



MONASH University

Oil/water separation by Nanocellulose Aerogel Sponge Filter

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Master of Engineering Science (By research)

A thesis submitted for the degree of *Master of Engineering Science (By research)* at
Monash University in 2017

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Abstract

The rapid industrial growth and occasional ocean spillage accidents have led to the large production of oily wastewater. With the greater demand of clean water, and the increasing concerns about environment issues associated with oily waste water, treating oily wastewater has become an inevitable challenge. Among all the techniques developed for the treatment of oily wastewater, membrane technology has attracted an ever increasing attention due to its advantages: no addition of chemicals, low energy requirement and high efficiency.

While many reported membranes showed promising performance on oil/water separation, they raised some environmental concerns regarding non-degradable and toxic chemicals used during the production. Therefore, using 'greener' materials and processes to produce membranes for oil/water separation has been a hot research topic recently. Cellulose is of technological interest as it is a renewable, sustainable and eco-and bio-friendly material. The research in this thesis focused on developing a 'green' membrane using cellulose for the application of oil/water separation.

In this research, a cellulose nanofibre aerogel filter with tuneable pore structure exhibiting super-hydrophilic and underwater-super-oleophobic behaviours is synthesized by a facile method of cross-linking between cellulose fibres and polyamideamine-epichlorohydrin (PAE). The prepared aerogel filter showed excellent oil/water separation efficiency for both oil/water mixtures (100%, even after 10 cycles), and oil/water surfactant-free emulsion (~98%), driven solely by gravity. In addition, the specific structure can de-emulsify oil/water emulsion. The results showed that the cellulose aerogel filter can be used for oil/water separation and recovery. However, the aerogel filter was still faced with difficulties in separating oil/water surfactant-stabilized emulsion due to its relatively large pores (about 100 microns) within the structure. Therefore, a second layer was coated onto the single layer cellulose aerogel by filtration to produce a double-layer aerogel filter in order to achieve the separation of oil/water surfactant-stabilized emulsion. As compared to the single-layer aerogel, this double-layer aerogel demonstrated improved performance due to its higher selectivity, achieving a 96% separation efficiency in separating oil/water stabilized emulsion, due to the reduced size of the surface pores. However, the two-layer structure was proved to be more prone to clogging, thus limiting its effectiveness over multiple cycles.

Chapter 1

1 Introduction

1.1 Research Background

A large amount of oily wastewater is produced daily in many industrial processes, including food processing, metallurgical, petrochemical industries, and petroleum refineries (Hong, Fane et al. 2003). The effect of this wastewater on the ecosystem is long term and lethal, which can be observed by the consequences of oil spill accidents that have occurred frequently (Peterson, Rice et al. 2003). From the 1967 Torrey Canyon oil spill to the latest 2011 Bohai bay oil spill (Wang, Liang et al. 2015), the leakage of oil into the ocean has brought many toxic compounds to the ocean and thus threatens every species along with the marine food chain, from low grade algae to higher mammals even including human beings (Dubansky, Whitehead et al. 2013). In addition, with the rapidly increasing population and steadily worsening climate, freshwater scarcity has become a severe issue in the world, especially in certain water-stressed regions (Oki and Kanae 2006, Iglesias, Garrote et al. 2007, Shannon, Bohn et al. 2008). Because of these environment and health requirements, these oil/water mixtures must be appropriately treated. Removing oil from wastewater is a significant aspect of pollution control. Apart from the burning of oil, artificial separation of oily water is a more favoured way since the oil separated from the oily waste water can be re-collected without causing any environment pollution and may be reused in various industries (Gaaseidnes and Turbeville 1999).

Traditional techniques such as gravity separation, skimming, and flotation have shown decent performance in separating oil and water. However, these conventional methods have their own drawbacks, such as, high cost, using toxic compounds, requiring large space for installation and generation of secondary pollutants. Keeping these drawbacks in view, membrane separation processes serve as an emerging technology in the 21st century (Padaki, Murali et al. 2015).

Membrane based separation methods are attractive because: (1) they show a higher energy efficiency than some of the other methods stated above; and (2) there are a range of materials that can be designed to selectively filter either water or oil (Rohrbach, Li et al. 2014). In the past years, various materials (Xu, Chung et al. 1999, Ochoa, Masuelli et al. 2003, Bowen, Cheng et al. 2005, Chakrabarty, Ghoshal et al. 2008, Chakrabarty, Ghoshal et al. 2010, Alsahy 2012) such as polydimethylsiloxane (PDMS) coated nanowire membranes, polytetrafluoroethylene (PTFE) coated metal mesh, carbon based porous materials, crosslinked polymer gels had been developed to produce membranes to effectively separate oil/water mixtures, and many of these materials have been demonstrated to filter or adsorb oil from water, referred to as 'oil-removing' materials. However, oil-removing materials are easily fouled and clogged by oil because of their oleophilic properties (Kota, Kwon et al. 2012). In most cases, the adhered oil is hard to remove and easily causes secondary pollution when discarded. Many of these filters run off pumps, consuming even more energy and decreasing efficiency (Wen,

Di et al. 2013). Secondary pollution, oil fouling, and increased energy needs have a detrimental impact to the environment. These factors are moving interest away from using ‘oil-removing’ materials towards hydrophilic/oleophobic filters in the separation of oil and water(Lemos, da Silva et al. 2010). Many existing hydrophilic/oleophobic filter(Kota, Kwon et al. 2012, Zhang, Zhong et al. 2013, Zhang, Zhu et al. 2014) are made of synthetic materials, which are derived from non-renewable sources and could cause issue during their disposal. Synthetic polymers are often non-biodegradable, in other words, they do not break down in the soil, and the chemicals used in their manufacture can leach out into the environment. Hence, improvements still need to be made to reduce their environmental impact.

Some researchers have examined the possibility of developing oil and water separation membranes(Li, Cao et al. 2006, Rohrbach, Li et al. 2014, Wang, He et al. 2015) using naturally derived materials, which are more environmentally friendly. However, these studies are still very limited. Among all these materials, cellulose and its derivatives were the focus for this study due to its accessibility and ‘Green’ properties such as renewability, biocompatibility and biodegradability(Pääkkö, Ankerfors et al. 2007). However, most of the previously published cellulosic membranes are modified using harmful chemicals such as those bearing fluoride groups to create the filter’s oleophobic behaviour(Feng, Zhang et al. 2004, Lemos, da Silva et al. 2010, Xue, Wang et al. 2011, Maphutha, Moothi et al. 2013). Hence, improvements still need to be made to decrease their environmental impact.

1.2 Research objectives

This research aims to minimize the environmental impact of cellulosic membranes specifically for the oil-in-water separation (termed as ‘oil/water separation’ in the rest of the thesis). This research will provide a feasibility study on producing a membrane using cellulose, without the modification of harmful chemicals.

1.3 Research Scopes

The specific scopes of this research are:

1. To develop a method to produce a membrane using cellulose without the addition of harmful chemicals.
2. To characterise the membrane in terms of surface structure, pore size distribution and surface wettability.
3. To examine the performance of the membrane in terms of the pure water flux, the separation efficiency to oil/water mixtures, oil/water surfactant-free emulsions and oil/water surfactant-stabilized emulsions.

