DEVELOPMENT OF FUNCTIONAL FLAX FIBERS THROUGH SELF-ASSEMBLED NANOPARTICLES FOR OIL-WATER SEPARATION

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Yunqiu Liu, candidate for the degree of Master of Applied Science in Environmental Systems Engineering, has presented a thesis titled, Development of Functional Flax Fibers Through Self-Assembled Nanoparticles for Oil-Water Separation, in an oral examination held on February 10, 2020. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

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ABSTRACT

Oil-water separation has attracted extensive attention since frequent oil leakage incidents and oily-wastewater discharge caused serious disaster to the environment. Traditional separation technologies have difficulties in dealing with rapid and widespread oil spills and may cause secondary pollution. The use of oil barriers with special wettability is a promising alternative for separating oil from water. Natural materials, such as biomass have advantages of biological degradability, resource abundance, and low cost. In this study, environmentally friendly, reusable, and low-cost functionalized flax fibers were fabricated to separate oil from water.

Flax fibers were modified by plasma-induced poly (acrylic acid) (PAA) polymerization followed by nano-TiO$_2$ self-assembly to obtain a hydrophilic surface. In order to identify the significant preparation parameters and reveal their complicated interactions, a two-level factorial design was employed. Plasma treatment power, plasma treatment gas flow rate, PAA concentration, and nano-TiO$_2$ concentration were found to be able to improve the hydrophilicity significantly. The modified fiber was characterized by synchrotron-based Fourier transform infrared spectroscopy (FTIR) and X-ray fluorescence (XRF). The chemical images of hydroxyl, carboxyl, and TiO$_2$ nanoparticles (TiO$_2$ NPs) on flax fiber surface were measured and analyzed. The TiO$_2$ NPs were found randomly fixed on flax fiber surface. The modified flax fiber was verified to have good capability of separating oil from water. The hydrophilicity of modified flax fiber was significantly improved, with water contact angle decreasing from 97.4° to 25.9° and almost doubled maximum oil
holding pressure. The modified flax fiber showed stable performance of immiscible light oil-water mixture separation in harsh conditions, such as alkaline (pH = 12) and saline (2%) conditions. These excellent performances remained stable after multiple cycles. Therefore, the modified flax fiber has potential to be used as an oil barrier for immiscible oil-water separation.

Furthermore, a photo-induced HDTMS-ZnO coated flax fiber was developed for on-demand oil-water separation. The HDTMS-ZnO coated flax fiber had properties of transferable hydrophobic/underwater oleophilic in the dark and hydrophilic/underwater oleophobic under UV irradiation. A full experimental design was applied to explore the impact between hexadecyltrimethoxysilane (HDTMS) and ZnO nanoparticles (ZnO NPs) concentrations on the modified fiber performance. The optimal combination was found to be 0.1 vol% HDTMS and 1.0 wt% ZnO NPs. The modified fiber samples before and after UV treatment were characterized by scanning electron microscope (SEM) and synchrotron-based FTIR and XRF. The hydrophobic functional groups and ZnO NPs distribution were investigated on flax fiber surface. It was interesting to find that the concentration of alkyl groups decreased with the increase of ZnO NPs concentration under UV irradiation, which contributed to reversible wettability. Hence, the developed flax fiber with this switchable behaviour has promising application including the separation of immiscible oil-water mixture and oil-in-water emulsion scenarios.
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CHAPTER 1

INTRODUCTION

1.1. Environmental Impacts of Oil Pollution

Recently, growing oily wastewater release and crude oil leakage have become a global issue. Oil expansion driven by wind and ocean currents could cause long-term risks to environment (Kingston, 2002). Potential contaminants in oil include ammonia, sulphides, phenol, and hydrocarbons. When exposed under the sunlight, some organic components in oil are oxidized into acidic and phenolic compounds, which show even more toxicity than their precursors (Wake, 2005). In addition, high-loading oil pollution could lead to aquatic environmental change, such as dissolved oxygen decrease, illumination reduction, and acidity increase. Consequently, the chain risks in ecosystems caused by these impacts should not be neglected. Furthermore, human health could also be threatened by oil contamination through the food-chain. Therefore, removing oil from water is in high demand for aquatic ecosystems and human beings.

1.2. Challenges in Oil Pollution Control

Traditional separation methods such as sedimentation, centrifugation, electrocoagulation, combustion, and some integrated treatment systems have drawbacks in dealing with rapid
and widespread oil spills and may cause secondary pollution. The use of oil barriers with special wettability is a promising alternative for separating oil from water, which has recently gained increasing attention. For example, Dai et al. (2019) converted skin collagen fibrous material waste to hydrophobic oil sorbent to separate oil from water. A cellulose-based paper filter modified with nanofibrillated cellulose hydrogel was successfully used as a hydrophilic oil barrier (Rohrbach et al., 2014). The hydrophilic or hydrophobic surface of an oil barrier is usually achieved by special bonding agents such as organic compounds or nanoparticles. However, some of the agents are toxic and fabrication processes are complicated. Hence, developing an effective, economical, and environmentally friendly material to separate oil from water is necessary.

1.3. Challenges in Fabricating Materials with Special Wettability

Both synthetic and natural materials have been used as oil barriers. Some studies have focused on artificially manufactured substrates. For example, Li et al. (2019) fabricated three-dimensional peanut hull/graphene aerogels for oil-water separation. Modifying old corrugated containers into a superhydrophobic coating on a suitable sponge material was also performed to deal with oil spills by Yuan et al. (2018). However, using synthetic materials still has problems in terms of complex preparation processes, high energy consumption, relatively high cost, and secondary pollution (Awual, 2017b). Compared with the synthetic materials, natural materials such as biomass materials have advantages of biological degradability, resource abundance, and low cost (Zahraee et al., 2019). Therefore, there is an increasing interest in modifying natural materials such as cotton, sisal cellulose, and kapok fiber into adsorbent or filter. Saskatchewan is the world’s largest
producer and exporter of flax (Boulos et al., 2017b). However, recently a large number of flax straws were disposed as solid wastes. Therefore, the use of flax fiber for fabricating oil barrier is a new initiative to convert agricultural solid wastes into recyclable, sustainable, and biodegradable composites.

Flax fiber is relatively hydrophilic in nature because there is a proportion of cellulose on the surface (Liu et al., 2018b). To change its surface wettability, hydrophobic or hydrophilic agents can be introduced. For example, Ibrahim et al. (2010b) reported that hydrophilic oxygen-containing functional groups were introduced by oxygen and air plasma treatment. An octadecanoyl chain was grafted on the flax fiber surface to obtain a hydrophobic surface (Wang et al., 2019b). However, the performances of these methods are limited. Perceptively, nanoparticles exhibit good chemical bonding capability owing to the high content of unsaturated atoms on their surfaces (Awual, 2017a). A special nanostructure with innovative performance has been obtained during the modification of materials (Awual, 2016b). Nevertheless, it has been found that it is difficult to bond nanoparticles with cellulose surface since the electrostatic interaction between –OH on flax fiber and nanoparticle is weak (Meilert et al., 2005). Therefore, further study is necessary to adhere nanoparticles on flax fiber surface for the application in the field of oil-water separation.

1.4. Objectives
In this study, flax fiber will be modified by nanoparticles to obtain special wettability, which will be further employed in oil-water separation. The main contents of this research include the following two aspects:

On the one hand, in order to separate immiscible oil-water mixture, flax fibers modified with self-assembled TiO$_2$ NPs were developed as a hydrophilic oil barrier (Chapter 3). On the other hand, to deal with various oil spill scenarios (immiscible light oil-water mixture, heavy oil-water mixture, and oil-in-water emulsion), a UV switchable hydrophobic-hydrophilic/underwater oleophobic flax fiber was proposed (Chapter 4). The feasibility and efficiency of the modified fibers were comprehensively investigated. In addition, the chemical imaging of functional groups and nanoparticles were obtained using synchrotron-based FTIR and X-ray technologies. Moreover, column experiments were set up for simulation of oil-water separation.

The aims of this study are expected (1) to explore the individual effect of process parameters and their interactions on the hydrophilicity of modified flax fiber; (2) to identify the optimal performance of transferable hydrophobic-hydrophilic/under water oleophobic performance; (3) to identify the interface process and mechanism of the fiber modification at micro-scale; and (4) to demonstrate the efficiency and reliability of the modified fibers for oil-water separation.
CHAPTER 2

LITERATURE REVIEW

Oil spilling caused by offshore oil industry and marine transportation is one of the most serious environmental issues. To meet environment challenges, researchers have devoted into oil pollution control. Many traditional physical and chemical methods, and their combinations have been developed to deal with water contamination due to oil spills. For example, adsorption, gravity separation, centrifugation, electrocoagulation, combustion, and some integrated treatment systems were investigated for oil-water separation (An et al., 2017; Awual, 2019; Zhang et al., 2019b). However, some methods have difficulties in handling large-scale polluted water and may cause potential secondary pollution (Farrow et al., 2018b). The use of oil barrier with special wettability is a promising alternative for oil-water separation, which has gained increasing attention recently.

This chapter has been divided into three sections. Section 2.1 reports the application of oil barrier as an effective and broadly employed oil-water separation method. Section 2.2 reviews surface wettability reconstruction methods, and Section 2.3 introduces modification of biomass in dealing with oil pollution problem.

2.1. Oil Barrier for Oil-Water Separation

Although some traditional physical and chemical methods of oil-water separation have
been investigated, they still have difficulties in dealing with large-scale polluted water and may cause potential secondary pollution. Therefore, some artificial materials have been used as oil barriers to separate oil from water. Generally, there are two kinds of oil barrier: oil removing type (oil affinity) and water removing type (water affinity) being employed (Li et al., 2018). Figure 2-1 shows the mechanisms of the two types of oil barriers used in oil-water separation. The water removing type of oil barrier is water affinity, which is able to filtrate water while repelling oil (Figure 2-1 (a)). On the contrary, as is shown in Figure 2-1 (b), water is defenced beyond oil affinity type of oil barrier while oil is filtrated.
Figure 2-1 Scheme of oil barrier in oil-water separation
The water removing type of oil barrier has been investigated in oil-water separation. For example, a cellulose-based paper filter modified with nanofibrillated cellulose hydrogel was successfully used as a water affinity oil barrier (Rohrbach et al., 2014). The water flux reached 89.6 L h\(^{-1}\) m\(^{-2}\) with more than 99% efficiency under gravitational force. A novel superhydrophilic/underwater superoleophobic polyacrylamide hydrogel-coated mesh was successfully applied for oil-water separation with a high efficiency and intrusion pressure (Xue et al., 2011). Aluminum oxide nanowires and graphene oxide nanosheets had been used to modify poly(vinylidene fluoride) membranes, performing as a water affinity oil barrier with a high separation efficiency up to 99.4% (Guo et al., 2019).

Oil removing type of oil barrier was also employed in oil-water separation. Graphene nanosheets have been modified using fluorosilane, and applied on LY12 aluminum substrate via spraying and a two-step coating system (Uzoma et al., 2019). The synthesized graphene nanosheets offered a promising application in oil-water separation with water contact angle over 152°. Modifying old corrugated containers into a superhydrophobic coating on a suitable sponge material was also performed to deal with oil spills by Yuan et al. (2018). A 3D porous FAS-modified ZnO-grown copper foam featured in superhydrophobic in air and superoleophilic under water. It had been used as an immiscible oil/organic solvent separation material, showing high adsorption capacity up to 3000% and high separation efficiency up to 99.4% (Rong et al., 2019). Compared with oil removing type of oil barrier, the water-removing type of oil barrier took advantage in being automatically utilized by gravity. The oil affinity oil barrier was suitable for oil-water emulsion and immiscible heavy oil-water mixture separation while the water affinity
oil barrier was usually utilized to deal with immiscible light oil-water mixture (Li et al., 2018).

