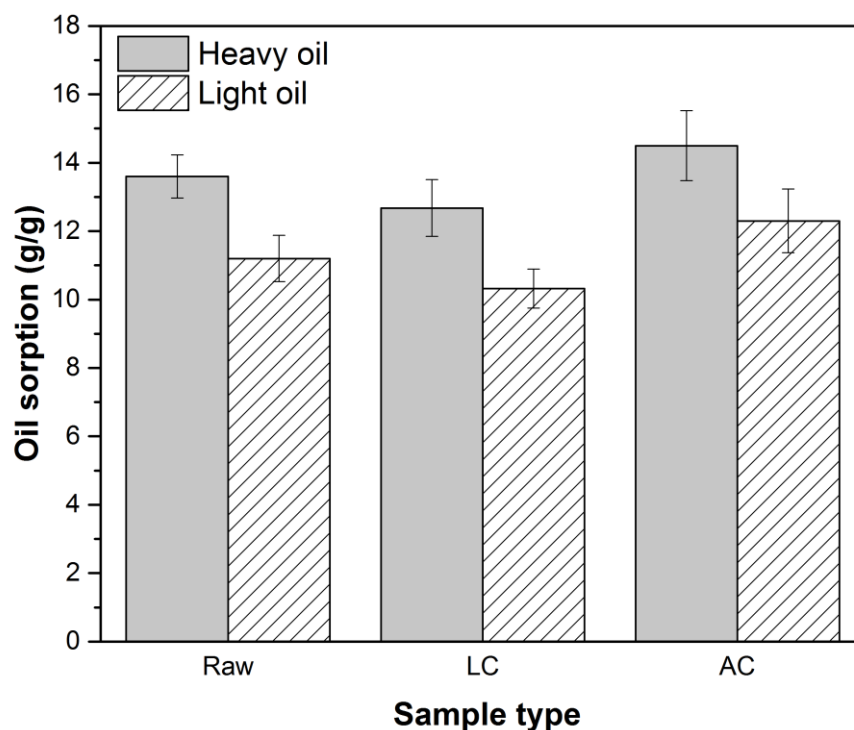


Figure 4.20. The oil sorption result of raw, linseed oil coated (LC) and acetylated (AC) flax straw samples.

Oil uptake of the sorbents in heavy oil media was generally higher than light oil. During the experiments, after removing the samples from the respective oils, the sorbents were hung for 30 s to allow excess oil to drain. High viscosity heavy oil did not flow easily which suggests a lower tendency of the liquid to leave the bulk sorbent. The low viscosity light oil drained more rapidly out of the bulk sorbent. This suggests the size of the intra-particle spaces of the sorbent are important for oil sorption of different oil viscosities.

The LC samples had the lowest oil sorption capacity. After the linseed oil coating treatment, the intra-particle spaces/void spaces where oil is generally deposited are no longer available. Also, the fiber lumens may have been obstructed due to the coating. Similarly, the porous shive particles may have been filled by the linseed oil.

The AC samples had the highest oil sorption capacities compared to the raw and LC samples. The acetylation treatment removed surface waxes from fibers resulting in more exposure of the fiber surface for oil uptake as shown in Figure 4.10. In addition, acetylation tended to damage the fibers to some extent and create micro-cracks on the surface of individual fibers [35]. Removing the wax

from the surface of the shives may result in more accessible pores for oil retention.

The acetylation showed a slight increase in oil sorption capacity while linseed oil coated samples showed a minor decrease in oil sorption capacity of the linseed oil coated samples. However, the result of ANOVA and LSD statistical analysis showed that these treatments did not significantly change the oil sorption capacity of linseed oil coated and acetylated sample (Appendix C). Therefore, for the situations where only oil exists as a sorbate, it is suggested that the raw flax straw be employed since the treatments do not have a significant impact on the oil sorption capacity.

4.5.2 Water uptake

The goal of the both LC and AC treatments were to decrease the water uptake of the flax straw. The result of water uptake for the three samples over a period of 45 min are plotted in figure 4.21.

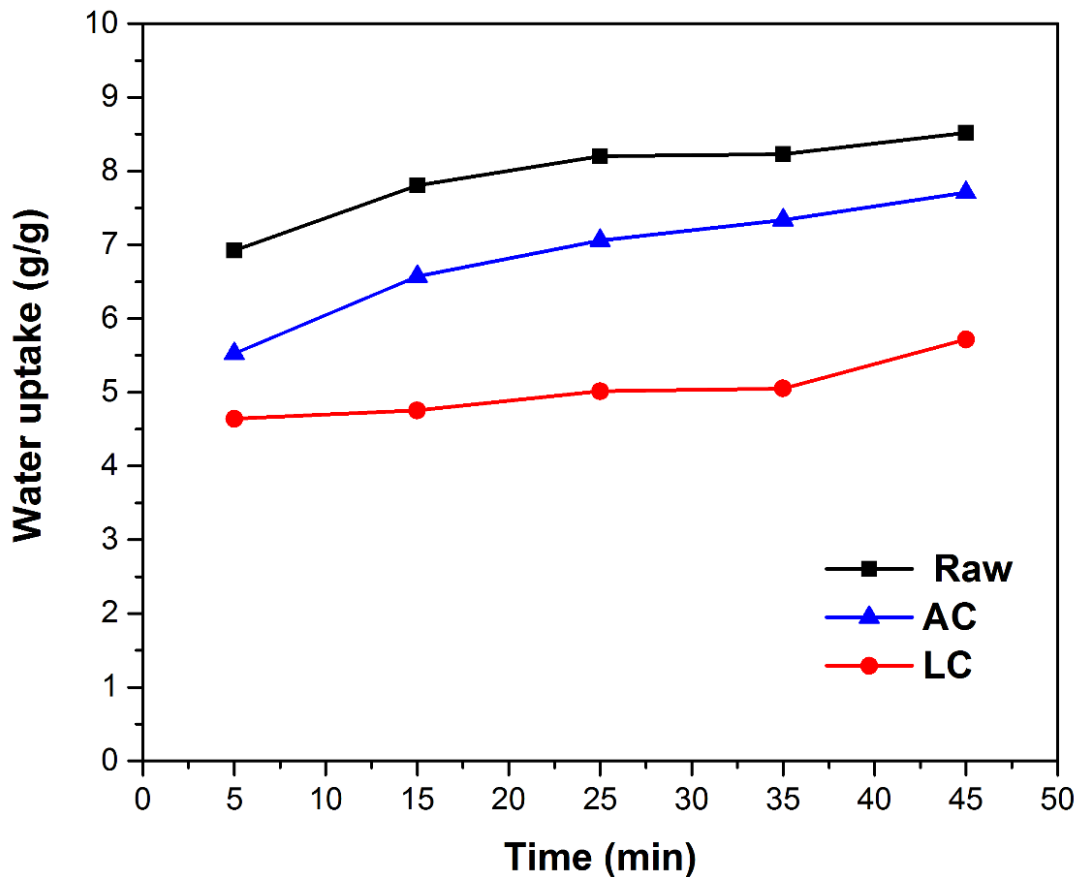


Figure 4.21. Water uptake of raw, linseed oil coated (LC) and acetylated (AC) flax straw samples as a function of time.

The increment in water uptake of all samples were observed as time increased. The raw sample had the greatest water uptake, while the LC samples had the least water uptake. At 5 min, the acetylated samples decreased the amount of water uptake by 20.1 % in comparison with raw samples. The difference is due to the removal of hydrophilic hydroxyl groups on the surface of the fibers and shives and replacing them with hydrophobic acetyl groups. Therefore, the sorbent behaves as a hydrophobic material and repels water. However, after 45 min the water uptake gap between the raw and AC samples closed gradually where the water uptake reached 8.8 g/g and 7 g/g, respectively. This shows that the hydrophobicity characteristic of AC samples gradually decreased over time.