4. To compare performance with reported membranes and create improvement plans.

Chapter 2

2 Literature Review

2.1 Oil and water mixtures and emulsions

Oily wastewater is from a broad range of sources and processes, such as oil refining, oil storage, agriculture and food operations, oil spillage in the ocean, the transportation and production in petrochemical industries. Common traditional methods for treating such contamination or spills are flotation, coagulation, biological treatment, advanced oxidation and membrane technology, which are discussed further in the section below.

Water and oil are normally immiscible. Sometimes oil-water mixtures are well layered, which, however, is not always the case. In fact, a large amount of oil-water mixtures to be processed exist in the form of an emulsion. In an emulsion(Young 1805), one liquid (the dispersed phase) is dispersed in the other (the continuous phase). The diameter of the dispersed phase droplet is normally lower than 20 μm (Khan, Talegaonkar et al. 2006). For water and oil systems, there are different types of emulsion: firstly, an ‘oil-in-water’ (O/W) emulsion, wherein the oil is the dispersed phase, and water is the dispersion medium; secondly, a ‘water-in-oil’ (W/O) emulsion, wherein water droplets are dispersed and encapsulated within the continuous phase of oil; lastly, multiple emulsions, such as a ‘water-in-oil-in-water’ (W/O/W) emulsion and an ‘oil-in-water-in-oil’ (O/W/O) emulsion(Khan, Talegaonkar et al. 2006).

Commonly emulsions do not form spontaneously due to their inherent instability(Walstra 1993). For any type of stable emulsion to form, three basic conditions must be met(Chen and Tao 2005):

- (1) The two liquids must be immiscible or mutually insoluble in each other;
- (2) Sufficient agitation must be applied to disperse one liquid into the other; and
- (3) An emulsifying agent or a combination of emulsifiers must be present.

Whether an emulsion of oil and water form a W/O emulsion or an O/W emulsion depends on the volume fraction of both phases and the type of emulsifier present(Ruckenstein 1996). In general, the Bancroft rule applies. Bancroft(Ruckenstein 1996) concluded that ‘the phase in which an emulsifier is more soluble constitutes the continuous phase’. In other words, the type of emulsion is dictated by the emulsifier present and that the emulsifier should be soluble in the continuous phase. Surfactants generally contain both a hydrophilic polar group and a hydrophobic (lipophilic) non-polar group, and they can be defined by their hydrophilic/lipophilic balance (HLB)(Guy 2007): low HLB surfactants with high affinity for oil phases will favour the formation of W/O emulsions and high HLB surfactants with high affinity for aqueous phase will favour the formation of O/W emulsions. An illustration of these two types of surfactant stabilized emulsion is shown in Figure 1(Guy 2007).

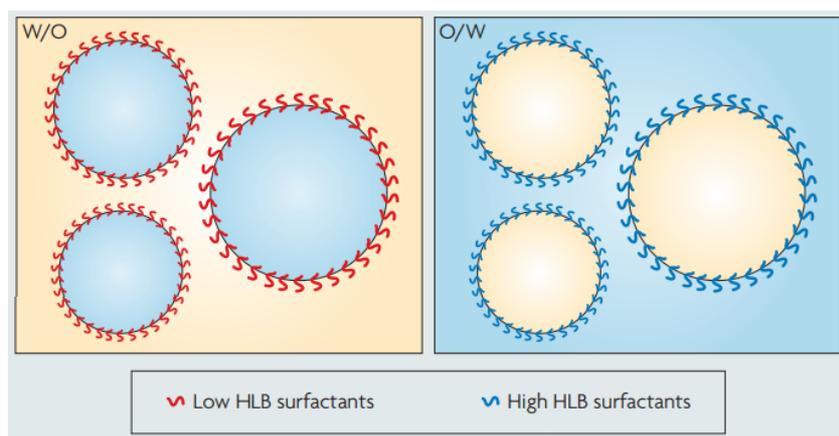


Figure 1 W/O emulsion and O/W emulsion(Guy 2007)

2.2 Separation strategies

2.2.1 Conventional treatments of oily wastewater

Conventional separation strategies include flotation, coagulation, advanced oxidation, biological treatment and membrane technology. Some of these methods such as flotation and biological treatment usually involve large energy consumption, heavy machinery and addition of chemicals during the separation process. Researchers and scientists are striving to develop strategies that have low energy requirement and are easy to apply, while maintaining high separation efficiency. Table 1 shows a summary of different methods for oil/water separation with separation efficiency, advantages and disadvantages.

Table 1 Different methods for oil/water separation

Methods	Advantages	Disadvantages	Separation efficiency (best reported results)	Ref
Flotation	Easy to apply and operate	Low efficiency, high energy consumption	~90%	(Wang 2007)
Coagulation	Effective for removing emulsified and dissolved oil, and some difficult bio-degradable organic polymers	Difficult in selection of coagulants, secondary pollution	~99%	(Zeng, Yang et al. 2007)
Biological treatment	Rapid, easy maintenance, effective for removing difficult bio-degradable organic polymers	Large energy requirement, Issues with the residue chemical waste	~97%	(Scholz and Fuchs 2000)
Advanced oxidation	Rapid, suitable for toxic and hazardous waste	Large amount of chemical required, issues with corrosion and salt deposition	~99%	(Kritzer and Dinjus 2001)

Membrane technology	Low energy requirement, easy to handle, high separation efficiency	Clogging, fouling	>99.9%	(Zhao, Zhang et al. 2016)
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a. Flotation

Flotation is a process to remove suspended oil and solids in wastewater by dissolving air under pressure and then releasing the air at atmospheric pressure. As the density of most oil is less than that of water; the tiny air bubbles with adhered oil particles will float, creating a scum layer, which can be separated from the water(Moosai and Dawe 2003). Currently, dissolved air flotation(Rubio and Tessele 1997), column flotation(Finch 1995), and jet impeller flotation(Clayton, Jameson et al. 1991) are the commonly used methods. Dissolved air flotation and column flotation are often plagued by maintenance issues, along with high energy consumption. On the other hand, the jet flotation method is relatively less energy-consuming, and easy to install and operate(Yu, Han et al. 2013). However, the major drawback of the flotation technique is relatively low separation efficiency (about 90%) compared to other conventional techniques(Yu, Han et al. 2013).

b. Coagulation

Coagulation is a process used to destabilize the particles in oily wastewater. Coagulants with charges opposite to those of the suspended solids are added to the oily wastewater to neutralise the charges on dispersed solids(Edzwald 1993). This technique has been widely used in recent years in oily wastewater treatment(Ahmad, Sumathi et al. 2006). Many coagulants such as zinc silicate and anionic polyacrylamide(Zeng, Yang et al. 2007) and $FeCl_3 \cdot 6H_2O$ (Amuda and Amoo 2007) were developed for this application. However, due to the complexity of oily wastewater composition, the selection of coagulants is difficult and requires enormous experiments to screen for the suitable coagulants.