2.2. Reconstruction of Material Surface for Changing Wettability

Although the manufactured oil barrier is a promising method in oil-water separation, problems still exist in low efficiency if using raw materials. Hence, reconstructing material surface with special wettability is necessary. Surface wettability is a specific characteristic of a solid surface, which determines the wetting behaviour when a liquid gets in touch with surface of a material (Gupta et al., 2017). The wetting property is determined by chemical components and geometric morphology of solid surfaces (Cassie and Baxter, 1944). As is seen in Figure 2-2, four typical wettability were illustrated: hydrophobicity (low water affinity), hydrophilicity (high water affinity), oleophobicity (low oil affinity), and oleophilicity (high oil affinity). Usually, a material featuring in hydrophilic surface also shows oleophobic behaviour, which characterizes in water affinity and oil repellence. On the contrary, hydrophobicity and oleophilicity can be obtained at the same time, showing oil affinity and water repellence (Li et al., 2018). The wettability/dewettability can be arbitrarily controlled by changing surface chemical deposition or surface morphology.
Figure 2-2 Scheme illustration for transferable surface wettability
2.2.1. Reconstruction of Hydrophobic Surface

As shown in Figure 2-2, hydrophobic materials have properties of water repellence and underwater oil affinity. Studies related to modification of hydrophobic surface by polymers have been investigated. For example, a super-hydrophobic surface was synthesized using adhesion of polydimethylsiloxane and magnesium palmitate to form roughness structure on various substrates including glass, textile, and stainless mesh (Xi et al., 2020). The water contact angle was up to 150° and the oil collection efficiency reached 91%. Multilayer films assembled by layer-by-layer technique through depositing polyallylamine hydrochloride and polyacrylic acid were coated on membranes, exhibiting high oil-water emulsion separation efficiency (Guo et al., 2020). A high-temperature reduced graphene oxide was coated on commercial polyurethane sponge to achieve superhydrophobic surface and employed in oil spills cleaning (Ma et al., 2020). In addition, nanoparticles were also widely used to change surface wettability of materials. Nanoparticles exhibit great chemical bonding capability owing to high content of unsaturated atoms on their surfaces (Awual, 2017a). Special nanostructures with innovative performance have been obtained during the modification of materials (Awual, 2016b). ZnO NPs prepared by hydrothermal reaction with a rod-like shape in nano-sizes showed high oil separation efficiency and a high oil flux (Wang et al., 2019a). SiO₂ nanoparticle-based spray was prepared to modify a superhydrophobic surface, which showed outstanding self-cleaning and anti-adhesion performance (Yu et al., 2019).

2.2.2. Reconstruction of Hydrophilic Surface
Opposite to hydrophobicity, hydrophilic surface shows water affinity and oil repellence properties (Figure 2-2). Methods in fabricating hydrophilic surface mainly include surface etching, chemical compounds decorating, and nanoparticles self-assembly. Plasma treatment was used to etch the surface of cellulose materials, clean impurities and introduce hydrophilic oxygen-containing functional groups (Ibrahim et al., 2010b). Hydrophilic graphene oxide was used as a coating material to modify oxidized copper mesh, exhibiting excellent anti-oil fouling property and stability in corrosive solutions (Chen and Chen, 2019). The oil-water separation efficiency could achieve 99.49% with good reusability. A cost-effective biomimetic coating system was designed and utilized to reconstruct membrane surface via the intermolecular "amino/mercapto-pyrogallol bridges" (Yang et al., 2019). The as-prepared membrane with hydrophilicity had high water flux up to 7900 L/m² h and oil rejection efficiency up to 95.4%. The surface of SiO₂ NPs was activated with amine groups to improve the polymeric membrane's performance (Khodadousti et al., 2019). The permeability and hydrophilicity of the modified membrane were tested and the oil rejection rate was over 98%. ZnO NPs were immobilized onto membrane surface, converting its hydrophobic nature to hydrophilic, and bringing about the dramatically improvement of membrane performance both in water permeation flux and oil rejection rate (Chen et al., 2019d).

### 2.2.3. Reconstruction of Surface with Switchable Wettability

Based on the traditional hydrophilic/underwater oleophobic and hydrophobic/underwater oleophilic surface properties, some innovative materials have been fabricated into
switchable wettability. Nowadays, attention has been paid to controllable surface wettability of solid substrates to solve oil pollution. Some chemicals are responsive to outside conditions such as pH, temperature, and light. After deposition, the surface wettability is transferable. A pH-sensitive P2VP-based blockcopolymer was fabricated with switchable wettability on a non-woven textile and apolyurethane sponge. The as-prepared membrane was hydrophobic and prevented the spread of water at pH 6.5 while achieved reverse separation when pre-treated by water at pH 2.0 (Zhang et al., 2012). A pH-responsive polymeric foam was used to adsorb micro-oil droplets. The switchable wettability was caused by protonation or dissociation of surface active functional groups (Cherukupally et al., 2017). Superhydrophobic ZnO nano-structures were synthesised on mesh and the surface wettability was reversibly switched from superhydrophobicity to hydrophilicity by altering the annealing temperature (Velayi and Norouzbeigi, 2018). A photo-induced oil-water mixture separation based on the switchable superhydrophobicity-superhydrophilicity and underwater superoleophobicity using aligned ZnO nanorod array-coated mesh films was reported. It showed excellent oil separation performance in a micro-reaction system (Tian et al., 2012).

2.3. Natural Bio-Materials for Oil-Water Separation

Both synthetic and natural materials surfaces were reconstructed to obtain special wettability in oil-water separation. Some studies have focused on artificially manufactured substrates. For example, a zeolite imidazole framework was developed by a porous hydrophobic-oleophilic nanoarchitecture 2D fluorinated graphene to separate oil-water
(Yogapriya and Datta, 2020). A new zwitterion, sulfonated N, N-Diethylethylenediamine was synthesized via the ring-opening reaction and co-deposited on the surface of PVDF membranes, which was employed in various oil-in-water emulsions separation with the efficiency beyond 96% (Sun et al., 2020). A superhydrophobic NiS nanorods/Ni mesh was synthesized by Yin et al. (2019) via the solvothermal reaction. The coated mesh collected oils or organic solvents with a high efficiency over 96%.

However, using synthetic materials still has problems of complex preparation processes, high energy consumption, relatively high cost, and secondary pollution (Awual, 2017b). Compared with the synthetic materials, natural materials such as biomass materials have advantages of biological degradability, resource abundance, and low cost (Zahraee et al., 2019). Therefore, there is an increasing interest in modifying nature materials such as cotton, sisal cellulose, and kapok fiber into adsorbent or filter with special wettability. For example, NH$_2$-MIL-125(Ti) (Ti-MOF) NPs were coated on cotton fabrics via in situ growing and further decorated by polydimethylsiloxane, achieving superhydrophobic wettability with anti-UV property (Yang et al., 2019). A cotton fiber surface was modified by SiO$_2$ NPs using a sol-gel method and subsequent octadecyltrichlorosilane assembly. The sorption capacity of the modified cotton was in excess of 25 ~ 75 g/g$^1$ its own weight (Lv et al., 2018). Silica nanoparticles were incorporated onto kapok fiber via sol-gel method (Wang et al., 2012). The superhydrophobic/oleophilic oil sorbent could quickly absorb diesel and soybean oil.

2.4. Literature Review Summary
In the past decades, many research efforts have been made in the area of oil-water separation. Among them, modifying surface wettability of a substrate is promising due to the facile process and broad use. All of the above technologies help to solve oil pollution problems, however, improvements in the following areas are still required:

(1) Most of the materials used as oil barriers are artificially manufactured substrates. When being applied in oil-water separation, the secondary pollutants might be introduced and they may be difficult to recycle. Although cellulose-based materials have been employed as green filtrate, the extraction process is complex and costly. Therefore, fabricating a kind of green material featured in biological degradability, resource abundance, and low cost is in high demand.

(2) Some of the biomass materials such as cotton, kapok fiber, rice shives, and flax fiber have been modified into oil absorbent to deal with oil spills. Hydrophobic agents were coated on their surfaces to achieve high oil absorption capability. However, the studies related to building a hydrophilic oil barrier made of biomass to filtrate water while repelling oil are rare. The hydrophilic and hydrophobic materials are suitable to deal with different types of oil-water mixture. The hydrophilic materials are usually made into oil barriers to filtrate water automatically by gravity. Some oil-water emulsion or immiscible light oil-water separation cases use such materials. Both oil absorbent and filter can be manufactured from hydrophobic materials, which can be employed in oil-water emulsion or immiscible heavy oil-water separation. Further studies are necessary in exploring an
innovative material which can deal with all kinds of oil-water mixture in demand.

(3) Surface reconstruction has been applied in many studies, among them, nanoparticles exhibiting great chemical bonding capability with innovative performance have been obtained during the surface wettability modification. The chemical bonds as well as valence variations have been investigated. Biomass is usually characterized in surface roughness and unevenly distributed organic contents. The distributions of chemical compounds and bonded nanoparticles still need to be investigated in future studies.
CHAPTER 3

FUNCTIONALIZATION OF FLAX FIBERS WITH SELF-ASSEMBLED TiO$_2$ NANOPARTICLES FOR IMMISCIBLE OIL-WATER SEPARATION

3.1. Background

Oil spilling caused by offshore oil industry and marine transportation is one of the most serious environmental issues (Awual, 2017b). Many traditional physical, chemical approaches and their combinations have been developed to deal with water contaminated by oil spills. For example, adsorption, gravity separation, centrifugation, electrocoagulation, combustion, and some integrated treatment systems were investigated for oil/water separation (An et al., 2017; Awual, 2019; Zhang et al., 2019b). However, some methods have difficulties in dealing with large-scale polluted water and may cause secondary pollution (Farrow et al., 2018b). The use of oil barrier with special hydrophilicity is a promising alternative for separating oil-water, which has recently gained increasing attention.

Both synthetic and natural materials with special wettability have been used as oil barriers. Some studies have focused on artificially manufactured substrates. For example, Dai et al. (2019) converted skin collagen fibrous material waste to oil sorbent to separate oil-water mixture. Li et al. (2019) fabricated three-dimensional peanut hull/graphene aerogels for
oil-water separation. Modifying old corrugated containers into a superhydrophobic coating on a suitable sponge material was also performed to deal with oil spills by Yuan et al. (2018). However, using synthetic materials still has problems in terms of complex preparation process, high energy consumption, relatively high cost and secondary pollution (Awual, 2017b). Compared with the synthetic materials, natural materials such as biomass feature in biological degradability, resource abundance, and low cost (Zahraee et al., 2019). Therefore, there is an increasing interest in modifying natural materials such as cotton, sisal cellulose, and kapok fiber into adsorbent or filter with special wettability.

Flax has a wide range of cultivation and high yield. Flaxseed is considered as an excellent source to produce oil, whereas the straws rich in flax fiber are often abandoned as residuals (Wang et al., 2017b). Therefore, the use of flax fiber as natural material for fabricating oil barrier is a new initiative to convert waste into recyclable, sustainable and biodegradable composite.

Flax fiber is relatively hydrophilic in nature because it has certain content of cellulose. However, oil can be absorbed on the fiber surface due to the existence of lignin, lumen, and wax (Liu et al., 2018b). To improve its hydrophilicity, hydrophobic components should be removed or hydrophilic agents can be introduced onto flax fiber surface. For example, Morrison et al. (2000) treated flax fiber by 4 M alkali solution at 170 °C for 2 h to remove lignin, wax, and oils covering the surface of the flax fiber, exposing cellulose components. Ibrahim et al. (2010b) reported that hydrophilic oxygen-containing functional groups were introduced by oxygen and air plasma treatment. However, the effects of such methods were limited. Nanoparticles have exhibited good chemical
bonding capability owing to high content of unsaturated atoms on their surfaces (Awual, 2017a). Special nanostructures with innovative performance have been obtained during the modification of materials (Awual, 2016b). TiO$_2$ nanoparticles (TiO$_2$ NPs) are attractive due to superhydrophilicity and low price (Liu et al., 2018a). Nevertheless, it had been found that nano-TiO$_2$ was difficult to be bonded with cellulose surface since the electrostatic interaction between –OH on flax fiber and nano-TiO$_2$ was weak (Meilert et al., 2005). In some studies, TiO$_2$ was immobilized onto nature fiber via immersing nature fiber into TiO$_2$ solution or TiO$_2$ sol-gel (Kemell et al., 2005). However, the entrapped nano-TiO$_2$ in small cracks were unstable and could be washed away easily.