For the LC sample, after 5 min the water uptake was 4.6 g/g which is a 32.9 % decrease in water uptake compared to raw samples. The reason for this improvement in water repellency is the hydrophobicity of linseed oil [87,88] distributed over the surface of sorbents. Unlike acetylated and raw samples, linseed oil coated samples resist more permeation of water over time.

The LC samples were able to resist diffusion of water up to 35 min as the water uptake increased by only 8.8 %, while the raw samples increased by 18.9 %. The results show a significant resistance of water uptake for the LC samples, but after 35 min the water uptake elevated more rapidly reaching 5.7 g/g at the 45 min.

4.5.3 Oil and water selectivity

The oil and water selectivity measurements were performed on raw, LC and AC samples using a ratio of water to oil (6:1). Figure 4.22 shows changes in the appearance and color of the sorbate after 15 min. The raw samples placed in the mixture of oil and water became murky after 5 min of stirring (Fig 4.22a). For AC samples this change was the same, however the mixture remained brighter to some extent compared to raw samples (Fig 4.22b). The mixture of LC samples and sorbate remained totally transparent during the experiment with no change in color (Fig 4.22c).

Figure 4.23 compares the water uptake and light oil uptake for the mixture of oil and water for three samples; raw, AC and LC. The AC samples decreased the water uptake by 43 % compared to the raw samples. In contrast to the literature, there was no significant increase in the amount of oil uptake [89-91]. For the LC samples, the amount of water uptake remarkably decreased by 81 % and oil sorption increased by 38 % compared to raw samples.

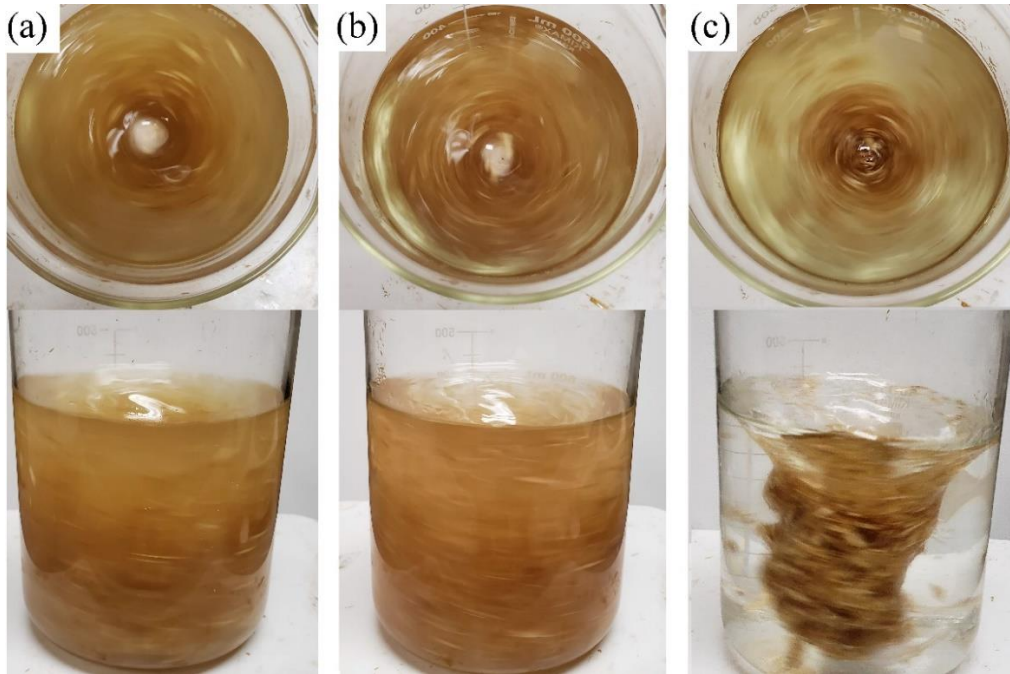


Figure 4.22. Oil and water selectivity experiment at 15 min on raw (a), acetylated (b) and linseed oil coated (c) flax straw samples.

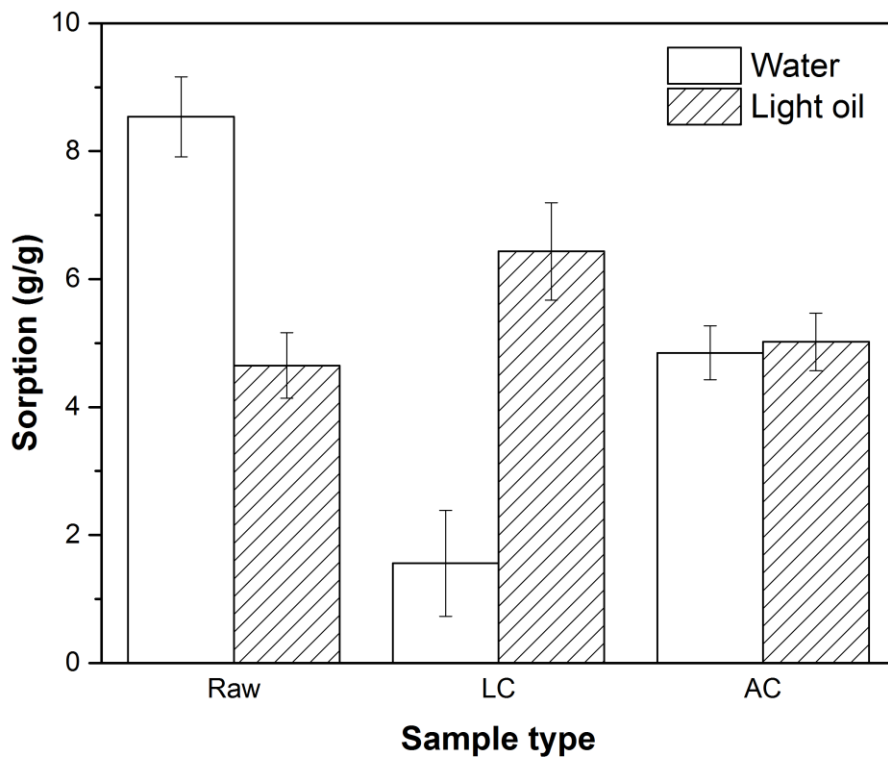


Figure 4.23. The sorption of raw, linseed oil coated (LC) and acetylated (AC) flax straw from the mixture of water and light oil.

The same experiment was performed on heavy oil and the results are plotted in figure 4.24. A small increase was observed in the uptake of heavy oil compare to light oil as well as a decrease in water uptake. The overall trend was similar. The acetylation treatment increased the uptake of heavy oil from 5.6 to 6.1 g/g while decreased the water uptake by 44 % compared to the raw samples. The water uptake decreased from 7.7 to g/g to 1.4 g/g for LC samples. In general, the sorption of heavy oil was higher than the light oil.