c. Biological treatment

Biological treatment involves the use of microbial metabolism to degrade, or decompose organic materials and produce clear effluent water(Kriipsalu, Marques et al. 2007). The treatment could be carried out in various ways: Woolard (Woolard and Irvine 1995) used a halophile organism to develop a halophilic sludge in a sequencing batch reactor; Suehara (Suehara, Kawamoto et al. 2005) used an oil degrading yeast, *Rhodotorula mucilaginosa*; Puay (Puay, Qiu et al. 2015) used zinc oxide nanoparticles in a sequencing batch reactor. The separation efficiency of biological treatment is usually higher than both flotation and coagulation, achieving about 93-97%(Scholz and Fuchs 2000). Although biological wastewater treatment is efficient in removing most organic contaminants,

studies indicate that some chemicals such as pharmaceuticals, detergents, cosmetic and industrial compounds, still remain after biological wastewater treatment. Membrane technologies may be able to address this problem(Wei, Van Houten et al. 2003).

d. Advanced oxidation process

Advanced oxidation processes include electrochemical oxidation catalysis(Li, Wang et al. 2003, Santos, Goulart et al. 2006), and supercritical water oxidation(Tester and Cline 1999). Electrochemical oxidation catalytic systems involve electrochemical oxidation of the hydroxyl radical with a highly organic matter through addition, substitution and electron transfer processes (Li, Wang et al. 2003, Koper 2005). Supercritical water oxidation (SCWO) is a process where organic solutes are oxidized in an aqueous medium with oxygen or hydrogen peroxide acting as oxidants, at temperatures and pressures above the critical point of water (374.3 C and 22.12 MPa)(Yu, Han et al. 2013). Various SCWO technologies were studied and reported by many researchers(Watanabe, Mochiduki et al. 2001, Liang, Shuzhong et al. 2006, Yu, Chen et al. 2015). However, this technique has drawbacks such as corrosion and salt deposition, high energy consumption and high operating cost(Vadillo, Sánchez-Oneto et al. 2013).

e. Membrane separation technology

Membrane technology has become a significant separation technology over recent decades(Lin, Liu et al. 2006). The applications of membrane technology have spread and become an essential separation technology.

Membrane separation technology is the use of special porous materials to physically remove trapped contaminants(Lin, Liu et al. 2006). The separation is not complicated to comprehend: the membrane acts as a semi-permeable layer between two phases and it regulates the transportation between those two phases. Specifically, the filter will allow water to penetrate through the membrane, while it retains suspended solids and other substances. Based on the pore sizes of filter membranes, membrane separation technologies are generally divided into 4 types: microfiltration, ultrafiltration, nanofiltration and reverse osmosis. A microfiltration filter membrane has a pore size around 0.1 microns, it removes microorganisms; an ultrafiltration filter membrane has a pore size around 0.01 microns, which allows it remove some viruses; a nanofiltration filter has a pore size around 0.001 microns, and it can be used to remove most organic molecules, nearly all viruses, most of the natural organic matter and a range of salts; Lastly, a reverse osmosis filter membrane has a pore size around 0.0001 microns, which allows it to remove all organic molecules, viruses and most minerals that are present in the water. Polymers such as polyvinylidene fluoride (PVDF) and polysulfone have been widely used for preparing microfiltration and ultrafiltration membranes(Li, Yan et al. 2006, Mansouri, Harrisson et al. 2010, Zhu, Wang et al. 2014). In addition, ceramic based membranes

(Yang, Zhang et al. 1998, Benito, Conesa et al. 2005, Cui, Zhang et al. 2008) are also of importance in the field of filtration due to their high chemical, thermal and mechanical stabilities (Zhu, Wang et al. 2014). For the application of oil/water separation, suitable membranes are selected based on the stability and droplet sizes of oil/water emulsion. Microfiltration filter membranes and ultrafiltration filter membranes are generally used for the separation of oil/water mixtures and surfactant-free micro-emulsions, while nanofiltration filter membranes and reverse osmosis filter membranes are used for oil/water surfactant-stabilized nano-emulsions.

The advantages of membrane technology are that it works without the addition of chemicals, with low energy requirement and is easy to handle. Membrane separation already shows better efficiency compared to some of the other conventional techniques (Padaki, Murali et al. 2015). A number of reported membranes can achieve oil removal efficiency around 99% (Cui, Zhang et al. 2008, Yang, Ma et al. 2011). Moreover, Zhao's group has reportedly achieved a efficiency higher than 99.9% (Zhao, Zhang et al. 2016).

2.2.2 Materials used for oil/water separation in recent research advances

Recently, researchers strive to help improve the existing technologies in the field, and to develop new advanced materials that ideally can selectively absorb oil (or water) while completely repelling the other phase. These are desired in the development of oil/water separation technologies (Xue, Wang et al. 2011, Wang, Lei et al. 2014). In the following sections, the types of materials used in recent research advances are reviewed and discussed from two different aspects: oil-removing materials versus water-removing material and synthetic materials versus natural materials. Lastly, cellulose and aerogels, the materials featured in this thesis, were then introduced and discussed.

a. Oil-removing materials vs water-removing materials

Oil-removing materials are materials, which allow the oil phase to spread easily, absorb (for porous bulk materials) and penetrate (for porous filter materials), while repelling the water phase. Oil can hence be separated from water in an oil/water mixture. These materials generally exhibit superhydrophobic and superoleophilic properties, which can be shown in Figure 2 (Zhang, Sèbe et al. 2014), water droplet remains spherical in shape, while dodecane droplet spreads on the surface of this silylated nano cellulose (NFC) sponge. There are commonly several types of oil-removing materials: fabric-based materials (Xue, Jia et al. 2008, Zhang, Wang et al. 2013, Zhang, Geng et al. 2013), sponge-based materials (Li, Sun et al. 2011, Zhu, Pan et al. 2011), metallic mesh-based materials (Feng, Zhang et al. 2004, Wang, Yao et al. 2009, Gao, Sun et al. 2013), carbon and its derived

materials (Dong, Chen et al. 2012, Fan, Qin et al. 2013, Singh, Chen et al. 2013), and particles and powder materials (Arbatan, Fang et al. 2011, Akhavan, Jarvis et al. 2013).

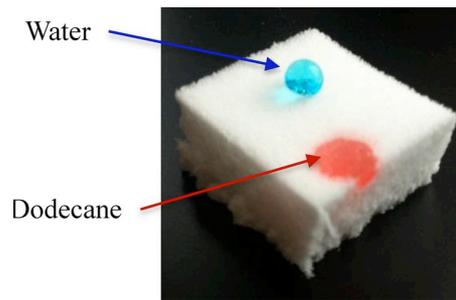


Figure 2 Demonstration of the combined hydrophobic and oleophilic properties of materials

As opposed to oil-removing materials, some researchers have also discovered water-removing materials, which let the water phase penetrate freely while repelling the oil phase. These materials can avoid problems commonly encountered when using oil-removal materials: due to the fact that as water has a higher density than most oil, water acts as a barrier between the substrate and the oil-phase, preventing contact between the oil and separation substrates (Zhang, Zhong et al. 2013). Moreover, oil-removal materials will produce waste from both the oils and the materials themselves, especially for oil with high viscosity. The as-absorbed oils are hard to be cleared away, easily causing secondary pollution during the post-treatment process of the materials(Xue, Wang et al. 2011).