Therefore, in this study, flax fibers were functionalized with nano-TiO$_2$ self-assembly on a plasma-induced poly (acrylic acid) (PAA) layer which covered flax fiber surface. The plasma treatment helped activate flax fiber surface by inducing electrons, forming free radicals, and generating oxidation groups. PAA grafted onto the plasma-activated flax fiber surface was used as binding agent to attach TiO$_2$ NPs. After modification, the hydrophilic/underwater oleophobic properties of modified flax fiber were investigated. In detail, (1) the modification process involved many factors with potential effects, and thus the individual effect of each factor and their interactions on the hydrophilicity of modified flax fiber were studied by using factorial design; (2) the modified fiber was comprehensively characterized with SEM, synchrotron-based FTIR and X-ray and the modification mechanism was analyzed; (3) the binding ability of TiO$_2$ NPs was investigated; and (4) the modified flax fiber was made into filter and applied to separate oil from water. The innovative flax fiber was featured in natural resources compared with
mostly used synthetic materials. In addition, instead of traditional hydrophobic oil absorbent, its surface was hydrophilic, which could achieve oil-water separation automatically by gravity. It can be used to substitute synthetic and hydrophobic materials in the field of oil-water separation.

3.2. Experiment and Methods

3.2.1. Materials

The flax fiber bundles (Figure 3-1) were obtained from Biolin Research Inc. (Saskatoon, Canada), with diameter ranging from 20 to 100 μm. The hydrophilic TiO₂ NPs (Degussa, P25) were used in the experiment. Diesel oil was purchased from a local gas station (Regina, Canada). All chemicals (i.e., acetone, acrylic acid (AA), Sudan III) with analytical standard or higher were purchased from Sigma-Aldrich (ON, Canada). They were used as received without further purification.
Figure 3-1 Flax fiber bundles
3.2.2. Flax Fiber Modification

The flax fiber was pretreated with acetone and deionized (DI) water under sonication at 40 KHz and 250 W for 4 times (15 min for one time) to remove impurities on the surface before drying in oven at 90°C for 3 hours to evaporate the remaining acetone and humidity. Three main procedures were involved: plasma treatment, PAA esterification and polymerization, and nano-TiO\textsubscript{2} self-assembly. Plasma treatment was applied to generate oxidized radicals as inducers for post PAA polymerization.

Plasma was generated by an IoN 40 Plasma System (PVA Tepla, USA) as shown in Figure 3-2 Plasma treatment system The pretreated flax fiber was stretched and fixed on a holder uniformly, so that plasma ions could transmit individual fiber during the plasma treatment process. The plasma process included Ar-plasma and O\textsubscript{2}-plasma to activate flax fiber surface and form oxidized groups. The reaction chamber was first pumped to provide a vacuum environment, then argon was introduced into reaction chamber. Argon was ionized and generated plasma by using electrical energy. Ablation and etching occurred on flax fiber surface, generating activated species. Oxygen was another active gas used in the process. Oxidation of free radicals on flax fiber surface was obtained when oxygen getting through. In order to enhance the oxidized species, another O\textsubscript{2}-plasma was then implemented.
Figure 3-2 Plasma treatment system
After plasma treatment under argon and oxygen environment, the fiber was immersed into AA solution for PAA polymerization in water bath. Then the PAA-grafted fiber was washed by DI water for several times to remove unbound AA monomers. The washed flax fiber was then dipped in TiO$_2$ NPs suspension for 1 hour with 200 rpm of shake. The TiO$_2$ NPs suspension was obtained by dissolving TiO$_2$ NPs in DI water, followed by sonication for 20 min. Next, the flax fiber was immersed in DI water for 6 h and then washed with DI water to remove weakly-bonded TiO$_2$ NPs. At last, the flax fiber was dried in oven at 40 °C for 6 hours.

3.2.3. Factorial Experiment Design

Environmental modeling methods have been widely applied in data analysis (Farrow et al., 2018a; Hu et al., 2018). Some decisions-making are based on modeling to figure out optimal environmental indicators (Remesan et al., 2018). Factorial design has been widely used to analyse influencing factors and the interactions between parameters (Huang et al., 2018; Song et al., 2018). There were many experimental factors that might have effects on the hydrophilicity of the modified flax fiber. In order to study the impact of individual processing parameters and their interactions on hydrophilic characteristic of modified fiber, a factorial experiment design was performed. The upper and lower levels of each parameter are listed in Table 3-1. Seven parameters (A-plasma treatment power, B-AA concentration, C-AA treatment time, D-AA treatment temperature, E-plasma treatment time, F-plasma treatment gas flow rate, and G-TiO$_2$ concentration) were studied as potential factors. However, it would be very time-consuming to run a 2-level full factorial
experiment, since at least 128 ($2^7$) runs were required in one experiment design. As a result, a $2^{7-2}$ fractional factorial design with a duplicate ($2 \times 2^{7-2}$) was applied in this research.
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3.2.4. Characterization Methods

Hydrophilicity of flax fiber was illustrated by water contact angle measured by OCA20 contact angle system (DataPhysics Instruments, Charlotte, USA). Contact angle is a widely-used parameter to evaluate surface wettability. It is generally accepted that smaller water contact angle indicated better hydrophilicity of flax fiber resulted from modification. In order to measure water contact angle, 0.03 g flax fiber was compressed into a round tablet under the pressure of 7 ton using Pellet Presses (Carver, USA), providing a relatively flat surface for measurement. A sessile drop method was adopted in the measurement, 7.5 µL water droplet from a micro-syringe was dropped onto the compressed flax fiber surface. The under-water oil contact angle was measured by dropping 10 µL dichloroethane onto compressed flax fiber surface which was fixed in DI water in advance. The data of contact angle was recorded and analyzed by SCA20 software (DataPhysics Instruments, Charlotte, USA). The initial contact angle was adopted using the average value of 5 repeated measurements from different samples.

Surface morphology and elemental investigation of flax fiber were detected with JSM-7001F Scanning Electron Microscope (SEM) and Pegasus XM2 Energy Dispersive X-ray (EDS) (Japan). The Specific surface area ($S_{BET}$) of flax fiber was determined by $N_2$ adsorption isotherms at 77 K using Brunauer-Emmett-Teller (BET) theory using TriStar II 3020 analyser (Micromeritics, USA). Synchrotron-based flourier transform infrared spectroscopy (FTIR) was carried out at the Mid Infrared (Mid-IR) Spectromicroscopy beamline (01B1-01) of the Canadian Light Source (Saskatoon, Canada) (Figure 3-3).
Synchrotron infrared light with an adequate signal-to-noise ratio was used to examine fiber samples after plasma treatment and PAA polymerization. The FTIR spectra were collected in reflection mode with 512 co-added scans. The data was analysed by OPUS 7.2 (Bruker, USA) and CytoSpec (CytoSpec Inc., USA), and the mapping plots were formed with Sigmaplot 14 (Systat Software Inc., USA). The synchrotron-based X-ray fluorescence (XRF) mapping of nano-TiO$_2$ on flax fiber surface was carried out at the Very Sensitive Elemental and Structural Probe Employing Radiation from a synchrotron (VESPERS, 07B2-1) beamline in Canadian Light Source (Saskatoon, Canada) (Figure 3-4). The polychromatic X-ray was applied to excite the sample, and the emitted XRF spectrum was recorded using a single element Vortex$^\circledR$ silicon drift detector. The scanning step-size was 8 μm, and the reported XRF spectrum was the average value of the selected mapping area. In addition, to test the nano-TiO$_2$ binding ability, the hydrophilicity of modified flax fiber was tested after ultrasonic treatment at 40 KHz and 250 W for 2.5, 5, 7.5, and 10 min, respectively.
Figure 3-3 FTIR end station at Canadian Light Source (http://midir.lightsource.ca/user-guide/infrared-microscopic-imaging/)
Figure 3-4 VESPERS end station at Canadian Light Source (http://www.lightsource.ca/)
3.2.5. Oil-Water Separation

The modified flax fiber was tested to evaluate its ability of oil-water separation. In the application, immiscible water and diesel oil were used. The diesel oil was dyed by Sudan III to distinguish from water. 0.03 g flax fiber was compressed and fixed at the bottom of a 10 mL pipette. 10 mL DI water was added into the pipette to immerse flax fiber completely and the water permeating flux was recorded. After pre-wetted by DI water, oil was poured into the pipette, and it was repelled by the flax fiber. At a certain oil height, the flax fiber could not hold the oil and started to leak. Thus, the maximum holding oil pressure was studied as another factor revealing its underwater oleophobic property, and the oil flux was also investigated when oil height was at 10 cm. Besides, to test whether the modified flax fiber could tolerate harsh environment, the flax fibers were immersed in acidic, alkaline, and salty solutions with pH values at 2, 4, 6, 8, 10 and NaCl concentrations at 0.5, 1, 1.5, 2, 2.5, 3, 3.5, and 4%, respectively. In addition, to further evaluate the performance of the modified flax fibers, they were recycled twenty times after simply washed by DI water.

The water and oil permeate flux can be expressed as $J$ (L/cm$^2$·s) (Chen et al., 2019a):\[ J = \frac{V}{A \times t} \] (1)

$V$ (L)-permeate water/oil volume; $A$ (cm$^2$)-effective flax fiber permeate area; $t$ (s)-permeation time.

The maximum pressure that flax fibers could hold can be expressed as $p$ (Pa) (Lian et al., 2018):\[ p = \rho gh \] (2)
\( \rho \) (0.832 kg/L)-density of diesel; \( g \) (9.8 N/kg)-gravitational constant; \( h \) (cm)-the maximum oil height.

### 3.2.6. Data Analysis

The quality assurance and quality control were followed to ensure the accuracy and reliability of data. All batch experiments were implemented in triplicate and the quantitative data were averaged. Main effects of individual factors and their interactions were analyzed through one-way Analysis of Variance (ANOVA) and least significance difference (LSD) for comparisons of treatment means with \( p < 0.05 \). The data analysis of factorial design was carried out by Design-Expert v8.0.6 (Stat-Ease Inc., Minneapolis, USA) and Minitab 17 (Minitab, Inc., Pennsylvania, USA). The figures were processed using Origin 8.0 (Origin Lab, Massachusetts, USA) and Sigmaplot 14 (Systat Software Inc., California, USA).

### 3.3. Results

#### 3.3.1. Modification of Flax Fiber Based on Factorial Design

Two-level fractional factorial design was engaged to analyze the effects of experimental factors on modification. Table 3-2 is the responded water contact angle based on \( 2^{7-2} \) fractional factorial design. Only individual parameters and two-factor combinations were implemented since higher order effects tended to be less necessary based on the effect
hierarchy principle (Wu and Hamada, 2011). Table 3-2 shows ANOVA analysis of significant parameters and their interactions. The $F$-value of model was 12.9605 and $P$-value was $< 0.0001$, indicating significance of the overall model. Parameters with a $P$-value less than 0.05 indicated that the factor had great influence on the result. In this study, the significant terms are A, B, F, G, AB, AE, AF, BC, BE, BF, BG, CD, CF, DE, and DF. The main effects of individual factors are shown in Figure 3-5. And the significant two-factor interactions are summarised in Figure 3-6.

There were three main procedures involved in the modification of flax fiber. Firstly, the flax fiber was treated with cold plasma to generate and oxidized free radicals, then PAA was grafted onto the activated flax fiber surface and finally nano-TiO$_2$ self-assembly occurred on the PAA-coated flax fiber surface. As each process had its potential influencing parameters, in the following sub-sections, parameters in each modification procedure and interactions between parameters from different procedures were investigated.
Table 3-2 Experiment design and result

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<th>AA temperature (℃)</th>
<th>Plasma treatment time (min)</th>
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<th>Nano-TiO$_2$ concentration (wt%)</th>
<th>Water contact angle (°)</th>
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Table 3-3 ANOVA analysis for significant operating factors and their interactions

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Figure 3-5 Main effect of modification parameters
Figure 3-6 Interactive effects of modification parameters
3.3.1.1. Effect of Plasma Treatment

In the plasma treatment, the accessed ions and atoms could collide with flax fiber surface, and the interactions between plasma and flax fiber surface depended on the selections of processing parameters (Wang et al., 2015). The plasma treatment in this study helped improve the adhesion between fiber and matrix through ablation, surface reactivity and cross-linking. Ablation referred to removing hydrophobic impurities and exposing the cellulose of flax fiber (Scalici et al., 2016). The surface was activated with induced electrons, contributing to the generation of free radicals or changing the reactive state of surface atoms (Ventura et al., 2016a). The free radicals interacted with each other and built covalent links, and thus the cross-linking occurred.