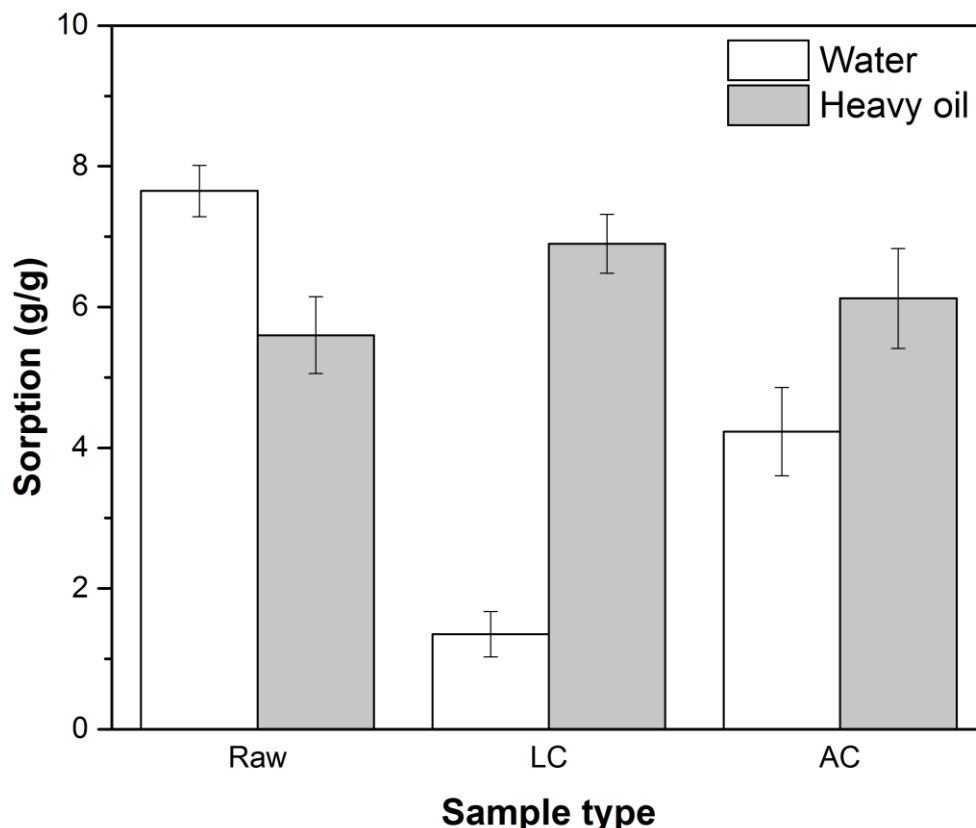


Figure 4.24. The sorption of raw, linseed oil coated (LC) and acetylated (AC) flax straw from the mixture of water and heavy oil.

There was a small increment in the oil sorption capacity of AC samples in the aqueous situation. This may be due to availability of increased void space within the bulk of the sorbents as the hydrophobic acetyl groups available on the surface of sorbent particles act to repel water and create more spaces for oil adsorption. For LC samples, the hydrophobicity was high enough to preserve the sorbent particles from wetting for a duration of 15 min. The polar water molecules repel the non-polar oil molecules within the sorbate mixture. Similarly, the linseed oil is non-polar and will also repel polar water. In the experiment both oil and the sorbent coated particles with linseed oil

were observed to be repelled by water, and therefore tended to attach to each other (Fig 4.25b). This is the main reason of high oil sorption in LC samples. Another important characteristic of LC sample was its high buoyancy compared to the raw sample. Figure 4.25 compares the raw and LC samples after 15 min of stirring within the oil and water media. Individual raw particles were observed to be floating in the test cell (Fig 4.25a) while the LC samples bonded to each other and floated to the surface of the water (Fig 4.25b).

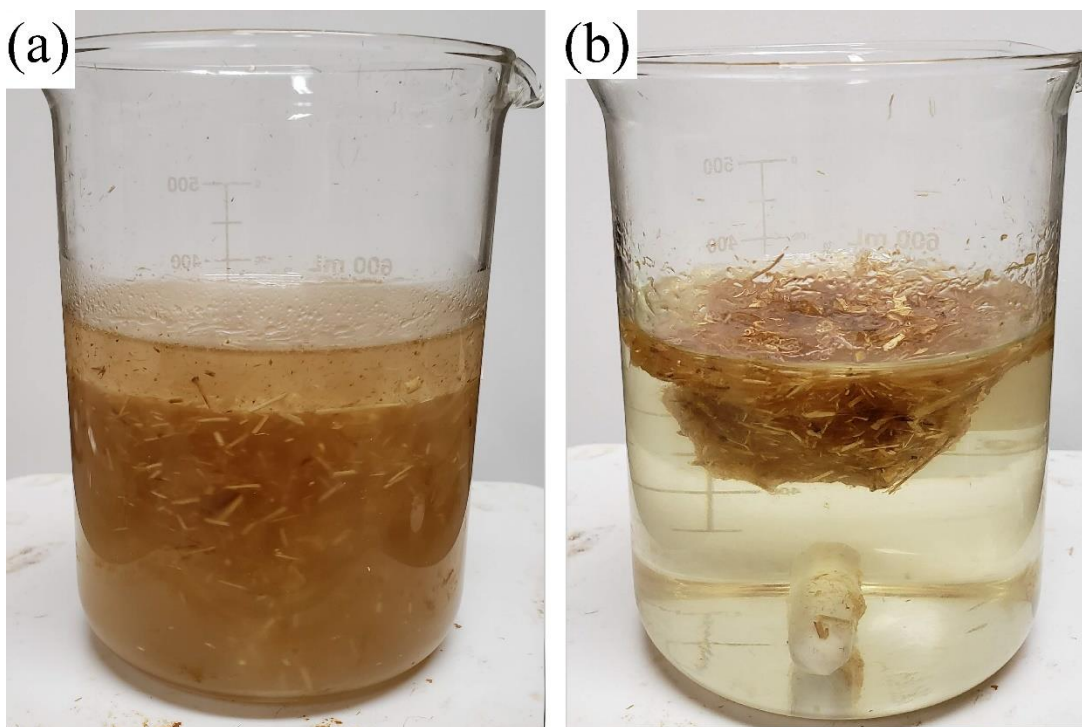


Figure 4.25. Comparison between buoyancy of raw (a) and linseed oil coated (LC) sample(b).

Although the AC samples considerably decreased in water uptake for the aquatic situation, there was no significant increase in its oil sorption capacity. The oil to water selectivity ratio of the AC samples was 1 and 1.5 for light and heavy oil, respectively (Fig 4.26). LC samples on the other hand, had 4 to 5 times more oil uptake compared to water in light and heavy oil, respectively. In this regard, the linseed oil coated samples are a good candidate for removing spilled oil in a marine environment.

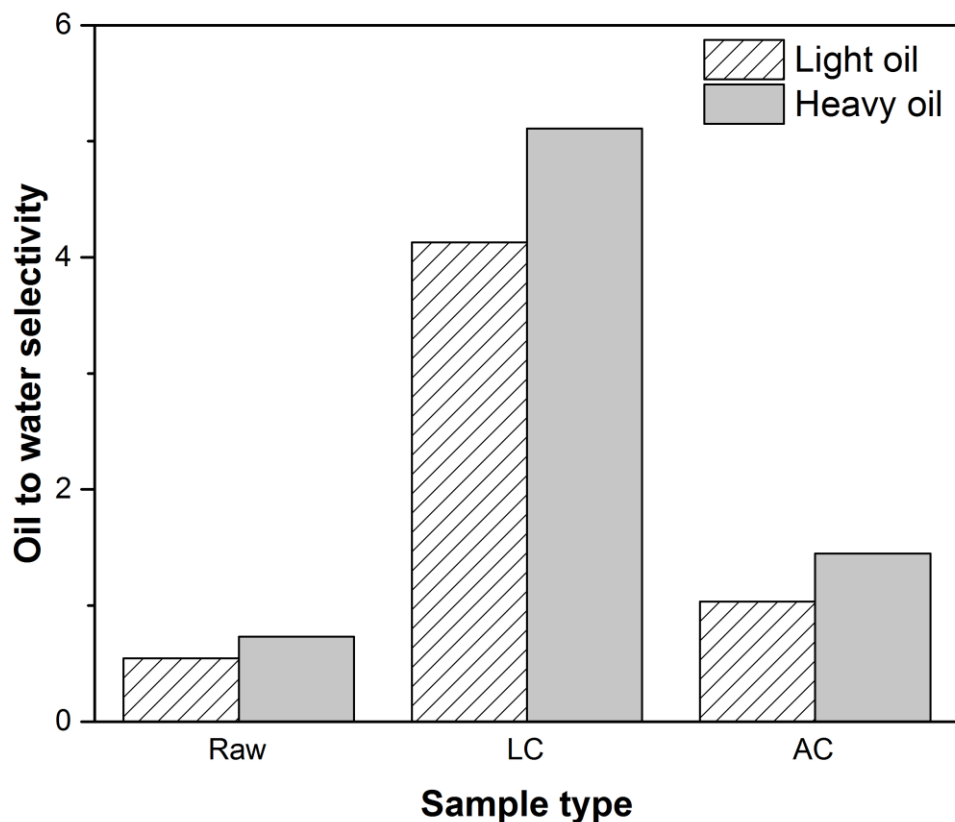


Figure 4.26. Light and heavy oil to water selectivity for raw, linseed oil coated (LC) and acetylated (AC) flax straw samples.