Water-removing materials can be categorized into two specific types based on their wettability characteristics: superhydrophilic-superoleophobic materials, and superhydrophilic-underwater-superhydrophobic materials. The former exhibits superoleophobic property in air (as shown in Figure 3(Zhou, Zhang et al. 2014): cellulose nanosheet), while the latter only exhibits superoleophobic property underwater (as shown in Figure 4(Zhang, Lu et al. 2013): a chitosan-coated film).

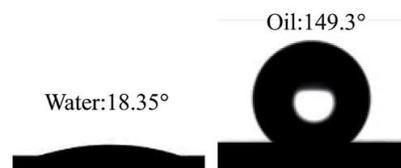


Figure 3 Demonstration of the combined hydrophilic and oleophobic properties of materials(Zhou, Zhang et al. 2014)

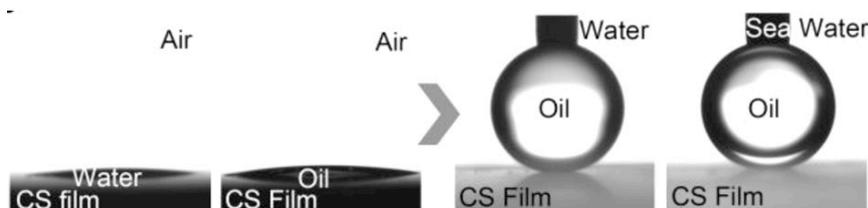


Figure 4 Demonstration of the combined hydrophilic and underwater-oleophobic properties of materials(Zhang, Lu et al. 2013)

To date, several superhydrophilic-superhydrophobic materials have gained some attention in the field, they include: (PDDA-PFO/SiO₂) coatings (Yang, Zhang et al. 2012), hydro-responsive membranes (Kota, Kwon et al. 2012), and other stimuli-responsive surfaces (Hutton, Crowther et al. 2000, Howarter, Genson et al. 2011).

Similarly, a few researchers also reported some interesting development of superhydrophilic-underwater superhydrophobic materials, such as PAM hydrogel-coated mesh (Xue, Wang et al. 2011), silicate/TiO₂ coated mesh (Zhang, Zhong et al. 2013), Cu(OH)₂ covered mesh (Liu, Chen et al. 2013).

b. Synthetic materials vs natural materials

Many of the research advances focus on synthetic materials(Oh, Maeng et al. 2000, Wei, Mather et al. 2003, Ceylan, Dogu et al. 2009, Wu and Zhou 2009, Karakutuk and Okay 2010, Rengasamy, Das et al. 2011) owing to their desirable properties: strength, flexibility, resistivity and chemical inertness. They have been frequently used in this field. The raw materials used to produce synthetic polymers are limited, as they are mostly derived from petroleum oil, and made by scientists and engineers. In addition, their disposal can sometimes lead to environmental issues. Synthetic polymers are often non-biodegradable, in other words, they do not break down in the soil, and the chemicals used in their manufacture can leach out into the environment.

On the other end of the spectrum, some researchers have developed oil/water separation strategies using naturally derived materials(Deschamps, Caruel et al. 2003, Huang and Lim 2006, Lim and Huang 2006, Lim and Huang 2007, Radetic, Ilic et al. 2008, Hussein, Amer et al. 2009). Natural polymers occur in nature and can be extracted. Examples of naturally occurring polymers are silk, wool, DNA, cellulose and proteins. Unlike synthetic polymers, the resources of natural polymers are renewable. Also, they generally require less energy to manufacture, and also lead to less amount of greenhouse gas (CO₂) emission during the manufacturing process(Oksman 1996). Moreover, some of these naturally derived materials such as wood, natural fibre, etc. are biodegradable, causing less harmful impact on environment. However, many naturally derived materials do not have the same level of mechanical strength and durability that synthetic materials provided. For example, a copper

filter mesh could withstand high-pressure flux during process while a paper one might not be strong enough.

c. Cellulose

One of the most promising natural polymers for the manufacture of materials for oil-water separation is cellulose. Cellulose is an organic compound with the chemical formula ($C_6H_{10}O_5$). It is one of the most abundant biopolymers on earth(Klemm, Heublein et al. 2005). It can be found in wood, cotton, hemp and other plant-based materials and serve as the dominant reinforcing phase in plant structures(Henriksson, Berglund et al. 2008). Although native cellulose in higher plants has a relatively simple chemical structure, its physical and morphological structure is complex and heterogeneous. In addition, cellulose molecules are intimately associated with other polysaccharides and lignin in plant cell walls, resulting in even more complex morphologies(Juniper 1968). Cellulose chains aggregate into the repeated crystal structure to form microfibrils in the plant cell wall, which also aggregate into larger macroscopic fibres(Eichhorn, Dufresne et al. 2010), as shown in Figure 5.

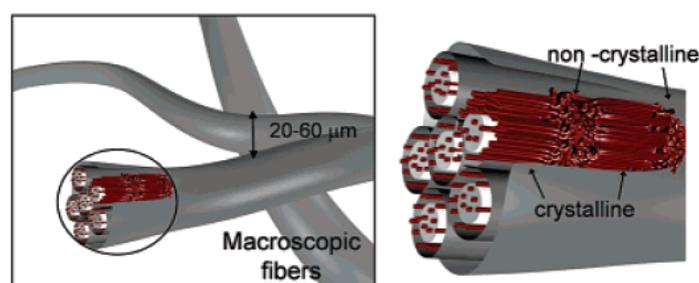


Figure 5 Natural Cellulose Fibres(Eichhorn, Dufresne et al. 2010)

Recently a new cellulose material has been produced; Cellulose nanofibrils, which are produced from any cellulose containing source including wood-based fibres (pulp fibres) through high-pressure, high temperature and high velocity impact homogenization, grinding or microfluidization to break down the cellulose fibres into single or bundled elementary fibrils(Isogai 2013). However, depending on the raw material and the degree of processing, chemical treatments may be applied prior to mechanical fibrillation(Henriksson, Berglund et al. 2008). The basic principle of these methods is that the cellulose microfibre suspension is subjected to strong mechanical shear forces to nano-fibrillate the micro fibres. This material has been called different names such as microfibrillated cellulose (MFC), cellulose nanofibres, nanocellulose and nanofibrils(Siró and Plackett 2010). The terms cellulose nanofibres and MFC are used interchangeably in this thesis. Cellulose nanofibres are available with diameters ranging from 5 to 100nm diameter and length in the range of microns as shown in Figure 6(Dong, Snyder et al. 2013). MFC was first reported in the early 1980s(Turbak, Snyder et al. 1983).