Plasma treatment was the first formulating procedure, followed by grafting of PAA. The flax fiber surface with more activated chemical states could provide excessive positions for post-grafting (Zhu et al., 2014). When the activated species were exposed to the ambient environment, free electrons were released due to absorbance of energy. Meanwhile, positively charged electron holes were left on the surface, stimulating surrounding oxygen or hydraulic substrate to generate hydroxyl radicals (\(\cdot\)OH) and reactive oxygen ions (\(O_2^-\)) (Wang et al., 2017a). Therefore, more hydroxyl groups were created owing to cellulose exposure as well as further plasma oxidation, creating more sites for post-grafting process. Morphology results reflected material ablation and surface etching. The number of active electrons increased with higher plasma power, leading to an increasing density of hot ions on flax fiber surface. At the same time, higher plasma
power tended to result in more serious etching on the surface of flax fiber, which can help clean the impurities and waxes while exposing more cellulose for further grafting of AA. Chemical oxidation of free radicals generated by Ar-plasma occurred when oxygen was applied and O$_2$-plasma treatment followed.

Understanding the effects of the experimental conditions and their interactions was of great significance for surface modification of flax fiber. According to Figure 3-5 and Figure 3-6 (a) and (b), the significant influencing factors were plasma treatment power (A), plasma gas flow rate (B), and interactions between AE and AF. Plasma power played a positive role in enhancing the wettability of flax fiber from the aspects of morphologic change and chemical oxidation. Morphology results reflected material ablation and surface etching. The number of active electrons increased with higher plasma power, leading to an increasing density of hot ions on flax fiber surface. Surface fragmentation and layer deterioration became more rapid compared to that with lower plasma power, providing more positions for polar groups to anchor (Sabharwal et al., 1993; Wang and Qiu, 2007). At the same time, higher plasma power tended to result in more serious etching on the surface of flax fiber, which can help clean the impurities and waxes while exposing more cellulose for further grafting of AA. Chemical oxidation of free radicals generated by Ar-plasma occurred when oxygen was applied and O$_2$-plasma treatment followed. From the chemical point of view, chemical bonds such as C-C, C-H were cleaved in Ar-plasma, and were further oxidized into C-O and C-OH (You et al., 2012). The cleavage and the combination of chemical bonds were strengthened with increasing power output.
Another significant factor was the gas flow rate in reaction chamber. The improvement of hydrophilic property was due to more polar radicals grafted or exposed on flax fiber surface. When introducing a higher flow rate, the gas travelled more quickly to the reaction chamber, increasing the amount of gas in a limited time. As more ions were activated, active particles grew faster on flax fiber surface (Jung and Choi, 2006). Therefore, the reaction efficiency increased with higher gas flow rate, which would bring more free radicals as well as more oxidation groups for further interact with AA. The effect of plasma treatment time was found to be less significant. Some researches hold a view that the etching and grafting efficiency were higher with the longer plasma exposure time (Ventura et al., 2016a; Wong et al., 1999). It was true that the concentrations of free radicals and activated ions increased with the increase of treatment time, leading to rougher surface and species accumulation (Mukhopadhyay et al., 2002). However, the saturation caused by recombination of generated groups were believed to occur in a short time. The active species were closely arranged on the surface, which tended to form connecting chain with each other (Sabharwal et al., 1993). Therefore, the insignificance of plasma treatment time could be attributed to that the saturation had been reached in low level of treatment time.

The whole plasma process involved both reactive species formation and monomer deposition, which could not be determined simply by individual parameters. As for the two-factor interactions, the interactive effects of plasma treatment power and time (AE), as well as plasma treatment power and gas flow rate (AF) were significant. The increasing of plasma power and treatment time both helped to decrease the water contact angle and enhance the wettability of flax fiber. However, according to Figure 3-6 (a), the treatment
time had negative effect at low level of plasma power while it had positive effect at high level of power. The lack of active species due to low plasma power would result in insufficient modification. In addition, longer treatment time in high-temperature plasma chamber might cause damage to flax fiber, inhibiting its wettability. Nevertheless, under the condition of higher plasma power, the activated ions were adequate and they could grow intensively on the flax fiber surface with longer treatment time. As for the interactive effect of AF, Figure 3-6 (b) describes that the impact of gas flow rate is significantly different between low and high plasma treatment power. At the low level of power, the water contact angles between low and high gas flow rate differed only within 5°. In contrast, 15° difference of water contact angle was observed between 60 sccm and 300 sccm of gas flow rate. This phenomenon could be explained by energy-deficient regime and monomer-deficient regime (Yasuda, 2011). In the energy-deficient regime, sufficient monomers were introduced, however, the level of plasma treatment power determined the reaction owing to the lack of active species. Contrarily, the number of monomers played the dominant role because the power was large enough for reaction in the monomer-deficient regime. Therefore, under the condition of high gas flow rate with sufficient monomers, energy-deficient regime functioned, contributing to obvious difference between two levels of power input.

3.3.1.2. Effect of PAA Polymerization

Nano-TiO₂ is difficult to be bonded with cellulose surface since the electrostatic interaction between –OH on flax fiber and nano-TiO₂ is weak. In order to strengthen the
combination and durability of nano-TiO$_2$, PAA was used as binding agent to attach nano-TiO$_2$ (Meilert et al., 2005). The reaction mechanism is esterification and polymerization between AA and plasma-activated fiber (Zafeiropoulos et al., 2002). The cellulose hydroxyl groups as well as oxidized hydroxyl groups could form covalent bonds with carboxylic group of AA, blocking hydroxyl groups of cellulose. In addition, vinyl group of AA could produce polycarboxylic acid to react with hydroxyl groups on the flax fiber surface to form a cross-linking network (Panda et al., 2016). As a result, the flax fiber surface was covered by a thin layer of PAA.

According to Figure 3-5, it was found that AA concentration (B) played an important role in grafting while grafting time (C) and grafting temperature (D) showed less significance. Based on previous research, in order to obtain an increased polar surface, the grafted layer could be modified under the condition of higher initial monomer concentration (Moses et al., 2018). As AA concentration increased, sufficient AA monomers were diffused on flax fiber surface, which would be favorable for higher degree of grafting. However, homopolymerization of AA and interaction of long chains occurred when the concentration reached a certain level, inhibiting further grafting (Xu et al., 2018). Chen et al. (2018) found that the longer treatment time, the more polar carboxylic groups on the surface. Thicker layer and longer chains were obtained with longer reaction time, but the chain growth was at a decreasing rate. In this study, however, there was no apparent difference between the low and high level of grafting time. The reason might be that 10 min of reaction time was long enough for the grafting of long-chain PAA on fiber surface, resulting in the similar responses. The grafting of PAA showed no significant variation.
between the temperature at 30 °C and 60 °C. Xu et al. (2018) drew a conclusion that the formation of PAA layer could be restrained at high temperature, and the amount of radicals fell down slightly when the temperature was over 60 °C. This could be explained that the formation of PAA would be too rapid at high temperature, leaving less monomers to interact with flax fiber. Therefore, further recombination and interaction were inhibited at high temperature.

When it referred to two-factor interactions during PAA grafting process, the interactive effects of AA concentration and treatment time (BC), as well as treatment time and grafting temperature (CD) were significant. As seen in Figure 3-6 (c), when the immersing time of flax fiber in AA solution was at low level, the change of water contact angles was only about 5° under the conditions of 20% and 80% AA concentration. However, approximately 20° difference was observed between the two levels of concentrations under the condition of 30 min grafting. This might be due to that the monomer deposition and growth needed sufficient time for AA spreading. Although the grafting time was considered to be an insignificant influencing factor, its greater impact was shown when connected with AA concentration. Another interesting result was that the main effects of AA treatment time and temperature were not significant individually, however, their interaction showed significant impact (Figure 3-6 (d)). From the analysis results of single-factor effects in this study, the increasing of temperature resulted in only slight improvement of PAA grafting. However, as for its interaction with treatment time, the influence of temperature showed completely contrary trend between the low and high grafting time. When the PAA grafting time was at low level, the increase of temperature
showed negative influence, contrarily, 60 °C AA showed better hydrophilic performance compared to 30 °C AA when PAA grafting time was at high level. The polymerization of AA monomers could be faster than the esterification between flax fiber and AA at high temperature. Therefore, the combination of PAA and flax fiber surface was limited when the grafting time was not long enough.

3.3.1.3. Effect of Nano-TiO$_2$ Self-assembly

After PAA polymerization, the flax fiber covered by PAA layer was dipped in aqueous nano-TiO$_2$ suspension. The result showed that nano-TiO$_2$ concentration played a significant role in hydrophilicity improvement. The formed PAA layer could catch nano-TiO$_2$ particles via electrostatic interaction, ion coordination and hydrogen bonding (Li et al., 2009). In electrostatic interaction, the modified flax fiber coated with PAA layer charged negatively, which was able to absorb positively charged titanium ions and this bond was found to be strong and durable (Ibrahim et al., 2012). The other two non-covalent interactions between TiO$_2$ and carboxyl groups included the monodentate, bridging bidentate, or chelating bidentate coordination of Ti$^{4+}$ cation with oxygen atoms of carboxyl groups and H-bonding of –COOH with –OH attached on Ti (Li et al., 2009; You et al., 2012). TiO$_2$ NPs functioned as excellent nano-adsorbents with abundant hydroxyl groups (Chen et al., 2019b). 0.1% of nano-TiO$_2$ had shown good hydrophilic character while the water contact angle decreased more obviously under the condition of higher concentration of nano-TiO$_2$ at 1%.
### 3.3.1.4. Interactions among Factors in Different Procedures

The two-factor interactions among different processing steps were also studied since all the steps were relevant and might affect each other. According to Figure 3-6, it was obvious that plasma treatment and AA grafting had interactions. As plasma treatment power and AA concentration increased, the corresponding water contact angles both showed apparent decreases (Figure 3-6 (e)). As for interactive effect of BE, when AA concentration was at its low level, plasma treatment time showed positive effect, while negative effect was shown by plasma treatment time when the AA concentration was at its high level (Figure 3-6 (f)). For interactive effect of BF as shown in Figure 3-6 (g), gas flow rate in plasma treatment had no significant difference when AA concentration was low while about 10° decrease was observed with increasing gas flow rate at high level of AA concentration. Figure 3-6 (i) demonstrated that AA immersion time showed positive effect at 300 sccm of plasma gas flow rate while the negative effect was witnessed at 60 sccm of gas flow rate. Factors D and E showed insignificant effect individually, but their interaction had significant influence (Figure 3-6 (j)). At the low level of AA temperature, the plasma treatment time restrained wettability improvement, contrarily, it impelled hydrophilicity at high temperature. The interactive effect of DF (Figure 3-6 k) showed opposite trend compared to BF (Figure 3-6 (g)). When investigating the gas flow rate, no apparent difference of water contact angle was seen at the high level of AA temperature, while the water contact angle showed great difference at the low AA temperature. Generation of free radicals was the initial step, followed by PAA grafting. The interactions between plasma treatment and AA grafting could be attributed to positively grafting
efficiency caused by increasing concentration and density of free radicals (Sun et al., 2011). As for the TiO$_2$ self-assembly, the interaction of BG also showed significant effect according to Figure 3-6 (h). At the low concentration of AA, the difference of water contact angle between the high and low level of nano-TiO$_2$ concentration was small, which could result insufficient PAA coating on flax fiber surface with less nano-TiO$_2$ bonding. The change between 0.1% and 1% TiO$_2$ was obvious at the high level of AA concentration. This could be explained by the strengthened combination of PAA layer and nano-TiO$_2$.

3.3.2. Surface Morphology and Component Analyses

The SEM images of flax fibers are shown in Figure 3-7. The surface of untreated fiber was rough and covered by some impurities such as waxes, line and bit-shaped pectin (Figure 3-7 (a)). From Figure 3-7 (b), we can see the surface of flax fiber became smooth with invisible impurities after PAA polymerization. The reason for this was the formation of a thin PAA layer on flax fiber surface (Ražić et al., 2017). Figure 3-7 (c) and (d) show flax fiber surfaces coated with nano-TiO$_2$ with the concentration of 0.1 and 1% respectively. It can be seen that TiO$_2$ NPs was successfully attached onto flax fiber surfaces and aggregation occurred on some positions. Some TiO$_2$ NPs could be trapped by cellulose or fragments on flax fiber surface to form aggregates (Karimi et al., 2010).