4.6 Reusability and disposal of the sorbent

The linseed oil coated samples showed promising results for oil sorption. In this section, the possibility of reusing this material along with the oil retention capacity of linseed oil coated samples are compared with raw samples. In addition, to determine the possibility of disposing used sorbent materials in landfills, the results of the paint filter liquid (PFL) test are reviewed.

4.6.1 Oil retention

The experimental findings of oil retention are shown in the figure 4.27. Light oil was observed to drain more easily out of the bulk of sorbent compared to heavy viscous oil which adhered to the bulk sorbent after 24 h. The LC material retained slightly less oil compared to the raw samples. For example, the LC light oil retained 7 % less, while the LC heavy oil retain 10 % less than the raw samples. This can be mainly due to lower oil sorption capacity of LC samples explained in the section 4.5.1.

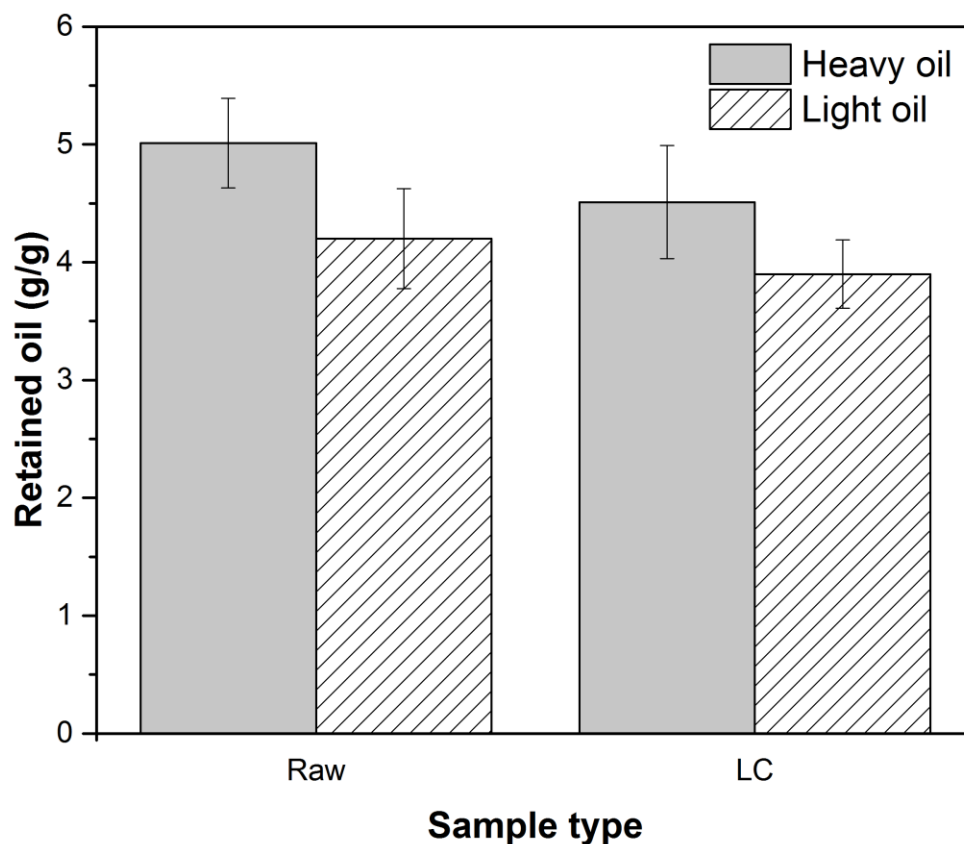


Figure 4.27. Heavy and light oil retention of raw and linseed oil coated flax straw samples (LC).

4.6.2 Reusability

Reusability of raw and LC flax straw samples for light oil is compared in figure 4.28. The oil sorption capacity of raw samples reduced by 14.8 % compared to 11.8 % for LC samples after the 4th sorption/desorption cycle. The oil sorption capacity of raw samples was reduced by almost 11 % after 1st cycle. This suggests a portion of oil is retained in the sorbent after being centrifuged. This may be due to the portion of oil that has been defused and absorbed into the bulk of the sorbent which cannot easily be removed by centrifuge. This remaining oil occupies part of the initial void spaces available to new oil to adsorb in the following cycle. Therefore, the sorbent oil uptake is decreases in the subsequent cycles. For example, a 2.8 % decrease in oil sorption capacity is observed from cycle two to cycle three and 0.8 % reduction from cycle three to cycle four. The decrease for the last two cycles was lower compared to first and second cycles. The centrifuge removed most of the adsorbed oil from the sorbent since this oil is mostly deposited in intra-particle spaces, and hence the sorbent was able to uptake almost the same amount of the oil during the next cycle.

For LC samples, as some opening of the pores had been closed by the coating layer, the penetration of the oil into the bulk of the sorbent was lower compared to the raw samples. Due to this reason, during the oil sorption process, most of the oil deposited in intra-particle spaces in sorbent and not in the bulk of sorbent particles. Because of this lower diffusion into the bulk, the centrifuge could push out most of the uptaken oil, and hence, the decline in oil sorption capacity of LC sample was not as high as the raw sample.

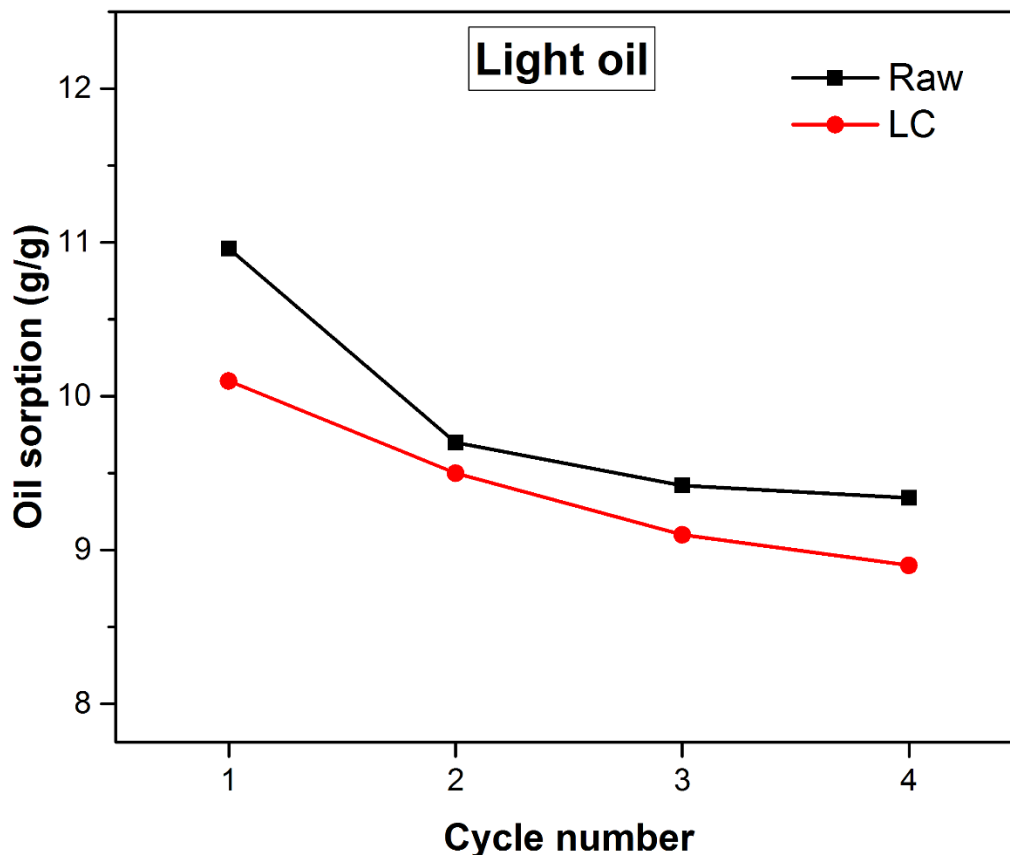


Figure 4.28. Comparison between the reusability of raw and linseed oil coated flax straw samples (LC) for light oil.