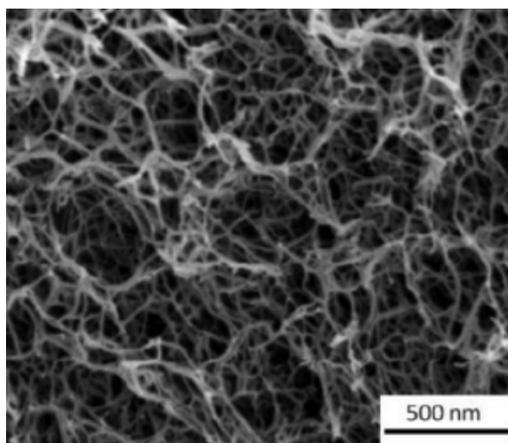


Figure 6 Microfibrillated Cellulose(Dong, Snyder et al. 2013)

Sustainability is expected from these naturally occurring raw materials, which are significantly advantageous for biomedical and environmental applications over synthetic organic and inorganic nanomaterials. In recent years, the synthesis of cellulose nanofibres and their applications in various fields have gained increasing attention because of their excellent properties and its potential to be used as new bio-based nanomaterials in various applications(Pääkkö, Ankerfors et al. 2007).

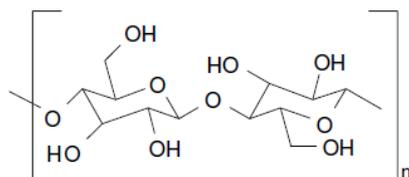


Figure 7 Repeating unit of cellulose

For the application of oil/water separation, MFC shows great potential due to the following reasons: cellulose itself is highly hydrophilic due to three active hydroxyls group in each repeating unit of cellulose molecule, which can be seen in Figure 7(Eichhorn, Dufresne et al. 2010). With this inherent hydrophilic property, MFC is ideal for developing water-absorbing material that repels oil. In addition, its nano-sized dimensions allow the creation of nano-structures that could selectively separate oil droplets of various sizes, even below micron-size.

d. Aerogels:

Aerogels are a class of materials, which are characterised by their highly porous structure and their low solids content. They are obtained from wet gels by drying largely maintaining the openness of the structure(Innerlohinger, Weber et al. 2006).

One of the cellulose-based low-density materials possessing highly porous structures are known as cellulose aerogels. Aerogels are porous materials of interconnected nanostructure made from gels

by replacing the liquid by gas, resulting in extremely low-density solids. Such structures have low density, high specific surface area and low thermal conductivity.(Nakagaito, Kondo et al. 2013) Materials with porosity at micro- and nano-scale made of renewable resources such as cellulose have potential applications in medical, cosmetic and pharmaceutical fields that require biocompatibility and biodegradability, in addition to environmentally friendly packaging and insulating materials(Jin, Nishiyama et al. 2004).

For the application of oil/water separation, various cellulosic aerogels have been developed, and most of them are designed as absorbents(Cervin, Aulin et al. 2012, Nguyen, Feng et al. 2013, Zhang, Sèbe et al. 2014, Wang, Xu et al. 2016), which selectively absorb oil from water. These oil-removing materials generally exhibit superhydrophobicity and superoleophilicity. However, they could easily lead to secondary pollution, as the as-absorbed oil is difficult to remove during post treatment. A few researchers have developed aerogels as water-removing materials(Lu, Chen et al. 2014, Rohrbach, Li et al. 2014). They need to be pre-wetted with water to create underwater superoleophobicity prior to usage. They then become hydrogel.

Hydrogel is one of the most typical hydrophilic materials, consisting of a cross-linked network with water filling the interstitial spaces(Gulrez, Phillips et al. 2011). Because of their excellent water-absorbing and water-retaining capacities, hydrogels are considered to be promising candidates for designing novel water-removing materials for oil/water separation. More importantly, they do not lead to secondary pollution issues, which commonly caused by absorbents.

2.3 Gap in knowledge

Although traditional techniques such as flotation, coagulation, biological treatment and advanced oxidation are widely used, they suffer from various drawbacks as mentioned previously. Membrane technology has become a significant due to its advantages of low energy requirement, easy to handle and high separation efficiency.

Many researchers have developed membranes using synthetic materials such as polydimethylsiloxane (PDMS) and polytetrafluoroethylene (PTFE). However, synthetic materials are often non-biodegradable, and are associated with environmental issues during their manufacture.

Therefore, some researchers focus on naturally derived materials instead because they generally require less energy to manufacture, and also lead to less amount of greenhouse gas (CO₂) emission during the manufacturing process. Cellulose has been many researchers' research focus due to its abundance, inherent hydrophilic properties and potential to create nano-structures as they can be homogenised to nanosize.

From the literature, some gap in knowledge was identified as following:

(1) Little research has been done on developing oil/water separation strategies using naturally derived materials, which could help reduce environmental impact that synthetic materials cause.

(2) For oil/water separation, aerogels have been widely designed as absorbents to remove oil from water. These aerogels exhibit superoleophilicity and superhydrobicity. However, little research has been done on using aerogel as a water removing filter membrane, which would overcome to secondary pollution issues that absorbents encountered.

(3) For water-removing materials, there is still large room to improve in terms of methods to create superoleophobic behaviour, which mostly were done by using toxic chemicals. It would be highly desirable to do it with more environmental friendly materials.

In this research, we aimed to explore the feasibility in developing an aerogel filter membrane for oil/water separation using cellulose nanofibres. More importantly, the membrane would demonstrate superhydrophilicity/superoleophobicity properties without the use of harmful chemicals. In terms of performance, it would be able to separate oil/water mixture, oil/water surfactant-free emulsion and oil/water surfactant-stabilised emulsion with high efficiency.

Chapter 3

3 Research Part 1: Single Layer nanocellulose sponge filter for oil-water separation

3.1 Introduction

Nano cellulose aerogel is commonly designed as an absorbent: an oil-absorbing material. However, many of these oil-absorbing sponges and membranes always have drawbacks such as their ease of fouling, difficulty to be cleaned and poor reusability, which restrict their applications (Wang, Zeng et al. 2014). A water-removing material, on the other hand, is a good candidate for oil/water separation with properties of antifouling and separation solely driven by gravity (Zhang, Zhu et al. 2014).

This chapter provides a detailed description on the development of a novel nanocellulose sponge filter from its production to characterization and performance testing. (The schematic of the production and application are shown in Figure 8) With the gap in knowledge mentioned previously, this nanocellulose aerogel was designed to demonstrate underwater superoleophobicity due to its inherent hydrophilicity, and this was to be done without additional chemical treatment such as that described for many reported materials. An ideal material should demonstrate good wet strength so that it could be used underwater. The aerogel would be characterized in terms of surface morphology, pores size distribution and wettability. Furthermore, the performance of this aerogel would be evaluated by its flux and separation efficiency to oil/water mixture, oil/water surfactant-free emulsion and oil/water surfactant-stabilized emulsion.