From Figure 3-7 (a), almost no apparent pores were observed on the surface. Regarding the structure of natural flax fiber, it can be considered as non-porous solid with small surface area (Bismarck et al., 2002). The specific surface area of untreated flax fiber in
this study was 0.76 m$^2$/g, which was similar with the results of Ouajai et al. (2004). Materials with larger pore size featured in better absorption performance (Awual, 2016a). The non-porous flax fiber had relatively small surface area, limiting its oil absorption, and therefore could be potentially used as oil defence or oil barrier. After modification by TiO$_2$ NPs, the specific surface area increased four times to 3.12 m$^2$/g, resulting from added nanoparticles.

Figure 3-8 (a) and (b) present results of elemental analysis for the modified flax fiber under the conditions of 0.1 and 1% TiO$_2$ NPs respectively. With the increase of TiO$_2$ NPs concentration from 0.1 to 1%, the content of Ti attached on fiber surface was almost doubled from 37.22 to 61.63% in elemental abundance and from 15.06 to 32.63% measured by atomic ratio. Both carbon and oxygen witnessed decrease in elemental abundance and atomic ratio. Carbon decreased from 22.1 Wt% at 0.1% TiO$_2$ to 12.43 Wt% at 1% TiO$_2$. The elemental abundance of oxygen also decreased from 40.68 to 25.94 Wt%. It could be attributed to TiO$_2$ NPs that covered flax fiber surface consisted of carbon and oxygen. As for atomic ratio, carbon and oxygen showed relatively small decreases from 35.66 to 26.24 At% and from 49.28 to 41.12 At%, respectively. The results proved the great increase in Ti content on the modified flax fiber surface with higher TiO$_2$ NPs concentration level.
Figure 3-7 SEM images of (a) untreated flax fiber; (b) PAA-coated flax fiber; (c) nano-TiO$_2$ coated flax fiber (0.1%); (d) nano-TiO$_2$ coated flax fiber (1%)
Figure 3-8 EDS results of the modified flax fiber: (a) nano-TiO$_2$ coated flax fiber (0.1%); (b) nano-TiO$_2$ coated flax fiber (1%)
3.3.3. Synchrotron-Based FTIR and X-ray Analyses

The synchrotron-based FTIR measurement takes advantage in light source being 100 ~ 1,000 times brighter than a conventional thermal infrared source, which is more suitable for investigating plant tissues (Zhang et al., 2017). In order to present the change of flax fiber surface in molecular scale, the synchrotron-based FTIR measurement was taken. The spectra of untreated flax fiber, plasma-treated fiber, and PAA-coated fiber with wavenumber ranges of 1,800 ~ 1,000 and 3,600 ~ 2,800 cm$^{-1}$ were summarized in Figure 3-9 (a) and (b).

During the first two modification steps, ablation, etching, and chemical reaction occurred on flax fiber surface, resulting in the breaking of some chemical bonds and the recombination of new species. According to Figure 3-9 (a) and (b), there was a broad peak in the wavenumber range of 3,500 ~ 3,100 cm$^{-1}$, which was referred to hydrogen-bonded –OH vibration existing in the cellulose and lignin structure of the flax fiber (Bozaci et al., 2013). The intensity became stronger after treated by plasma, which was due to that the surface ablation exposed more cellulose on fiber surface. In addition, hydroxyl groups were formed when free radicals reacted with surrounding oxygen or hydraulic substrate (Wang et al., 2017a). The peaks at 2,916 cm$^{-1}$ and 2,849 cm$^{-1}$ suggested the C-H stretching from aliphatic saturated compounds in cellulose and hemicellulose components (Bozaci et al., 2013). The decrease in intensity of C-H stretching was observed after plasma treatment, whereas the peak showed an incredible increase after PAA polymerization. This could be explained by the cleavage of C-H and formation of more oxidation groups instead during
plasma treatment (Ventura et al., 2016b). However, when immersed in AA solution with vinyl groups, polymerization among AA monomers occurred on flax fiber surface, introducing a larger amount of C-H stretching (Panda et al., 2016). The peak at 1,730 cm$^{-1}$ corresponded to carbonyl linkage C=O of acetyl ester group in hemicelluloses and lignin (Chen et al., 2019a). This peak became stronger after plasma treatment, and the intensity increased after PAA polymerization. The plasma treatment could stimulate more polar groups (C=O and C-O) through oxidation, thus decreased the amount of non-polar groups (Kafi et al., 2011). In addition, esterification reaction happened between carboxyl groups of acrylic acid and hydroxyl groups on flax fiber surface, contributing to the formation of C=O in ester groups (Liu et al., 2018a). The peak at 1,629 cm$^{-1}$ was attributed to conjugated C=O bond (Mooktzeng and Zulkifli, 2018). The peak intensity increased after plasma treatment and shifted to 1,643 cm$^{-1}$ after PAA coating. This might be due to the oxidation of plasma treatment and the reflection of PAA cross-linking on fiber surface. Two peaks at 1,542 cm$^{-1}$ and 1,578 cm$^{-1}$ were obviously strong in the spectrum of PAA-coated flax fiber, which were assigned to asymmetric C-H and -COOH group formed by polymerization of AA monomers (Sdrobiş et al., 2013). A new peak at 1,456 cm$^{-1}$ was discovered in PAA-coated flax fiber. It suggested methylene non-symmetry changing angle vibration, which might be caused by the broken of C=C and polymerized CH$_2$ (Chen et al., 2013).

To further investigate the distribution and concentration of increased functional groups, synchrotron-based FTIR mapping and spectra for hydroxyl groups with wavenumber range of 3,500 ~ 3,100 cm$^{-1}$ and carbonyl groups with wavenumber range of 1,740 ~ 1,720
cm\(^{-1}\) are shown in Figure 3-9 (c) ~ (f). It was clear that the intensity of –OH of plasma treated flax fiber was higher than that of the untreated one (Figure 3-9 (c) and (d)). Figure 3-9 (e) and (f) illustrate stronger intensity of –COOH in PAA-coated fiber compared to the sample in previous treatment step (plasma treatment), indicating a PAA layer covering flax fiber surface. However, the distributions of both groups were uneven with higher density in centre and lower density on the edge. This might be caused by the various density of flax fiber substrate on different areas. Around the middle of the fiber, the substrate was thick and with high density, providing more sites for –OH to anchor.

Synchrotron-based X-ray has been applied to investigate metal ions complexation on the solid surface (Awual et al., 2017). In order to analyze the presence and occurrence of TiO\(_2\) NPs on modified flax fiber, synchrotron-based XRF mapping was used. Mappings of Ti distributions on original flax fiber and modified flax fiber are shown in Figure 3-10 (a) and (b). There was almost no Ti on the untreated flax fiber surface. After modification, TiO\(_2\) NPs were immobilized on fiber surface, though the distribution was relatively uneven due to the various density of flax fiber substrate mentioned above. The XRF spectra in Figure 3-10 (c) demonstrates the average intensity of Ti extracted from the selected area according to Figure 3-10 (a) and (b). The peak at about 3000 eV was referred to Ar in environment, and the peaks at 4500 eV and 5000 eV were energy characteristic peaks of Ti K\(\alpha\) and Ti K\(\beta\) respectively, which was apparent on the modified flax fiber. Combining the results of synchrotron-based FTIR and X-ray analyses, it could be comprehensively proved that the PAA layer and TiO\(_2\) NPs were successful coated on the modified flax fiber surface.
Figure 3-9 Synchrotron-based analysis of flax fiber: (a,b) FTIR spectrum results of untreated, plasma treated and AA treated flax fiber between the range of 3,600 ~ 2,800 cm\(^{-1}\) and 1,800 ~ 800 cm\(^{-1}\); (c,d) FTIR mapping results of untreated and plasma treated flax fiber from 3,500 to 3,100 cm\(^{-1}\); (e,f) FTIR mapping results of plasma treated and AA treated flax fiber from 1,740 to 1,720 cm\(^{-1}\);
Figure 3-10 Synchrotron-based XRF of flax fiber: (a,b) XRF mapping of untreated and nano-TiO$_2$ modified flax fiber; (c) XRF spectra of the selected areas from (a, b).
3.3.4. Mechanism of Nano-TiO$_2$ Self-Assembly on Flax Fiber

Based on the analyses above, Figure 3-11 (a) shows the modification scheme and mechanism of nano-TiO$_2$ self-assembly on flax fiber. Three main procedures were involved: plasma treatment, PAA esterification and polymerization, and nano-TiO$_2$ self-assembly. Plasma was first induced to etch the surface of flax fiber, exposing cellulose and introducing free oxidized groups (Mukhopadhyay and Fangueiro, 2009). During the process of low-temperature plasma treatment, argon was introduced to make the cleavage of C-C bonds, then the formed free radicals were exposed to oxygen, contributing to more oxidation groups such as C=O, C-O, COOH and -OH (Ventura et al., 2016a). Meanwhile, ablation occurred on flax fiber surface, cleaning impurities and exposing cellulose. Although TiO$_2$ NPs were possible to be trapped by cellulose on flax fiber surface, the combination was easy to eliminate. Potential grafting agents which hold at least two carboxyl groups such as PAA was in need as reported in previous studies (Chen et al., 2019c). In this study, the plasma-treated fiber was immersed into AA solution to generate PAA layer covering flax fiber surface via esterification and polymerization. Esterification reaction happened between carboxyl groups of acrylic acid and hydroxyl groups formed on flax fiber surface. Vinyl groups of AA could also combine with oxidation groups on flax fiber surface and then reaction of polymerization among AA monomers occurred, forming long-chain PAA layer. Finally, PAA with long chain was supposed to immobilize TiO$_2$ NPs firmly and stably by electrostatic interaction, ion coordination and hydrogen bonding (Li et al., 2009). In electrostatic interaction, PAA layer charged negatively was able to absorb positively charged titanium ions. The other two possible non-covalent
interaction was monodentate, bridging bidentate, or chelating bidentate coordination of Ti$^{4+}$ cation with oxygen atoms of carboxyl groups and H-bonding of –COOH with –OH attached on Ti (You et al., 2012). Figure 3-11 (b) presents the different performances of flax fibers for oil-water separation before and after modification. The flax fiber was compressed and pre-wetted with DI water. Compared to the untreated flax fiber, it was expected that the modified fiber had better hydrophilic/underwater oleophobic performance. The modified flax fiber was supposed to perform as oil barrier by filtrating water and repelling oil, while no specific wettability was observed on untreated flax fiber.
Figure 3-11 (a) Modification process and mechanism; (b) scheme of water-oil separation
3.3.5. TiO$_2$ NPs Bonding Performance

To better demonstrate the use of modified flax fiber as separator, TiO$_2$ NPs bonding performance was investigated. The untreated flax fiber, modified flax fiber, and modified flax fiber through various ultrasonic treatments were tested. Compared to the original flax fiber, the modified flax fiber took advantages in hydrophilic in air and underwater oleophobic. Figure 3-12 shows that the original flax fiber is neutral in hydrophilic-hydrophobic property with the water contact angle at 97.4° and under water oil contact angle at 95.8°. 7.5 μL water droplet disappeared after 25.95 s. After modification, the water contact angle decreased to 25.9°, and the underwater oil contact angle increased to 134.6°, indicating the hydrophilic in air and underwater oleophobic properties. In addition, the water droplet on the modified flax fiber surface only took 1.903 s to disappear due to the significant improvement of hydrophilicity. TiO$_2$ NPs bonding ability was tested through ultrasonic treatment. The results showed almost no variation on contact angles and water droplet extinction time after even 10 min ultrasonic treatment, which meant that TiO$_2$ NPs was firmly bonded on flax fiber.
Figure 3-12 Water and oil contact angle and water droplet extinction time of untreated and modified fiber and TiO$_2$ binding performance
3.3.6. Application in Oil-water Separation