As shown in figure 4.29, the oil sorption capacity of LC samples in heavy oil dropped by 7.9 %, while in light oil decreased by about 11.8 % after four cycles of reusability. This may be attributed to the different oil viscosities. Heavy oil does not penetrate within the bulk of sorbent as quickly as light oil due to its higher viscosity. Therefore, most of the heavy oil that had been up taken by the LC samples drained out of the sorbent during centrifuge. As a result, the sorbent did not lose most of its oil sorption capabilities.

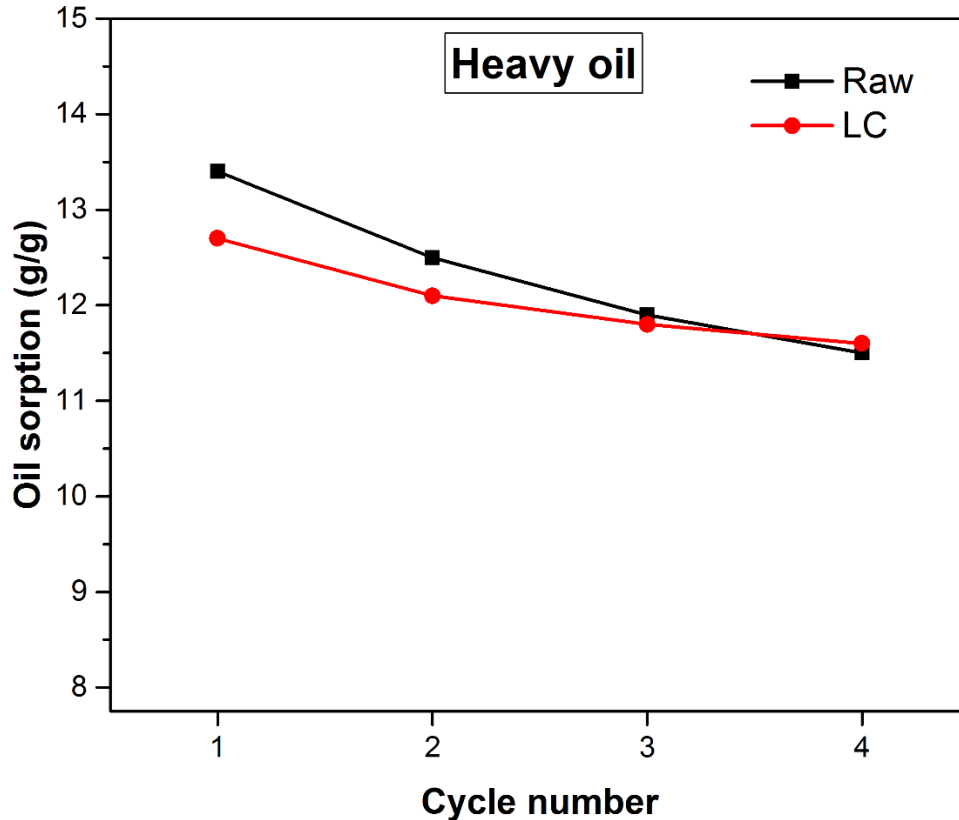


Figure 4.29. Comparison between the reusability of raw and linseed oil coated flax straw samples (LC) for heavy oil.

4.6.3 PFL test result

The PFL tests were performed on three different contaminated LC samples with light oil. The first sample was the oily sorbent from the oil sorption experiment where the sample had been immersed in light oil for 15 min and drained for 30 s. The other sample was the result of the oil retention experiment which had been hung for 24 h after the oil sorption experiment. The last sample was the oily sample which had been centrifuged for 30 second after 15 min of soaking in oil. The first did not pass the test which means that a free liquid still existed in the sorbent and it is not appropriate for landfill deposition. However, the second and third samples passed the test. This suggested that hanging the oily sorbent for 24 h or applying the centrifuge right after the oil sorption can clean the sorbent from hazardous free liquid and make it ready for transferring to the landfill.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

5.1 Conclusions

In this research work, flax straw was examined for its oil and water uptake. Raw flax straw was submitted to the acetylation treatment and a novel linseed oil coating treatment to enhance its oil sorption properties. The main findings from these experimental investigations are highlighted as follows:

- Cutting the straw with a knife milling machine is an effective practice for producing the oil sorbent since it uses both shear and impact forces to simultaneously crush and cut the straw. The results showed cutting the flax straw to sizes less than 4 mm was not practical as the flax fibers had a tendency to weave into each other. This prevented the fibers from passing through the sieving of the milling machine.
- The untreated flax straw (cut by knife milling machine using the sieve with 6x6 mm opening) was capable of adsorbing up to around 11 and 14 g/g of light and heavy oil, respectively in the absence of water.
- The water uptake of untreated flax straw (cut by knife milling machine using the sieve with 6x6 mm opening) in kinetic water uptake tests where only water existed was 6.9 g/g at 5 min. This amount was raised to 8.5 g/g after 45 min of soaking. This was found to be an issue when utilizing natural sorbents in aqueous conditions.
- Both proposed treatments did not substantially impact the oil sorption capacity of the samples made of untreated flax straw where only oil exist as a sorbent. Therefore, using the pulverized untreated flax straw (cut by knife milling machine using the sieve with 6x6 mm opening) is proposed for the situation that only oil exist.
- Acetylation treatment decreased the water uptake of flax straw by 44 % from the mixture of light oil and water (1:6) while improving the oil sorption uptake by 9 %.
- Linseed oil coating using the proposed centrifuge method will provide an inexpensive yet effective coating results. This thin coating can reduce the water uptake of flax straw by 81 %

and improve the oil sorption by 38 % compared to the untreated straw in an aqueous situation.

- Linseed oil coating decrease the water uptake of flax straw by 33 % after 5 min of immersing in the artificial sea water. Also, the resistance of flax straw toward water adsorption was improved by coating. The increase in the amount of water uptake for LC sample was only 8.8 % after 35 min of soaking in the water.

5.2 Recommendations for future work

Based on the present research, some recommendations for future work are listed below:

- Linseed oil coated samples can resist the water diffusion up to 35 min after soaking in water. In the coating practice, by changing the time that sorbent exposed to the coating agent, centrifugal speed and drying time, the water resistance capacity can be improved further.
- After harvesting of flax straw, moisture and bacteria may rot and decompose. Providing a linseed oil coating may prevent moisture sorption and last longer. Therefore, the effect of linseed oil coating on storage capacity of the sorbent is an important subject to investigate.
- In real oil spill situation, applying a loose sorbent is impractical as it cannot be easily collected after the sorption of oil. A material that can hold the sorbent particle together such as a mat would ease the application. The mat properties such as sorption, density, buoyancy and reusability will need to be investigated.