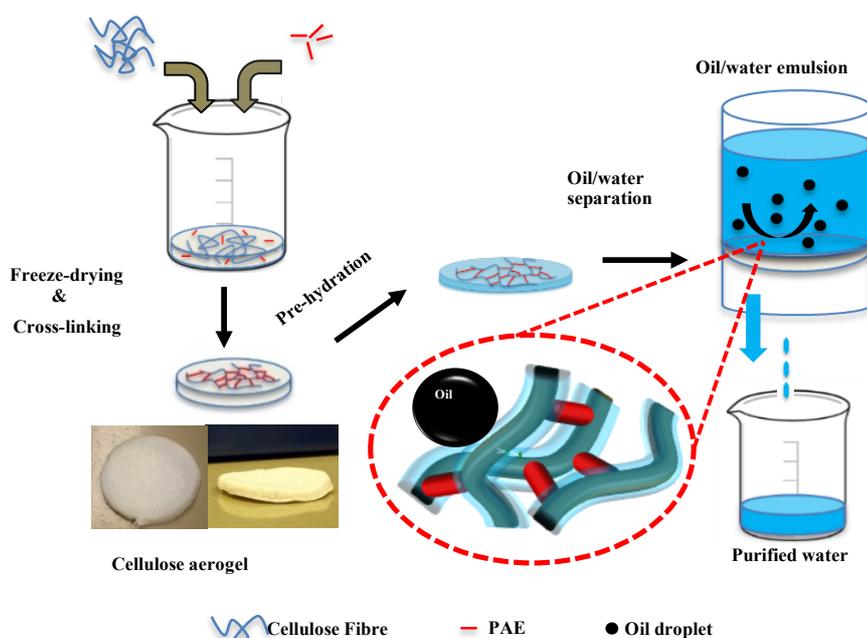


Figure 8 Schematic of fabrication process of the cellulose aerogel filter and its application in oil/water separation.

3.2 Methodology

3.2.1 Materials

Microfibrillated cellulose (MFC) purchased from DAICEL Chemical Industries Limited (Celish KY-100G) was used as the primary material for preparing nanocellulose hydrogel. This MFC sample contains fibres that are approximately 73 nm in width and several microns in length (Varanasi, He et al. 2013). Oil Red-o purchased from Sigma Aldrich Pty Ltd, Australia was used to dye the hexadecane. Sodium dodecyl sulfate (SDS) purchased from Sigma Aldrich Pty Ltd, Australia was used as an emulsifier for stabilizing oil/water emulsion. Hexadecane and mineral oils were provided by Sigma Aldrich Pty Ltd, Australia. Canola and peanut oils were bought from Coles Pty Ltd, Australia. Commercial PAE was provided by Nopco Paper Technology Pty Ltd, Australia (33% w/w solids content). PAE was used as a cross-linker in the fabrication of the hydrogel.

3.2.2 Manufacture of Nanocellulose aerogel

Firstly, a measured amount of wet MFC was weighed (MFC has water content of 75%). A measured amount of PAE (15% Wt) was then weighed (0.05 g/g dry weight MFC) and dissolved in 50 mL of water. The MFC and PAE were mixed together with water to make up to 1.5 L because the minimum volume required in the disintegrator is 1.5 L. Solids content of the MFC in this mixture determines the density of the final aerogel product. Therefore, aerogel with different densities were produced by varying the solids content of MFC in the mixture (60 g, 30 g and 15 g wet MFC were used for making aerogel filter with density of 0.0197 g/ml, 0.0239 g/ml and 0.0337 g/ml, respectively). The mixture was then mixed thoroughly with a disintegrator (Messmer Disintegrator MK3C) for 15000 revolutions. After mixing, the mixture was poured into 50 mL containers, forming suspensions that weight 15 g each in order to achieve a consistent sponge size later. The containers were allowed to freeze in the freezer for 24 hours at -25 °C to maintain its porous structure. Lastly, they were freeze-dried in a freeze dryer for another 24 hours to remove all moisture in the sponge while maintaining their porous structure. The freeze-dried samples were then placed in the oven for 3 hours at 120 °C to promote crosslinking between MFC and PAE.

3.2.3 Performance testing



Figure 9 Experimental set up

Figure 9 above shows the experiment setup for the pure water flux (PWF) and oil/water separation experiments. For all tests, the cellulose aerogel was pre-wetted using deionized (DI) water and was placed in between two glass plates, which have holes with a diameter of 3.2 cm at the centre. Note that the experiments were conducted in open atmosphere, which has a humidity level of 40-50%.

a. Water Flux Testing

34 mL of deionised water was poured into the glass chamber for this test. A beaker, which was placed on a weighing scale, was used to collect the filtrate. The weight of the filtrate was measured and recorded within a certain timeframe (I.e. ranging from 5 seconds to 100 seconds depending on the samples. Details can be seen in the raw data in Appendix I). For tests that were less than 20 seconds, the tests were video-recorded using a phone camera for the entire duration and data were determined later from the recording, as the processes were too quick to do both at the same time. The flux, J , ($\text{Lm}^{-2}\text{h}^{-1}$) was calculated using $J=V/(A.t)$, where V is the volume of the water filtered (L), A is the effective membrane area (m^2) and t is the filtration time (h). In this research, the results were plotted and fitted with a trend-line to calculate the slope at the start of the test (The linear section of the plot; the first 3 points were used). The slope of this trend line was used as V/t .

b. Gravimetric analysis for separation efficiency

The concentration of oil in initial emulsion C_0 was firstly quantified by calculating the weight percentage of oil in the emulsion. Weight of the empty bottle W_1 used to collect filtrate was determined. Weight of filtrate (including bottle) W_2 was then determined. The filtrate was then placed in a ventilated oven for 8 hrs at 60 °C for evaporation of water content in the filtrate. Only oil was

expected left in the bottle, which was then weighed (W3). The concentration of oil in filtrate C_f was quantified by $(W3-W1)/(W2-W1)$. The oil rejection ($R\%$) was calculated as follows:

$$R (\%) = (1 - C_f/C_o) \times 100 \quad (1)$$

c. Water /Oil Mixture Separation Testing

34 mL of a water and selected oil mixture of 50:50 ratios were prepared by simply mixing it together without stirring (oil floats on top of water due to lower density) and poured into the chamber. 1mg of Oil Red-O was added to the mineral oil to enable oil droplets to be more distinguishable. The prepared mixture is as shown in Figure 10 below.



Figure 10 Oil and Water Mixture

A beaker, which was placed on a weighing scale, was used to collect the filtrate. The weight of the filtrate was measured and recorded within a certain timeframe (I.e. ranging from 2 seconds to 30 seconds depending on the samples. Details can be seen in the raw data in Appendix I). For tests that were less than 20 seconds, the tests were video-recorded using a phone camera for the entire duration and data were determined later from the recording, as the processes were too quick to do both at the same time. The respective graphs were plotted as shown in the results. The efficiency is calculated using the gravimetric analysis described in section 3.2.3 b. Repeat measurements were done 3 times. In between repeats, aerogel sample was cleaned by spraying water to wash off the oil on the surface of the samples.

d. Water/ Oil Emulsion Surfactant-free Separation Testing

Emulsion was prepared using 10 mL canola oil and 90 mL deionised water. Mixture was then mixed with a magnetic stirrer for 2 hours to produce a homogenized emulsion that is milky white in colour, indicating that the oil and water were well mixed as shown in Figure 11 below.