In order to investigate the practical application of modified flax fiber, the performance of flax fiber in oil-water separation was tested under different conditions of pH value and NaCl concentration, and the reutilization was also considered. Figure 3-13 shows the results of oil-water separation performance of the modified flax fiber. The superhydrophilicity of TiO$_2$ NPs is favorable for effective separation of oil-water (Liu et al., 2018a). After nano-TiO$_2$ self-assembly, the flax fiber became hydrophilic and under water oleophobic, which means the modified flax fiber was featured in high water affinity and oil repellency. It was seen that both oil and water permeated the untreated flax fiber while the oil was rejected by modified flax fiber. After 6 min, only water permeated through the modified flax fiber while oil was repelled, in contrary, both oil and water permeated through the untreated flax fiber. After 12 min, no oil and water remained in untreated fiber filling pipe, but the modified flax fiber still rejected oil without leaking.
Figure 3-13 Comparison of oil-water separation performance between untreated and modified flax fiber: (a) pipettes with compressed flax fibers at the bottom tip; (b) the magnified view of the compressed flax fiber; (c) 10 mL of immiscible oil-water; (d) the initial stage of immiscible oil-water separation; (e) immiscible oil-water separation at 6 min; (f) immiscible oil-water separation at 12 min.
Furthermore, Figure 3-14 summarizes the performance data of flax fibers when applied in water permeating and oil prohibiting cases. The water flux implied hydrophilic character of flax fiber, and the maximum oil pressure that flax fiber could hold as well as the oil flux under the pressure of 10 cm oil height revealed the property of underwater oleophobicity. Figure 3-14 (a) compares performance data of untreated and modified flax fiber. The untreated flax fiber showed water flux at 38.76 L/(cm$^2$ s) and the oil flux under the pressure of 10 cm oil height reached 7.62 L/(cm$^2$ s). The maximum oil pressure it could hold was 366.9 Pa. Compared with the untreated flax fiber, the performance data of modified fiber was obviously improved owing to the enhanced hydrophilicity and underwater oleophobicity. The modified fiber had increased water flux, almost half of oil flux at the same oil height pressure, and an incredible increase in maximum oil pressure it could hold (693 Pa).

The effects of harness environment such as extreme acidity, alkalinity and salinity were also taken into consideration to further evaluate the performance of modified flax fiber comprehensively, and the results are presented in Figure 3-14 (b) and (c). Figure 3-14 (b) shows the performance data of modified flax fiber under various salty conditions. As NaCl concentration increased, both water flux and oil flux fluctuated but showed increase trends. The maximum oil pressure illustrated two apparent decreases at 1% and 2% of NaCl concentration. It could be concluded that with higher salty concentration, the oil prohibition ability of modified fiber became weaker. The acidity and alkalinity that the modified flax fiber could tolerate are shown in Figure 3-14 (c). The water flux showed a slight decrease trend as pH value increased and the oil flux under the pressure of 10 cm oil
height showed almost no difference. The maximum oil pressure was the smallest (407.7 Pa) at acidity condition when the pH value was 2, and it increased to 570.8 Pa when pH value was 8 and 652.3 Pa in alkaline condition (pH = 12). The reason for this might be that PAA with carboxyl groups was a pH-responsive material, which could accept or donate protons as pH changes (Philippova et al., 1997). Under alkaline condition, protons were donated, contributing to negatively charged layer. TiO$_2$ NPs tended to be bonded with the negatively charged layer firmly via electrostatic interaction. Taken all these three parameters into consideration, the modified flax fiber showed better performance below 1% salty concentration and in neutral or alkaline condition.

Another important criterion to evaluate the performance of modified flax fiber for oil-water separation is reuse capacity. Figure 3-14 (d) shows the results of three performance data after 20 cycles. In each cycle, the used flax fiber was washed by DI water ($\sigma = 62.9 \, \mu$S/cm) several times to remove oil existing in the narrow gaps of fibers. The adhering oil was easily removed by DI water owing to the oleophobic character. The water flux fluctuated slightly and kept a relatively high permeation during 20 cycles. The oil flux at the pressure of 10 cm oil increased a little after cycle 11. There was a decrease of maximum oil holding pressure at cycle 10. Thus, the modified flax fiber kept good performance within 10 times of recycles. After that, some of the unfirmly attached nano-TiO$_2$ on flax fiber surface might be washed away, leading to weaker oleophobicity.

The performances of modified flax fiber and other reported oil barriers were compared. The produced flax fiber oil barrier was capable of holding 693 Pa oil. An organogel-coated stainless steel mesh was used to separate oil and water from its mixture, however, the
intrusion pressure was no more than 500 Pa (Lai et al., 2018). Ou et al. (2016) fabricated the poly(N-isopropylacrylamide) hydrogel-coated thermoplastic polyurethane microfiber membrane, achieving high maximum oil holding pressure up to 3000 Pa. Nevertheless, the fabrication process was complex and the material had low degradability. A 3D porous copper material was also modified by a facile and environmentally friendly method (Wang et al., 2017). Although its oil separation performance was good, the substrate was copper foam with a relatively high price compared with natural biomass.
Figure 3-14 Hydrophilic and underwater oleophobic performance: (a) untreated compared with modified flax fiber; (b) modified flax fiber in salty condition; (c) modified flax fiber in acidic and alkaline condition; (d) modified flax fiber after times of recycles
3.4. Summary

In this study, environmentally friendly, reusable and low-cost functionalized flax fibers were fabricated to separate immiscible light oil from water. Free radicals and oxidation groups were introduced on flax fiber surface through plasma treatment, providing radical initiators for AA to form the PAA layer via esterification and polymerization. TiO₂ NPs were immobilized through the coated PAA to obtain a hydrophilic surface for modified flax fiber. A two-level factorial design was used to find out the influencing parameters and their interactions. It was interesting to find that plasma treatment power, plasma treatment gas flow rate, AA concentration and TiO₂ NPs concentration helped improve the hydrophilicity significantly. The modified fiber was comprehensively characterized and the modification mechanism was studied by contact angle, SEM, and synchrotron-based FTIR and XRF. For the first time, the distribution of functional groups and coated TiO₂ on flax fiber surface were investigated by synchrotron-based analysis. The modified flax fiber was verified to have great capability to filtrate water while repelling oil. Compared with the untreated flax fiber, the water contact angle decreased from 97.4° to 25.9°, and the under-water oil contact angle increased from 95.8° to 134.6°. The modified flax fiber showed stable performance of oil-water separation in alkaline and salty conditions, and it could be used up to 10 cycles. The modified flax fiber could be further constructed into oil barrier with special wettability to separate oil.
CHAPTER 4

HDTMS-ZnO COATED FLAX FIBER WITH PHOTO-INDUCED SWITCHABLE WETTABLEITY FOR ON-DEMAND OIL-WATER SEPARATION

4.1. Background

The growing oily wastewater release and crude oil leakage have brought serious threat to both human health and ecosystem balance, heightening the interest in technological oil-water separation (Yan et al., 2016). Traditional oil-water separation methods include adsorption, gravity separation, centrifugation, electrocoagulation, combustion, and some integrated treatment systems (An et al., 2017; Zhang et al., 2019b). However, these methods have difficulties addressing rapid and widespread oil leakage and could cause secondary pollution (Farrow et al., 2018b). The use of an oil barrier with special wettability is a promising alternative to separate oil from water and has recently gained increasing attention.

Natural materials, such as raw bagasse, cotton fabric, and kapok, have been used as oil barriers in oil-water separation (Gupta and Tai, 2016). For example, TiO$_2$-composited cotton fabrics with silanized surfaces were fabricated, exhibiting superhydrophobic and oleophilic properties toward the application of oil-water separation (He et al., 2020). A
superhydrophobic CeO$_2$-modified kapok fiber with superhydrophobicity and good sorption capacity was also used as an oil absorbent (Zhang et al., 2018). Among them, flax fiber featuring biological degradation, wide resources, and low cost, offer great potential in the fields of residual recycling and environmental protection. However, flax fiber characterizing neutral wettability owing to cellulose, lignin, lumen, and wax has limited oil-water separation ability (Liu et al., 2018b). Hence, flax fiber needs to be modified to obtain special surface wettability to reinforce its applicability in oil-water separation.

Some studies have focused on reconstructing flax fiber surface wettability. A hydrophilic and underwater oleophobic surface has been investigated. For example, a remarkable improvement in the hydrophilic property was obtained by oxygen and air plasma treatment (Ibrahim et al., 2010a). An alkali treatment was induced to remove lignin, wax, and oils that covered the surface of the flax fiber, exposing cellulose components and building a hydrophilic surface (Morrison III et al., 2000). However, for some heavy oil, the hydrophilic surface is not suitable, since the heavy oil layer is resisted and accumulated at the bottom layer. In addition, it cannot be applied in oil-water emulsion separation due to the wide interspace and surface hydrophilicity. Studies related to fabricating a hydrophobic surface have also been reported. Modification of the surface of the flax fibers with a thin film of ZrO$_2$ was explored by Boulos et al. (2017a), demonstrating enhanced hydrophobicity and reduced water absorption. An exclusive hydrophobic surface with silane as a bonding agent was also studied by Gogoi and Tyagi (2019). The hydrophobic materials were typically used as an oil absorbent in oil-water separation. However, when employed as an oil filter, they failed to separate the immiscible light oil-water mixture.
automatically by gravity. Therefore, a material with switchable wettability is desirable to separate various types of oil pollution.

In this study, a UV-induced switchable surface modified by HDTMS-ZnO was investigated to address the immiscible light oil-water mixture, immiscible heavy oil-water mixture, and oil-in-water emulsion. Previous research was dedicated to investigating the ZnO switching behavior from hydrophobic to hydrophilic under UV light exposure. For example, Ennaceri et al. (2016) fabricated superhydrophobic ZnO nanorod arrays coating on FTO substrates, which demonstrated switchable wettability from superhydrophobic to superhydrophilic after UV exposure. Switchable superhydrophobicity–superhydrophilicity/underwater superoleophobicity was also achieved based on the UV-induced aligned ZnO nanorod array-coated mesh films to separate oil from water (Tian et al., 2012). However, the substrates used were synthetic materials that were not recyclable. Therefore, in this study, a photo-induced HDTMS-ZnO coated flax fiber for on-demand oil-water separation was investigated. In detail, (1) the flax fiber was modified with ZnO nanoparticles (ZnO NPs) and hexadecyltrimethoxysilane (HDTMS) using plasma-induced poly (acrylic acid) (PAA) as a binding agent; (2) the amounts of ZnO NPs and HDTMS were balanced, and the optimal transferable hydrophobic-hydrophilic/underwater oleophobic performance was determined; (3) the modified fiber was comprehensively characterized based on the contact angle, SEM, synchrotron-based FTIR and X-ray; (4) the as-modified flax fiber was applied in several scenarios of on-demand oil-water separation, including oil-in-water emulsion, immiscible light oil-water, and heavy oil-water mixture.
4.2. Materials and methods

4.2.1. Materials

The flax fiber bundles, with diameters ranging from 20 to 100 μm, were obtained from Biolin Research Inc. (Saskatoon, Canada). The hydrophilic ZnO NPs (< 100 nm) were purchased from Innochem (Beijing, China). Hexadecyltrimethoxysilane (> 85%) and acrylic acid (99%) were purchased from Sigma-Aldrich (ON, Canada). They were used as received without further purification.

4.2.2. Fabrication of PAA-HDTMS-ZnO Flax Fiber

The flax fiber bundles were washed three times with acetone and distilled water in an ultrasonic bath before drying in an oven at 40°C. As illustrated in Figure 4-1, a facile approach was employed to produce the HDTMS-ZnO flax fiber. First, the flax fiber was ablated by 300 sccm Ar plasma at 200 W for 2 min, followed by exposure in an O₂ environment. After the plasma treatment, the flax fiber was immersed into an 80% acrylic acid (AA) solution for 30 min at 60°C to form a layer of poly acrylic acid (PAA) on its surface. To obtain the HDTMS-ZnO solution, ZnO NPs and HDTMS were added into ethanol and stirred to achieve homogeneous dispersion. Finally, the HDTMS-ZnO was assembled onto plasma-induced PAA flax fiber.
Figure 4-1 Schematic illustration of the fabrication process of PAA-HDTMS-ZnO flax fiber
4.2.3. *Optimization of HDTMS and ZnO NPs Amount*

The hydrophobic behavior resulted from long-chain alkyl groups (–C\textsubscript{16}H\textsubscript{33}) of HDTMS, while the UV-induced hydrophilic/underwater oleophobic property was due to the photo-catalytic property of the ZnO NPs. To obtain both hydrophobicity and UV-induced hydrophilicity/underwater oleophobicity, the optimal balance of the HDTMS and ZnO NPs concentrations should be determined. Therefore, in this study, a 4 × 4 matrix full design was developed to explore the effects of HDTMS and ZnO NPs concentrations on the surface wettability of flax fiber. The water contact angle was detected using the OCA20 contact angle system (DataPhysics Instruments, Charlotte, USA) to investigate surface wettability. A UV wave at 254 nm was induced by an Ultraviolet Crosslinker at 300,000 µJ/cm\textsuperscript{2} (Analytik Jena US, Upland, USA) to transfer the surface hydrophobicity to hydrophilicity. The water contact angle after modification and UV time when the water contact angle was less than 60° were two responses. The optimal combination with the appropriate contact angle and UV time was determined.