LIST OF REFERENCES

- (1) Cojocaru, C.; Macoveanu, M.; Cretescu, I. Peat-Based Sorbents for the Removal of Oil Spills from Water Surface: Application of Artificial Neural Network Modeling. *Colloids Surfaces A Physicochem. Eng. Asp.* **2011**, *384*, 675-684.
- (2) Quintana-Rizzo, E.; Torres, J. J.; Ross, S. W.; Romero, I.; Watson, K.; Goddard, E.; Hollander, D. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in Deep-Living Fishes and Shrimps after the Deepwater Horizon Oil Spill, Gulf of Mexico. *Mar. Pollut. Bull.* **2015**, *94*, 241–250.
- (3) Bozeman, B. The 2010 BP Gulf of Mexico Oil Spill: Implications for Theory of Organizational Disaster. *Technol. Soc.* **2011**, *33*, 244–252.
- (4) Swedmark, M.; Granmo, Å.; Kollberg, S. Effects of Oil Dispersants and Oil Emulsions on Marine Animals. *Water Res.* **1973**, *7*, 1649-1672.
- (5) Bellino, P. W.; Flynn, M. R.; Rangwala, A. S. A Study of Spreading of Crude Oil in an Ice Channel. *J. Loss Prev. Process Ind.* **2013**, *26*, 558–561.
- (6) Kujawinski, E. B.; Kido Soule, M. C.; Valentine, D. L.; Boysen, A. K.; Longnecker, K.; Redmond, M. C. Fate of Dispersants Associated with the Deepwater Horizon Oil Spill. *Environ. Sci. Technol.* **2011**, *45*, 1298–1306.
- (7) Ventikos, N. P.; Vergetis, E.; Psaraftis, H. N.; Triantafyllou, G. A High-Level Synthesis of Oil Spill Response Equipment and Countermeasures. *Journal of Hazardous Materials.* **2004**, *107*, 51–58.
- (8) Crini, Grégorio, and P.-M. B. *Sorption Processes and Pollution: Conventional and Non-Conventional Sorbents for Pollutant Removal from Wastewaters*; Presses Univ. Franche-Comté, **2010**.
- (9) Ceylan, D.; Dogu, S.; Karacik, B.; Yakan, S. D.; Okay, O. S.; Okay, O. Evaluation of Butyl Rubber as Sorbent Material for the Removal of Oil and Polycyclic Aromatic Hydrocarbons from Seawater. *Environ. Sci. Technol.* **2009**, *43*, 3846–3852.
- (10) Pasila, A. A Biological Oil Adsorption Filter. *Mar. Pollut. Bull.* **2004**, *49*, 1006–1012.

- (11) Suni, S.; Kosunen, A. L.; Hautala, M.; Pasila, A.; Romantschuk, M. Use of a By-Product of Peat Excavation, Cotton Grass Fibre, as a Sorbent for Oil-Spills. *Mar. Pollut. Bull.* **2004**, *49*, 916–921.
- (12) Abdullah, M. A.; Rahmah, A. U.; Man, Z. Physicochemical and Sorption Characteristics of Malaysian *Ceiba Pentandra* (L.) Gaertn. as a Natural Oil Sorbent. *J. Hazard. Mater.* **2010**, *177*, 683–691.
- (13) Melvold, Robert W., Steven C. Gibson, and R. S. Sorbents for Liquid Hazardous Substance Cleanup and Control. *Noyes Publ.* **1988**.
- (14) Choi, H. M.; Cloud, R. M. Natural Sorbents in Oil Spill Cleanup. *Environ. Sci. Technol.* **1992**, *26*, 772–776.
- (15) Wahi, R.; Chuah, L. A.; Choong, T. S. Y.; Ngaini, Z.; Nourouzi, M. M. Oil Removal from Aqueous State by Natural Fibrous Sorbent: An Overview. *Separation and Purification Technology.* **2013**, *113*, 51–63.
- (16) Praba Karana, C.; Rengasamy, R. S.; Das, D. Oil Spill Cleanup by Structured Fibre Assembly. **2011**.
- (17) Adebajo, M. O.; Frost, R. L.; Kloprogge, J. T.; Carmody, O.; Kokot, S. Porous Materials for Oil Spill Cleanup: A Review of Synthesis and Absorbing Properties. *Journal of Porous Materials.* **2003**, *10*, 159–170.
- (18) Wang, J.; Zheng, Y.; Wang, A. Superhydrophobic Kapok Fiber Oil-Absorbent: Preparation and High Oil Absorbency. *Chem. Eng. J.* **2012**, *213*, 1–7.
- (19) Said, A. E. A. A.; Ludwick, A. G.; Aglan, H. A. Usefulness of Raw Bagasse for Oil Absorption: A Comparison of Raw and Acylated Bagasse and Their Components. *Bioresour. Technol.* **2009**, *100*, 2219–2222.
- (20) Tijani, M. M.; Aqsha, A.; Mahinpey, N. Development of Oil-Spill Sorbent from Straw Biomass Waste: Experiments and Modeling Studies. *J. Environ. Manage.* **2016**, *171*, 166–176.
- (21) Li Loong, M.; Cree, D. Enhancement of Mechanical Properties of Bio-Resin Epoxy / Flax

- Fiber Composites Using Acetic Anhydride. *J. Polym. Environ.* **2018**, *26*, 224-234.
- (22) Nič, M. IUPAC Compendium of Chemical Terminology 2nd Edition. *IUPAC Compend. Chem. Terminol. Gold B.* **1997**.
- (23) Hyung-MIn, C.; Cloud, R. M. Natural Sorbents in Oil Spill Cleanup. *Environ. Sci. Technol.* **1992**, *26*, 772-776.
- (24) Zhu, H.; Qiu, S.; Jiang, W.; Wu, D.; Zhang, C. Evaluation of Electrospun Polyvinyl Chloride/Polystyrene Fibers as Sorbent Materials for Oil Spill Cleanup. *Environ. Sci. Technol.* **2011**.
- (25) Wu, D.; Fang, L.; Qin, Y.; Wu, W.; Mao, C.; Zhu, H. Oil Sorbents with High Sorption Capacity, Oil/Water Selectivity and Reusability for Oil Spill Cleanup. *Mar. Pollut. Bull.* **2014**, *45*, 4527-4531.
- (26) Marambe, H. K.; Wanasundara, J. P. D. Ch. 8: Protein From Flaxseed (*Linum Usitatissimum* L.). In *Sustainable Protein Sources*, **2016**, *1*, 133-144.
- (27) Physical Properties of Agricultural Materials. *Dev. Agric. Eng.* **1986**.
- (28) Baley, C.; Goudenhooff, C.; Gibaud, M.; Bourmaud, A. Flax Stems: From a Specific Architecture to an Instructive Model for Bioinspired Composite Structures. *Bioinspiration and Biomimetics*, **2018**.
- (29) Charlet, K.; Jernot, J. P.; Breard, J.; Gomina, M. Scattering of Morphological and Mechanical Properties of Flax Fibres. *Ind. Crops Prod.* **2010**, *32*, 220-224.
- (30) Buranov, A. U.; Mazza, G. Lignin in Straw of Herbaceous Crops. *Industrial Crops and Products.* **2008**, *28*, 237-259.
- (31) Aqsha, A.; Tijani, M. M.; Moghtaderi, B.; Mahinpey, N. Catalytic Pyrolysis of Straw Biomasses (Wheat, Flax, Oat and Barley) and the Comparison of Their Product Yields. *J. Anal. Appl. Pyrolysis* **2017**, *125*, 201-208.
- (32) Ansari, I. A., G. C. East, and D. J. J. Structure–Property Relationships in Natural Cellulosic

- Fibres: Part III: Flax—an Oil Sorbent. *J. Text. Inst.* **2003**, *94*, 1–15.
- (33) Ansari, I. A.; East, G. C.; Johnson, D. J. Structure–property Relationships in Natural Cellulosic Fibres. Part I: Characterisation. *J. Text. Inst.* **1999**, *90*, 469–480.
- (34) Tamaki, Y.; Mazza, G. Measurement of Structural Carbohydrates, Lignins, and Micro-Components of Straw and Shives: Effects of Extractives, Particle Size and Crop Species. *Ind. Crops Prod.* **2010**, *31*, 534-541.
- (35) Bledzki, A. K.; Mamun, A. A.; Lucka-Gabor, M.; Gutowski, V. S. The Effects of Acetylation on Properties of Flax Fibre and Its Polypropylene Composites. *Express Polym. Lett.* **2008**, *2*, 413-422.
- (36) Zhang, X.; Yang, W.; Blasiak, W. Modeling Study of Woody Biomass: Interactions of Cellulose, Hemicellulose, and Lignin. *Energy and Fuels* **2011**, *25*, 4786-4795.
- (37) Liu, W.-J.; Jiang, H.; Yu, H.-Q. Thermochemical Conversion of Lignin to Functional Materials: A Review and Future Directions. *Green Chem.* **2015**, *17*, 4888-4907.
- (38) Murphy, J. D.; McCarthy, K. Ethanol Production from Energy Crops and Wastes for Use as a Transport Fuel in Ireland. *Appl. Energy* **2005**.
- (39) Singh, V.; Kendall, R. J.; Hake, K.; Ramkumar, S. Crude Oil Sorption by Raw Cotton. *Ind. Eng. Chem. Res.* **2013**, *52*, 6277-6281.
- (40) Cao, S., Dong, T., Xu, G., & Wang, F. Study on Structure and Wetting Characteristic of Cattail Fibers as Natural Materials for Oil Sorption. *Environ. Technol.* **2016**, *37*, 1–21.
- (41) Dong, T.; Wang, F.; Xu, G. Sorption Kinetics and Mechanism of Various Oils into Kapok Assembly. *Mar. Pollut. Bull.* **2015**, *91*, 230-237.
- (42) Nwadiogbu, J. O.; Ajiwe, V. I. E.; Okoye, P. A. C. Removal of Crude Oil from Aqueous Medium by Sorption on Hydrophobic Corncobs: Equilibrium and Kinetic Studies. *J. Taibah Univ. Sci.* **2016**, *10*, 56-63.
- (43) Norman Louis Allinger, Melvin Jerome Bigelow, H. C. M. An Introduction to General,