Figure 11 Preparation of Emulsion

34 mL of emulsion was poured into the chamber for this test. A beaker, which was placed on a weighing scale, was used to collect the filtrate. The weight of the filtrate was measured and recorded within a certain timeframe (I.e. ranging from 15 seconds to 8 minutes depending on samples, details can be seen in the raw data in Appendix I). For tests that were less than 20 seconds, the tests were video-recorded using a phone camera for the entire duration and data were determined later from the recording, as the tests were too quick to do both at the same time. The respective graphs were plotted as shown in the results. The efficiency is calculated using the gravimetric analysis described in section 3.2.3 b.

e. Water/ Oil Surfactant Stabilised Emulsion Testing

Surfactant stabilized emulsion were prepared using 10 mL canola oil and 90 mL deionised water. 1:0.02 ratio of oil and SDS were then added to create a surfactant stabilise oil and water emulsion. Mixture was then mixed with a magnetic stirrer for 2 hours to produce a homogenized emulsion that is milky white in colour, indicating that the oil and water were well mixed. 34 mL of the surfactant stabilized emulsion was then added into the chamber for the test. A beaker, which was placed on a weighing scale, was used to collect the filtrate. The weight of the filtrate was measured and recorded within a certain timeframe (I.e. ranging from 90 seconds to 10 minutes depending on the samples. Details can be seen in the raw data in Appendix I). The respective graphs were plotted as shown in the results. The efficiency is calculated using the gravimetric analysis described in section 3.2.3 b.

3.2.4 Characterization of hydrogel

a. Surface structure-SEM

Scanning electron microscope (SEM) images of the hydrogel samples were taken using Field Emission Scanning Electron Microscopy, JEOL7001F FEG SEM (located in Monash Centre for Electron Microscopy (MCEM)) to capture images at the cross-section of the sample in order to study the structure of the surface, pore size and pore distribution. Samples were cut into small pieces due to the size requirement for the measurement. To prevent the compression of the sample when cutting, samples were frozen by liquid nitrogen and broken down into pieces using tweezers. The small pieces of samples then underwent freeze drying and vacuum oven drying. A segment of the sample, with cross-section facing up, was placed on a metal plate, which was then coated with platinum and used for SEM analysis.

b. Pore size pore distribution-Mercury Porosimetry

Pore size distribution of the hydrogel samples were characterised by using Micromeritics' AutoPore IV 9500 Series. Samples were cut into small pieces due to the size requirement for the measurement. To prevent the compression of the sample when cutting, samples were frozen by liquid nitrogen and broken down into pieces using tweezers. The small pieces of samples then underwent freeze drying for 24 hours and vacuum oven drying for another 24 hours. Finally, these samples were placed inside the designated test globes to be analysed using Micromeritics' AutoPore IV 9500 Series.

c. Surface wettability

Surface wettability was evaluated by measuring contact angles of oil and water on surface. Measurement was conducted on OCA 15EC (Dataphysics), a measuring device for professional contact angle measurements and drop shape analysis. Samples were cut into small pieces due to the size requirement for the measurement. To prevent the compression of the sample when cutting, samples were frozen by liquid nitrogen and broken down into pieces using tweezers. The small pieces of samples then underwent freeze drying and vacuum oven drying. During the oil contact angle under water measurement, 3 μ L oil drop was ejected from a syringe underwater, then raised to be in contact with the aerogel surface, which was floating at the interface between water and air. Images of the droplet on the surface were taken with the built-in camera of the device, followed by contact angle measurement using its analysis software. For water contact angle in air measurement, 3 μ L water was pipetted and dropped on the aerogel surface. The droplet shape was then recorded real-time with the camera and the contact angle was measured followed using analysis software.

3.3 Results & Discussion

3.3.1 Characterisation

a. Digital images



Figure 12 Digital images of wetted aerogels (From left to right: 0.0197 g/ml, 0.0239 g/ml and 0.0337 g/ml)

The digital images shown in Figure 12 displayed the physical appearance of the wetted aerogels, which were wetted by water. It has shown that the lower the density, the more opaque it appears. This set of aerogels was produced by altering the solids content of the starting MFC suspension. A lower solids content resulted in a lower density of the aerogel, vice versa.

b. SEM images

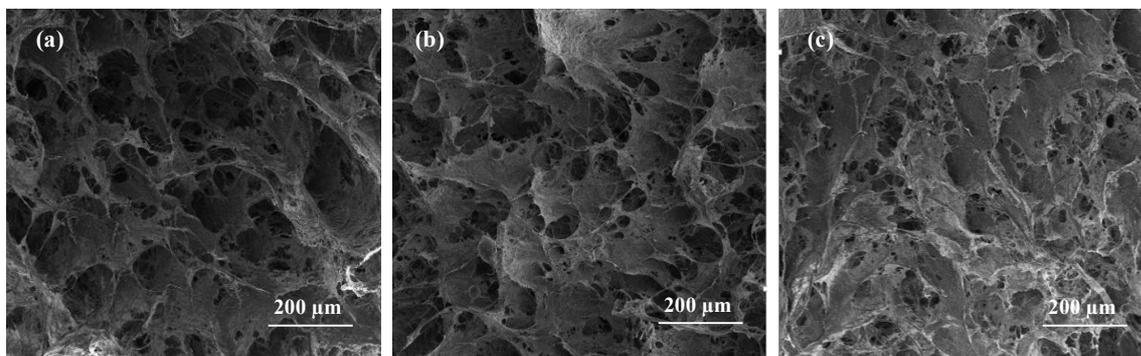


Figure 13 SEM images of the surface of aerogels made with (a) 0.0197 g/ml. (b) 0.0239 g/ml. (c) 0.0337 g/ml starting solids concentration.

The surface structure of the cellulose aerogel was characterized using scanning electron microscopy (SEM) as shown in Figure 13. As mentioned, the pore structures of the cellulose aerogels can be controlled by altering the solids content in the starting MFC suspension before freeze-drying. As expected, the material is more compact with the increasing solids content in the starting MFC suspension, which can be observed in Figure 13. The direct drying of these suspensions usually results in total collapse of porosity, due to the strong surface tension of leaving water causing cohesion of

cellulose molecules forming a tight mass. The freeze-drying method, on the other hand, is effective in perserving the MFC network structure formed in the MFC suspension(Jin, Nishiyama et al. 2004). Therefore, altering the solids content in the starting MFC suspension can effectively tailor the tightness of the structue, as well as the pore sizes.

c. Mercury porosimetry

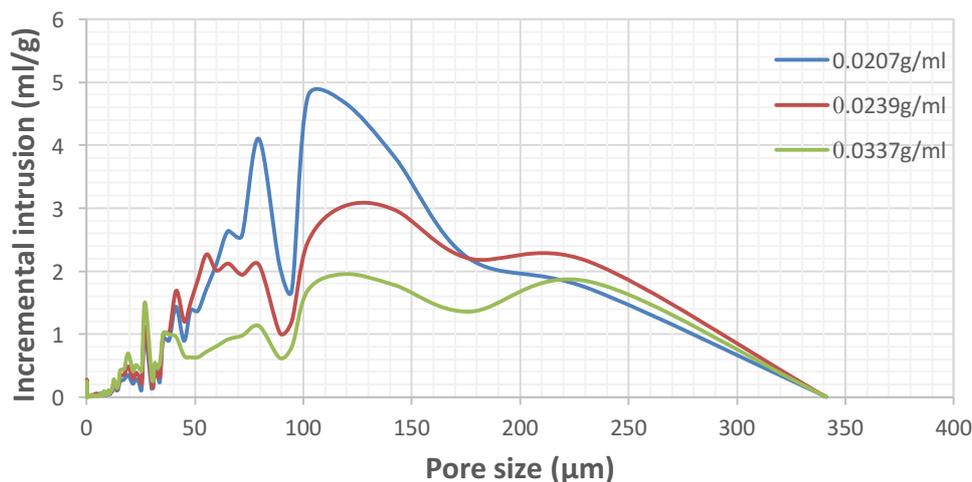


Figure 14 Pore size and distribution of aerogel as a function of the starting suspension density