4.2.4. *Characterization Methods*

A scanning electron microscope (SEM) and energy dispersive X-ray (EDS) of flax fiber were used by ZEISS Sigma 500 (Germany) and Ultim Max 100 (Oxford Inst., UK). Synchrotron-based Fourier transform infrared spectroscopy (FTIR) was performed at the mid infrared (Mid-IR) spectromicroscopy beamline (01B1-01) of the Canadian Light Source (Saskatoon, Canada). Synchrotron infrared light with an adequate signal-to-noise
ratio was used to detect HDTMS-ZnO fiber samples. The spectra were collected in reflection mode with 512 co-added scans. The synchrotron-based X-ray fluorescence (XRF) mapping of ZnO NPs on the flax fiber surface was conducted at the Very Sensitive Elemental and Structural Probe Employing Radiation from a synchrotron (VESPERS, 07B2-1) beamline in the Canadian Light Source (Saskatoon, Canada). The distribution of ZnO NPs on flax fiber surface was also investigated by synchrotron-based X-ray fluorescence (XRF). The polychromatic X-ray was applied to excite the sample, and the emitted XRF spectrum was recorded using a single element Vortex® silicon drift detector. The scanning step size was 25 μm, and the reported XRF spectrum was the average value of the selected mapping area.

4.2.5. On-Demand Oil-Water Separation

The UV switchable hydrophobic-hydrophilic/underwater oleophobic flax fiber was used to separate oil-water emulsion, floating oil, and immiscible heavy oil from water. The oil-water emulsion was artificially synthesized by mixing diesel oil and DI water with stirring at 2500 rpm for 6 h. The emulsified oil-water was stabilized for 24 h, and the floating oil was removed prior to treatment. The chemical oxygen demand (COD) concentrations of emulsion were detected by a COD analyzer (Hach 2800, London, Canada). 0.05 g of HDTMS-ZnO flax fiber was immersed into a 6 mL oil-water emulsion, and the oil absorption occurred at 200 rpm shaking. The separation efficiency was expressed as follows:

\[
R (\%) = \frac{(C_0 - C)}{C_0}
\]
where $C_0$ (mg/L) is the COD concentration in the original oil-water emulsion, and $C$ (mg/L) is the COD concentration after HDTMS-ZnO flax fiber absorption.

The commercial diesel oil and dichloroethane were dyed by Sudan III to distinguish from water and were used as float oil and heavy oil, respectively. Heavy oil separation was realized by compressing 0.05 g of HDTMS-ZnO flax fiber at the bottom of a pipette, after which immiscible heavy oil-water was poured onto its surface. In addition, an immiscible diesel oil-water mixture was separated in the pipette to verify the performance of the hydrophilic character after the UV treatment.

4.3. Results and Discussion

4.3.1. Optimal Combination of HDTMS and ZnO NPs Concentration

The wettability of the HDTMS-ZnO coated flax fiber was investigated. The flax fiber was hydrophilic in nature, given the large amount of hydroxyl group in cellulose (Li et al., 2007). Both HDTMS and ZnO NPs played important roles in the switchable oil-water separation performance. Table 4-1 displays all possible combinations of HDTMS and ZnO NPs concentrations, presenting the corresponding water contact angle and transferable UV time when the water contact angle < 60° as two responses. In general, after modification, the surface changed into hydrophobicity with increasing water contact angle. The weakened wettability was attributed to HDTMS with hydrophobic long-chain alkyl groups. The hydrophilic hydroxyl groups were blocked by hydrolysis of HDTMS (Xie et al., 2019).
In addition, the formation of the nanostructure roughened the flax fiber surface and trapped air on the surface, therefore increasing the hydrophobicity (Zhang et al., 2019a).

Figure 4-2 illustrates the changing of the water contact angle for different HDTMS and ZnO NPs concentrations. From Figure 4-2(a), the water contact angle demonstrates a decreasing trend as the ZnO NPs concentration increases. This could be explained by the presence of hydrophilic ZnO NPs demonstrating a high affinity of water (Balta et al., 2012). At the low HDTMS concentration, decreasing of the water contact angle was most apparent when the ZnO NPs concentration changed from 0.1% to 0.5%; afterward, an increase of the ZnO NPs concentration resulted in almost no variation. When the HDTMS concentration was at 0.4%, the water contact angle exhibited no obvious change with an increasing ZnO NPs concentration. This was because at low concentration of HDTMS, more unreacted ZnO NPs were bonded onto the PAA-flax fiber surface, enhancing the surface wettability. The surface reached saturation after 0.5% ZnO concentration. When there was a sufficient amount of HDTMS, silanol groups of HDTMS reacted with the hydroxyl groups surrounding the ZnO NPs and thus blocked hydrophilicity (Agrawal et al., 2019). As illustrated in Figure 4-2(b), increasing the HDTMS concentration resulted in continuously increased hydrophobicity. This was caused by the silane coupling agents of HDTMS reducing the number of cellulose hydroxyl groups on the flax fiber surface (Li et al., 2007). The water contact angle increased to nearly 130° at all levels of ZnO NPs concentration, which is consistent with the result presented in Figure 4-2(a). Figure 4-2(c) presents the water contact angle of all ZnO NPs and HDTMS concentration combinations. It was apparent that the highest hydrophobicity lay in 0.4% HDTMS. However, according
to Table 4-1, either 0.1% ZnO NPs or 0.4% HDTMS revealed a transferable UV time of more than 90 min. Considering both the highest water contact angle and least switchable UV time, the optimal combination was 0.1% HDTMS and 1% ZnO NPs. The flax fiber modified by optimal HDTMS and ZnO NPs was characterized and applied in the following sections.
Table 4-1 Water contact angle and switchable UV time under all combinations

<table>
<thead>
<tr>
<th>HDTMS concentration (vol%)</th>
<th>ZnO NPs concentration (wt%)</th>
<th>Water contact angle (°)</th>
<th>UV time (min)</th>
</tr>
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<tr>
<td>0.05</td>
<td>0.1</td>
<td>112.63</td>
<td>160</td>
</tr>
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<td></td>
<td>0.5</td>
<td>97.40</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>96.20</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>103.35</td>
<td>30</td>
</tr>
<tr>
<td>0.10</td>
<td>0.1</td>
<td>123.50</td>
<td>&gt; 180</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>103.98</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>111.86</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>112.60</td>
<td>60</td>
</tr>
<tr>
<td>0.20</td>
<td>0.1</td>
<td>124.00</td>
<td>&gt; 180</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>109.01</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
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</tr>
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<td>60</td>
</tr>
<tr>
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<td>0.1</td>
<td>128.96</td>
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<td>2.0</td>
<td>129.91</td>
<td>100</td>
</tr>
</tbody>
</table>
Figure 4-2 Water contact angle changing as: (a) various concentration of ZnO NPs; (b) various concentration of HDTMS; (c) combination of HDTMS and ZnO NPs concentration.
4.3.2. Surface Morphology and Component Analyses

To explore the bonding performances of ZnO NPs and HDTMS on a modified flax fiber surface, SEM observation and EDX analysis were performed. Figure 4-3 displays the results of original flax fiber, HDTMS-ZnO flax fiber, and HDTMS-ZnO flax fiber after UV treatment. Figure 4-3 (a) and (b) illustrate that the flax fiber surface was smooth except for some inconspicuous cracks and impurities. It was primarily composed of carbon (C) and oxygen (O), owing to cellulose-based substrate. After HDTMS and ZnO NPs grafting, the flax fiber surface became rough with some tiny holes (Figure 4-3 (c)). The nanostructure caused by ZnO NPs was covered with hydrophobic HDTMS, contributing to water repellent. From Figure 4-3 (d), 0.56 Wt% of silicon (Si) and 4.62 Wt% of zinc (Zn) were witnessed, which indicated that HDTMS and ZnO NPs were successfully deposited onto the flax fiber surface. However, the amount of Si was low, which might have been because the amount of HDTMS added was relatively low at 0.1%. The amount of O after being modified by HDTMS and ZnO NPs also exhibited an increase, from 27.41 Wt% to 33.89 Wt%, which resulted from oxygen groups containing in HDTMS or ZnO NPs. Figure 4-3 (e) illustrates the surface morphology of HDTMS-ZnO flax fiber after UV treatment. Compared with Figure 4-3 (c), there are some fragments on the surface, and nanostructures are more evident. This is because that layer of HDTMS was ablated under UV light, partially causing HDTMS to destroy and expose ZnO NPs (Yong et al., 2015). This result could also explain the wettability switching from hydrophobic to hydrophilic after UV treatment. In addition, compared with Figure 4-3 (d), in Figure 4-3 (f), the component of Zn witnessed an increase from 4.62 Wt% to 6.89 Wt%, consistent with the
HDTMS ablation and ZnO NPs exposure.
Figure 4-3 SEM images and elemental analyses of (a) and (b) original flax fiber; (c) and (d) PAA-HDTMS-ZnO flax fiber; (e) and (f) PAA-HDTMS-ZnO flax fiber after UV treatment
4.3.3. Mechanism of UV-Induced Switchable Surface Wettability

After modification by HDTMS and ZnO, the flax fiber featured in switchable surface wettability between hydrophobic-hydrophilic/underwater oleophobic before and after UV irradiation. Similar to the modification process in Chapter 3, plasma was first induced to activate the flax fiber surface by introducing electrons, forming free radicals, and generating oxidation groups. Meanwhile, ablation occurred on the flax fiber surface, cleaning impurities and exposing cellulose. Then, PAA as a binding agent was grafted onto plasma-activated flax fiber to further react with ZnO NPs. The covered PAA layer holding carboxy groups formed bidentate species with Zn\(^{2+}\) during the process of nano-ZnO self-assembly (Chen et al., 2019a). However, nanoparticles tend to aggregate and are not easy to disperse, thus deteriorating their functionality. In this case, HDTMS was used to increase the dispersibility of ZnO NPs (Ryu et al., 2019). In addition, the main content of flax fiber was cellulose containing free hydroxyl groups, which is responsible for its hydrophilic surface in nature. To convert cellulose-based material from hydrophilic to hydrophobic, HDTMS coupling agents were involved to block the hydroxyl groups on the flax fiber surface and thereby reduce water sorption sites (Li et al., 2007).

The silanol groups of HDTMS bonded with the free hydroxyl groups presented on the flax fiber cellulose surface and ZnO NPs (Agrawal et al., 2019). Figure 4-4 (a ~ b) and (e ~ f) present the distribution of stretching vibration of the alkyl groups caused by HDTMS on HDTMS-ZnO modified flax fiber before and after UV treatment, respectively. It can be seen that after UV treatment, the concentration of alkyl groups decreased due to
hydrophobic HDTMS deteriorating slightly by UV light. The concentration distribution of ZnO NPs before and after UV treatment was illustrated in Figure 4-4 (c) and (g). Compared with the original HDTMS-ZnO flax fiber, more ZnO NPs were exposed during UV irradiation, contributing to the hydrophilic surface. In a dark environment, due to a long alkyl chain of HDTMS, the modified flax fiber exhibited high hydrophobicity (Figure 4-4 (d)). As a photo-responsive semiconducting oxide material, ZnO NPs determined the switchable wettability of the modified flax fiber. After UV irradiation, electron-hole pairs were generated on the ZnO surface. These holes interacted with lattice oxygen to form unstable oxygen vacancies. The water in the surrounding atmosphere was adsorbed on oxygen vacancies to produce hydroxyl radicals, which helped to change surface hydrophobicity to hydrophilicity (Figure 4-4 (h)). When stored in a dark environment, the free hydroxyl groups were replaced by ambient oxygen, reconverting to a hydrophobic surface (Fakhru’l-Razi et al., 2009).