Organic, and Biological Chemistry; *Wadsworth Publishing Company*, **1976**.

- (44) Choi, H.-M.; Kwon, H.-J.; Moreau, J. P. Cotton Nonwovens as Oil Spill Cleanup Sorbents. *Textile Research Journal*. **1993**, *63*, 211–218.
- (45) Lim, T. T.; Huang, X. Evaluation of Kapok (*Ceiba Pentandra* (L.) Gaertn.) as a Natural Hollow Hydrophobic-Oleophilic Fibrous Sorbent for Oil Spill Cleanup. *Chemosphere* **2007**, *66*, 955–963.
- (46) Dong, T.; Xu, G.; Wang, F. Oil Spill Cleanup by Structured Natural Sorbents Made from Cattail Fibers. *Ind. Crops Prod.* **2015**, *76*, 25-33.
- (47) Cui, Y.; Xu, G.; Liu, Y. Oil Sorption Mechanism and Capability of Cattail Fiber Assembly. *J. Ind. Text.* **2014**, *43*, 330–337.
- (48) Pooya Ghasemi; Duncan Cree; and Alvin Aldrich., " Development of Raw and Treated Flaw Straw for Oil Spill Clean up", *CSME International Congress – York University, Toronto, Ontario*, **2018**.
- (49) Law, K. Y.; Zhao, H. Surface Wetting: Characterization, Contact Angle, and Fundamentals; *Springer*, **2015**.
- (50) Behnood, R.; Anvaripour, B.; Fard, N. J. H.; Farasati, M. Petroleum Hydrocarbons Adsorption from Aqueous Solution by Raw Sugarcane Bagasse. *Int. J. Emerg. Sci. Eng.* **2013**, *1*, 96–99.
- (51) Hussein, M.; Amer, A. A.; El-Maghraby, A.; Taha, A. Availability of Barley Straw Application on Oil Spill Clean Up. *Int. J. Environ. Sci. Technol.* **2009**, *6*, 123–130.
- (52) Kast, W. Principles of Adsorption and Adsorption Processes. *Chem. Eng. Process. Process Intensif.* **1985**, *118*, 433-450.
- (53) Choi, H. M.; Moreau, J. P. Oil Sorption Behavior of Various Sorbents Studied by Sorption Capacity Measurement and Environmental Scanning Electron Microscopy. *Microsc. Res. Tech.* **1993**, *25*, 447–455.
- (54) Thomas L. Lemke. Review of Organic Functional Groups: Introduction to Medicinal Organic

Chemistry 4th Ed.; *Lippincott Williams & Wilkins*, **2003**.

- (55) Dehabadi, L.; Mahaninia, M. H.; Soleimani, M.; Wilson, L. D. Miscanthus Biomass for the Sustainable Fractionation of Ethanol-Water Mixtures. *ACS Sustain. Chem. Eng.* **2017**, *5*, 2970-2980.
- (56) Espert, A.; Vilaplana, F.; Karlsson, S. Comparison of Water Absorption in Natural Cellulosic Fibres from Wood and One-Year Crops in Polypropylene Composites and Its Influence on Their Mechanical Properties. *Compos. Part A Appl. Sci. Manuf.* **2004**, *35*, 1267–1276.
- (57) Li, X.; Tabil, L. G.; Panigrahi, S. Chemical Treatments of Natural Fiber for Use in Natural Fiber-Reinforced Composites: A Review. *Journal of Polymers and the Environment.* **2007**, *15*, 25-33.
- (58) X. L. Sun.; Study On The Surface Adsorption Characteristics Of Natural Cellulose Fiber To Oil, **2012**.
- (59) Wong, Chris, McGowan, Tyler, Bajwa, Sreekala, AND Bajwa, Dilpreet. “Impact of Fiber Treatment on the Oil Absorption Characteristics of Plant Fibers” *BioResources*, **2016**, *11*, 6452-6463.
- (60) Sun, X. F.; Sun, R. C.; Sun, J. X. Acetylation of Sugarcane Bagasse Using NBS as a Catalyst under Mild Reaction Conditions for the Production of Oil Sorption-Active Materials. *Bioresour. Technol.* **2004**, *95*, 343–350.
- (61) Joana M.Lopes. Effect of ScCO₂ on the Kinetics of Acetylation of Cellulose Using 1-Allyl-3-Methylimidazolium Chloride as Solvent. Experimental Study and Modeling. *J. Supercrit. Fluids* **2018**, *141*, 97–103.
- (62) Teli, M. D.; Valia, S. P. Acetylation of Banana Fibre to Improve Oil Absorbency. *Carbohydr. Polym.* **2013**, *92*, 328-333.
- (63) Babak Karimi, H. S. N -Bromosuccinimide (NBS), a Novel and Highly Effective Catalyst for Acetylation of Alcohols under Mild Reaction Conditions, **2001**, *4*, 0519-0520.
- (64) Höfle, G.; Steglich, W.; Vorbrüggen, H. 4-Dialkylaminopyridines as Highly Active Acylation

- Catalysts. [New synthetic method (25)]. *Angewandte Chemie International Edition in English*. **1978**, *17*, 569-583.
- (65) Pries, M.; Wagner, R.; Kaesler, K. H.; Militz, H.; Mai, C. Acetylation of Wood in Combination with Polysiloxanes to Improve Water-Related and Mechanical Properties of Wood. *Wood Sci. Technol.* **2013**, *47*, 685-699.
- (66) Sabir, S. Approach of Cost-Effective Adsorbents for Oil Removal from Oily Water. *Crit. Rev. Environ. Sci. Technol.* **2015**, *45*, 1916-1945.
- (67) Jähn, A.; Schröder, M. W.; Fütting, M.; Schenzel, K.; Diepenbrock, W. Characterization of Alkali Treated Flax Fibres by Means of FT Raman Spectroscopy and Environmental Scanning Electron Microscopy. *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2002**, *58*, 2271-2279.
- (68) Schrader, B. Infrared and Raman Spectroscopy-Methods and Applications; *John Wiley & Sons*, **1994**.
- (69) Gabbot, P. Principles and Applications of Thermal Analysis, *John Wiley & Sons*, **2008**.
- (70) Nwankwere, E. T.; Omolaoye, J. A.; Nwadiogbu, J. O.; Nale, B. Y. Thermal and Dimensional Stability of NBS-Catalyzed Acetylated Rice Husk. **2011**, *2*, 189–196.
- (71) Calado, V.; Barreto, D. W.; D’Almeida, J. R. M. The Effect of a Chemical Treatment on the Structure and Morphology of Coir Fibers. *J. Mater. Sci. Lett.* **2000**, *19*, 2151–2153.
- (72) ASTM D1141-98(2013), Standard Practice for the Preparation of Substitute Ocean Water, ASTM International, West Conshohocken, PA, **2013**, www.astm.org.
- (73) ANKOM Method 5. Acid Detergent Fiber in Feeds-Filter Bag Technique. ANKOM Technology. Macedon, New York; **2006**.
- (74) ANKOM Method 6. Neutral Detergent Fiber in Feeds-Filter Bag Technique. ANKOM Technology. Macedon, New York; **2006**.
- (75) ANKOM Method 8. Determining Acid Detergent Lignin in Beakers. ANKOM Technology.