Corresponding with Figure 4-4, the synchrotron-based FTIR (Figure 4-5 (a)) and XRF spectra (Figure 4-5 (b)) before and after UV treatment are displayed. The broad peak between 3,600 and 3,000 cm\(^{-1}\) was due to the hydroxyl (-OH) groups of the cellulose, which was abundant in substrate (Bozaci et al., 2013). Two peaks, at 2,853 and 2,916 cm\(^{-1}\), corresponded with the C-H stretching band caused by alkyl groups of HDTMS (Pipatchanchai and Srikulkit, 2007). After UV treatment, a decrease of intensity was witnessed on the modified fiber due to the deterioration of HDTMS. However, the Si–O–Si stretching vibration at about 1,100 cm\(^{-1}\) was not discovered. The reason for this might be that only one drop of HDTMS was enough to obtain the hydrophobic surface and was
thus difficult to detect via FTIR spectroscopy. Figure 4-5 (b) displays the XRF spectra before and after UV treatment. No obvious metal element was found on untreated flax fiber. The small peak, at about 2,960 eV, was due to the occurrence of Ar in the environment. The two new peaks, at about 8,640 and 9,570 eV, corresponded with the characteristic X-ray emission lines of Zn Kα and Zn Kβ caused by immobilized ZnO NPs. It can be observed that after UV treatment, the peak of Zn was stronger than that of freshly modified flax fiber, contributing to hydrophilic wettability.
Figure 4-4 (a, b) Synchrotron based FTIR mapping results of HDTMS-ZnO modified flax fiber between the range of 2,850 ~ 2,853 cm\(^{-1}\) and 2,916 ~ 2,919 cm\(^{-1}\); (e, f) Synchrotron based FTIR mapping results of HDTMS-ZnO modified flax fiber after UV treatment between the range of 2,850 ~ 2,853 cm\(^{-1}\) and 2,916 ~ 2,919 cm\(^{-1}\); (c, g) Synchrotron-based XRF of HDTMS-ZnO modified flax fiber before and after UV treatment; (d, h) Mechanism scheme of HDTMS-ZnO modified flax fiber before and after UV treatment.
Figure 4-5 (a) Synchrotron based FTIR spectra results of HDTMS-ZnO modified flax fiber before and after UV treatment; (b) Synchrotron based XRF spectra of untreated, HDTMS-ZnO modified flax fiber, and UV treated HDTMS-ZnO modified flax fiber.
4.3.4. Performance of Oil-water Separation

The modified HDTMS-ZnO flax fiber was characterized as being hydrophobic/underwater lipophilic in nature and hydrophilic/underwater oleophobic after UV treatment. It can be employed in various oil pollution scenarios, including immiscible light oil-water, immiscible heavy oil-water, and oil-in-water emulsion. In addition, it can be fabricated into an oil sorbent or oil barrier to address different types of oil-water mixtures.

Figure 4-6 illustrates HDTMS-ZnO flax fiber used as an oil sorbent. The light and heavy oil were dyed red by Sundan III to distinguish it from water. Figure 4-6 (a) and (b) display modified flax fiber applied in the absorption of light oil and heavy oil spilling, respectively. It could be seen that both light and heavy oil were collected by the modified flax fiber. Figure 4-6 (c) presents the absorption result after 12 h. The initial concentration of oil-water emulsion was 7,060 mg/L COD; after absorbed by HDTMS-ZnO flax fiber, the COD concentration decreased to 112 mg/L, achieving a high oil removal efficiency of 98.4%.

The modified flax fiber could also be fabricated into an oil filter. As displayed in Figure 4-7 (a), the original HDTMS-ZnO flax fiber was compressed at the bottom of a pipette tip. Afterward, 10 mL of immiscible heavy oil-water was poured onto the filter. Only oil was permeated, and water was repelled. After 7 s, all oil was permeated, and the remaining water could be held more than 3 h. The water contact angle was greater than 130°, and the underwater oil contact angle was too small to measure. This was primarily caused by the
hydrophobic surface of HDTMS-ZnO flax fiber, which demonstrated an affinity for oil and a repulsion to water. However, due to the switchable wettability of ZnO caused by UV irradiation, the flax fiber surface was converted to hydrophilicity and underwater oleophobicity. Figure 4-7 (b) displays that the water contact angle was less than 30°, and the underwater oil contact angle was more than 150°. Accordingly, when used as an oil barrier, water was filtrated via UV treated HDTMS-ZnO flax fiber while light oil was held.
Figure 4-6 HDTMS-ZnO modified flax fiber as oil sorbent employed in (a) immiscible light oil-water mixture; (b) immiscible heavy oil-water mixture; (c) oil-in-water emulsion.
Figure 4-7 (a) HDTMS-ZnO modified flax fiber as oil filter before UV treatment employed in immiscible heavy oil-water mixture; (b) HDTMS-ZnO modified flax fiber as oil filter after UV treatment employed in immiscible light oil-water mixture.
4.4. Summary

In this study, a UV controllable hydrophobic–hydrophilic/underwater oleophobic HDTMS-ZnO flax fiber was developed for oil-water mixture separation on demand. The HDTMS-ZnO coated flax fiber was hydrophobic and underwater oleophilic in the dark, while demonstrating transferrable wettability of hydrophilicity and underwater oleophobicity after UV treatment. The wettability switching was reversible when stored in the dark. Based on the modification process presented in Chapter 3, this chapter introduces two new determining factors: HDTMS and ZnO concentration. A 4 × 4 matrix full design was employed to explore the relationship between the HDTMS and ZnO concentrations. Considering both the highest water contact angle and least switchable UV time, the optimal combination was 0.1% HDTMS and 1% ZnO NPs. The water contact angle could achieve 111.86°, and it took 40 min to switch its surface wettability to hydrophilicity under UV treatment. The modified fiber was comprehensively characterized, and the modification mechanism was studied based on the contact angle, SEM, and synchrotron-based FTIR and XRF. The functional groups and ZnO NPs distribution before and after UV treatment were investigated on a flax fiber surface. It was interesting to find that the concentration of alkyl groups decreased, while the ZnO NPs concentration increased after UV treatment, which attributed to reversible wettability. The as-prepared flax fiber was successfully applied in several oil pollution scenarios, including oil spilling, immiscible light and heavy oil-water separation, and oil-water emulsion separation.
CHAPTER 5

CONCLUSIONS

5.1. Summary

In this study, environmentally friendly, reusable and low-cost functionalized flax fibers were fabricated to separate oil from water. A TiO₂-modified flax fiber with a hydrophilic/underwater oleophobic property and a HDTMS-ZnO-modified flax fiber with a UV-induced switchable hydrophobic–hydrophilic/underwater oleophobic property were developed and employed to deal with various oil pollution. Based on cold plasma-induced PAA polymerization and esterification, TiO₂ NPs and HDTMS-ZnO NPs were self-assembled on PAA-coated flax fiber surfaces. A factorial experiment design was carried out to investigate the significant preparation parameters and reveal their complicated interactions on flax fiber modification. Furthermore, a full experiment design was carried out to balance the amounts of HDTMS and ZnO to obtain an optimal combination. Surface functionality and mechanism were comprehensively explored by contact angle, SEM, and Synchrotron-based FTIR and XRF. The distributions of functional groups as well as self-assembled nanoparticles were analyzed on flax fiber surfaces. Both the as-prepared two kinds of flax fiber were applied in oil-water separation. The hydrophilic/underwater oleophobic flax fiber modified with TiO₂ NPs was successfully used as an oil barrier to separate immiscible light oil from water. The HDTMS-ZnO coated flax fiber with a UV-induced switchable hydrophobic-hydrophilic/underwater oleophobic property exhibited good performance in separating oil-in-water emulsion, immiscible light oil-water mixture,
and heavy oil-water mixture.

5.2. Research Achievements

A functional flax fiber was developed through self-assembled TiO$_2$ NPs. Free radicals and oxidation groups were introduced on flax fiber surface through plasma treatment, providing radical initiators for AA monomers to form the PAA layer via esterification and polymerization. TiO$_2$ NPs were immobilized through the coated PAA layer to obtain a hydrophilic surface for the modified flax fiber. A $2^7$-$2$ two-level factorial design was used to find out the effects of significant parameters and their interactions. It was interesting to find that plasma treatment power, plasma treatment gas flow rates, AA concentration, and nano-TiO$_2$ concentration helped improve the hydrophilicity significantly. The significant interactions in the fabrication process indicated that the factors affected hydrophilic property in various aspects. The modified fiber was comprehensively characterized and the modification mechanism was studied by contact angle, SEM, and synchrotron-based FTIR and XRF. For the first time, the distribution of functional groups and coated TiO$_2$ on flax fiber surfaces was investigated by synchrotron-based analyses. After plasma treatment, the amount of hydroxyl groups increased due to the oxidation of free radicals and the exposure of cellulose in the ablation process. Acrylic acid reacted with hydroxyl groups through esterification and polymerization. A thin PAA layer was formed through plasma-induced polymerization to immobilize TiO$_2$ NPs. The bonding of TiO$_2$ NPs was stable, therefore the modified flax fiber kept its hydrophilic property after 10 minutes of ultrasonic shaking. The modified flax fiber was verified to have great capability to filtrate water while
repelling oil. Compared with the untreated flax fiber, the water contact angle decreased from 97.4° to 25.9°, and the underwater oil contact angle increased from 95.8° to 134.6°. The modified flax fiber showed stable performance of oil-water separation both in alkaline and salty conditions, and it could be used up to 10 cycles. The modified flax fiber could be further constructed into oil barriers with special wettability to separate oil from water.

The above mentioned TiO$_2$ NPs modified flax fiber can usually be used as an oil barrier for immiscible light oil-water separation. Furthermore, in order to deal with broader oil pollution problems, a UV controllable hydrophobic-hydrophilic/underwater oleophobic HDTMS-ZnO flax fiber was developed for oil-water mixture separation on demand. The HDTMS-ZnO coated flax fiber was hydrophobic and underwater oleophilic in the dark. However, it demonstrated transferrable wettability of hydrophilicity and underwater oleophobicity after UV treatment. The wettability switching was reversible when stored in the dark. Based on the modification processes presented in Chapter 3, two new determining factors were introduced: HDTMS and ZnO concentration. A 4 × 4 matrix full design was employed to explore the relationship between the HDTMS and ZnO concentrations. Considering both the highest water contact angle and least switchable UV time, the optimal combination was 0.1% HDTMS and 1% ZnO NPs. The water contact angle could achieve 111.86°, and it took 40 minutes to switch its surface wettability to hydrophilicity under UV treatment. The modified fiber was comprehensively characterized, and the modification mechanism was studied based on the contact angle, SEM, and synchrotron-based FTIR and XRF. The functional groups and ZnO NPs distribution before and after UV treatment were investigated on flax fiber surface. It was
interesting to find that the concentration of alkyl groups decreased, while the ZnO NPs concentration increased after UV treatment, which attributed to reversible wettability. The as-prepared flax fiber was successfully applied in several oil pollution scenarios, including oil spilling, immiscible light and heavy oil-water separation, and oil-in-water emulsion separation.

5.3. Recommendations for the Future Study

Modification of bio-materials will have important implications for risk assessment and site remediation regarding overall environmental performance. The modified flax fiber has been comprehensively characterized by synchrotron-based FTIR and XRF technologies. The reaction mechanism was explored in this study; however, the bonding formation and valence changes of self-assembled nanoparticles still need to be further studied. In addition, further studies are desired to apply the modified flax fiber in a field experiment. Although it has already demonstrated good performance in oil-water mixture separation in a lab-based experiment, the performance of on-site application is unknown. Based on the research of their characteristics in the environment, the flax fibers are expected to have extensive applications on the environmental simulation, ecological system modeling and pollutant migration estimations. In the future, the absorption of other petroleum organic pollutants such as naphthenic acid, hydrocarbon, and aromatic compounds can also be explored.
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