Macedon, New York; **2005**.

- (76) Official Methods of Analysis of AOAC INTERNATIONAL (2012) 19th Ed., AOAC 50INTERNATIONAL, Gaithersburg, MD, USA, “Www.Eoma.Aoac.Org.”
- (77) Silverman, B. L. Particle Size Analysis in Industrial Hygiene; *Elsevier*, **1971**.
- (78) ASTM F726-17, Standard Test Method for Sorbent Performance of Adsorbents for use on Crude Oil and Related Spills, ASTM International, West Conshohocken, PA, **2017**, www.astm.org.
- (79) 40 CFR 264.314 - Special Requirements for Bulk and Containerized Liquids, Code of Federal Regulations (Annual Edition), **2011**.
- (80) SW-846 Test Method 9095B: Paint Filter Liquids Test, Title 40 of the Code of Federal Regulations, Sections 264.314, **2004**.
- (81) Dufresne, A.; Cavaille, J.-Y.; Vignon, M. R. Mechanical Behavior of Sheets Prepared from Sugar Beet Cellulose Microfibrils. *J. Appl. Polym. Sci.* **1997**, *64*, 1185-1194.
- (82) ASTM WK58359, Standard New Practice for Drying Flax Fiber Prior to Moisture Sensitive Processing or Testing, ASTM International, West Conshohocken, PA, **2017**, www.astm.org.
- (83) Parsi, R. D.; Kakde, M. V; Pawar, K.; Police Patil, R. S. Influence of Fibre Length on Ring Spun Yarn Quality. **2016**.
- (84) Singha, K.; Maity, S.; Singha, M.; Paul, P.; Gon, D. P. Effects of Fiber Diameter Distribution of Nonwoven Fabrics on Its Properties. *Int. J. Text. Sci.* **2012**, *1*, 7-14.
- (85) Rana, A. K.; Basak, R. K.; Mitra, B. C.; Lawther, M.; Banerjee, A. N. Studies of Acetylation, of Jute Using Simplified Procedure and Its Characterization. *J. Appl. Polym. Sci.* **1997**, *64*, 1517-1523.
- (86) Pang, J.; Liu, X.; Yang, J.; Lu, F.; Wang, B.; Xu, F.; Ma, M.; Zhang, X. Synthesis of Highly Polymerized Water-Soluble Cellulose Acetate by the Side Reaction in Carboxylate Ionic Liquid 1-Ethyl-3-Methylimidazolium Acetate. *Sci. Rep.* **2016**, *6*, 33725-33733.

- (87) Nunes, C.; Slížková, Z. Hydrophobic Lime Based Mortars with Linseed Oil: Characterization and Durability Assessment. *Cem. Concr. Res.* **2014**, *61*, 28-39.
- (88) Craven, J. M.; Swithenbank, J.; Sharifi, V. N.; Peralta-Solorio, D.; Kelsall, G.; Sage, P. Hydrophobic Coatings for Moisture Stable Wood Pellets. *Biomass and Bioenergy* **2015**, *80*, 278-285.
- (89) Asadpour, R.; Sapari, N. B.; Isa, M. H.; Kakooei, S.; Orji, K. U. Acetylation of Corn Silk and Its Application for Oil Sorption. *Fibers Polym.* **2015**, *16*, 1830-1835.
- (90) Behnood, R.; Anvaripour, B.; Jaafarzadeh, N.; Farasati, M. Oil Spill Sorption Using Raw and Acetylated Sugarcane Bagasse. *J. Cent. South Univ.* **2016**, *23*, 1618-1625.
- (91) Teli, M. D.; Valia, S. P. Acetylation of Jute Fiber to Improve Oil Absorbency. *Fibers Polym.* **2013**, *14*, 915-919.

APPENDIX A

Table A.1: ANOVA and LSD test result for oil sorption of untreated flax straw with respect to heavy oil and light oil.

SUMMARY				
<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
Heavy oil(A)	7	82.19	11.74143	12.23639
Light oil(B)	7	75.0425	10.72036	10.92629

ANOVA						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between						
Groups	3.649054	1	3.649054	0.315081	0.58491	4.747225
Within						
Groups	138.9761	12	11.58134			
Total	142.6251	13				

P-value is higher than the level of significance (0.05). Hence, based on the ANOVA the difference is not significant.

$$LSD_{A,B} = t_{(0.05/2,DFW)} \sqrt{S_{within} \left(\frac{1}{n_A} + \frac{1}{n_B} \right)} = 3.963717$$

T critical (from critical value of t-Distribution for df=12) = 2.179

MS_w (from ANOVA) =11.58134

n_A=n_B=7

If A(average) -B(average) > LSD_{A,B} , the difference is statistically significant

11.74143-10.72036 = 1.2107 < LSD_{A,B} .Based on LSD the difference is not significant.

APPENDIX B

Table B.1: ANOVA and LSD test result for light oil sorption of untreated samples with changing in samples packing density (PD) (1.5×10^5 , 2.5×10^5 and 3.5×10^5 g/m³)

SUMMARY						
<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>		
1.5×10^5 PD (A)	3	60.48	20.16	0.81		
2.5×10^5 PD(B)	3	68.94	22.98	1.21		
3.5×10^5 PD(C)	3	43.8	14.6	0.7225		

ANOVA						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	109.0904	2	54.5452	59.66658	0.00011	5.143253
Within Groups	5.485	6	0.914167			
Total	114.5754	8				

P-value is lower than the level of significance (0.05). Hence, based on the ANOVA the difference is significant.

$$LSD_{A,B} = t_{(0.05/2, DFW)} \sqrt{MS_{within} \left(\frac{1}{n_A} + \frac{1}{n_B} \right)} = 1.9102979$$

T critical (from critical value of t-Distribution for df=6) = 2.447

MS_w (from ANOVA) = 0.914167 and n_A=n_B=3

If A(average) - B(average) > LSD_{A,B}, the difference is statistically significant

Comparing 1.5×10^5 PD(A) with 2.5×10^5 PD(B):

$22.98 - 20.16 = 2.82 > LSD_{A,B}$. Based on LSD the difference is significant between A and B.

Comparing 2.5×10^5 PD(B) with 3.5×10^5 PD(C):

$22.98 - 14.6 = 8.38 > LSD_{B,C}$. Based on LSD the difference is significant between B and C.

APPENDIX C

Table C.1: ANOVA and LSD test result for light oil sorption with varying the sorbent treatment (raw, linseed oil coated and acetylated).

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
Raw(A)	3	40.8	13.6	0.3969
LC(B)	3	38.025	12.675	0.6889
AC(C)	3	43.5	14.5	1.0404

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>Df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	4.99625	2	2.498125	3.524774	0.0972	5.143253
Within Groups	4.2524	6	0.708733			
Total	9.24865	8				

P-value is higher than the level of significance (0.05). Hence, based on the ANOVA the difference is not significant.

$$LSD_{A,B} = t_{(0.05/2,DFW)} \sqrt{MS_{within} \left(\frac{1}{n_A} + \frac{1}{n_B} \right)} = 1.9102979$$

T critical (from critical value of t-Distribution for df=6) = 2.447

MS_w (from ANOVA) = 0.708733 and n_A=n_B=3

If A(average) - B(average) > LSD_{A,B}, the difference is statistically significant

Comparing raw sample(A) with LC sample(B):

13.6-12.675 = 0.925 < LSD_{A,B} .Based on LSD the difference is not significant between A and B.

Comparing raw sample (A) with AC sample(C):

14.5-13.6 = 0.9 < LSD_{A,C} .Based on LSD the difference is not significant between A and C.

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