The pore size distribution of the aerogels was measured by mercury porisimetry. It is shown in Figure 14 that majority of the pores are ranging from 50 to 250 microns. As expected, the structure is more porous with a decreasing density. This trend aligns with the observation in SEM images shown in Figure 13. Interestingly, the shape of the pore distribution curves is relatively similar for the three sets of samples. Pores with size over 200 µm are the same for the three curves likely due to that these large pores would be the defects on the surface as well as the gaps between the pieces of aerogel in the testing tube. All of the other smaller pores have a distribution that scaled with starting density of the suspension. In addition, majority of the pores lie between 70 µm to 150 µm. It is interesting to understand why the distribution scales with the starting density of suspension instead of shifting to the left with an increasing density. This could possibly be due to the way samples were frozen.

Freeze-drying techniques are efficient ways to produce interconnected porous structures. These methods use rapid cooling to produce thermodynamic instability within a system and cause phase separation. The solvent (water in this case) is removed by sublimation under vacuum leaving behind voids in the regions it previously occupied(Thomson, Wake et al. 1995). Common issues associated with these techniques are the low structural stability and generally weak mechanical properties of the fabricated materials(Ho, Kuo et al. 2004).

It was suspected that many of the small pores in the samples with a higher density (0.0337 g/ml) collapsed at the scaffold-air interface due to the interfacial tension caused by solvent evaporation. The bigger pores remained in the structure, and they are less in quantity than those samples with a lower density (0.0197 and 0.0239 g/ml), however, have a similar distribution pattern. Therefore, it appeared that the pore size distribution of all the samples scales with the starting density of the suspension instead of shifting to the left with an increasing density.

d. Contact angle measurement

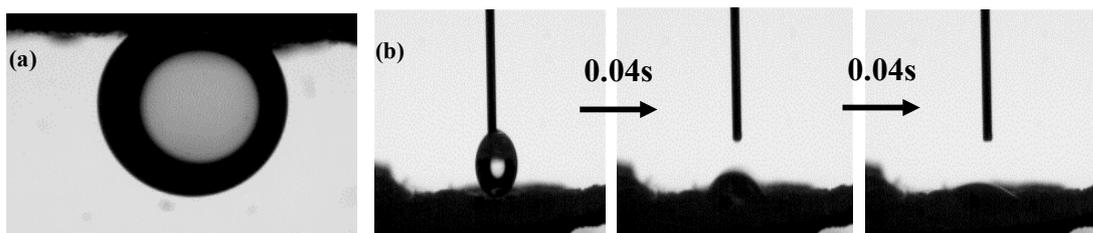


Figure 15 (a) Underwater oil wettability. (b) water wettability.

The wettability of water and mineral oil on the cellulose aerogel was also characterized. The contact angle is determined by both the properties of the water/oil and the surface of nanocellulose aerogel filter, and the cohesive and adhesive interactions between all the phases (gas, liquid and solids). On the other hand, capillary action occurs when a wetting liquid has a low contact angle with the solid surface. In the test, the oil contact angle ($156^{\circ} \pm 3^{\circ}$) was measured by placing 3 μL of oil on the surface of the cellulose aerogel underwater (Figure 15a). A larger contact angle indicates that cohesive forces are stronger than adhesive forces, in other words, the molecules of the oil tend to interact more with each other than with the aerogel filter. The capillary action thus did not occur so that the oil was able to sit on the surface of the aerogel. It suggested that the aerogel filter has a high oleophobicity underwater. On the contrary, the cellulose aerogel exhibits a high hydrophilicity with a contact angle of almost 0° for water in air (Figure 15b). The cohesive interactions of the water droplet were weaker than its adhesive interactions in this case, resulting an extremely small contact angle with the aerogel surface. Capillary forces pulled the water into the aerogel filter (it wetted the filter). In summary, the combination of a high oleophobicity and an excellent hydrophilicity is highly promising for oil-water separation as discussed in the literature review in previous chapter.

3.3.2 Pure water flux

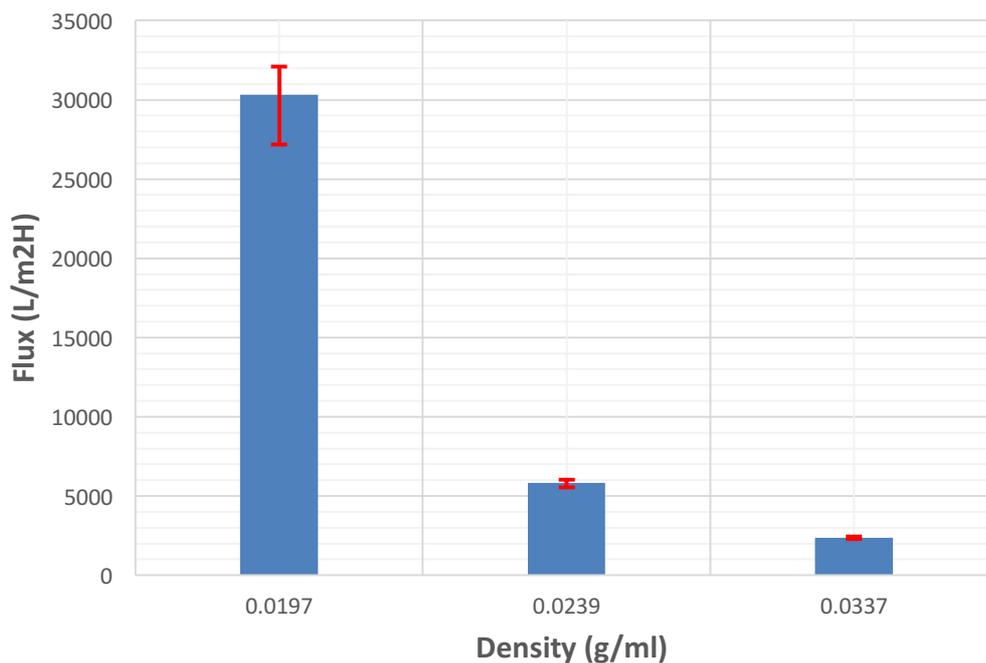


Figure 16 Flux for DI water filtration

It can be observed in Figure 16 that the pure water flux decreases dramatically with increasing density of the aerogel samples. The flux tested with samples of 0.0197 g/ml was ranging from around 27000 to 32000 L/m²h, while that with sample of 0.0337 g/ml only reduced to about 2300 L/m²h. This is due to the structure difference of samples as their density varied. This was expected based on the observation obtained in SEM images shown in Figure 13 and the pore distribution shown in Figure 14. Note that the data plotted were average value, and error bars indicate real range of results from all experiments. The full set of raw data is given in Appendix I.

3.3.3 Oil/water mixture



Figure 17 Experiment for oil/water mixture

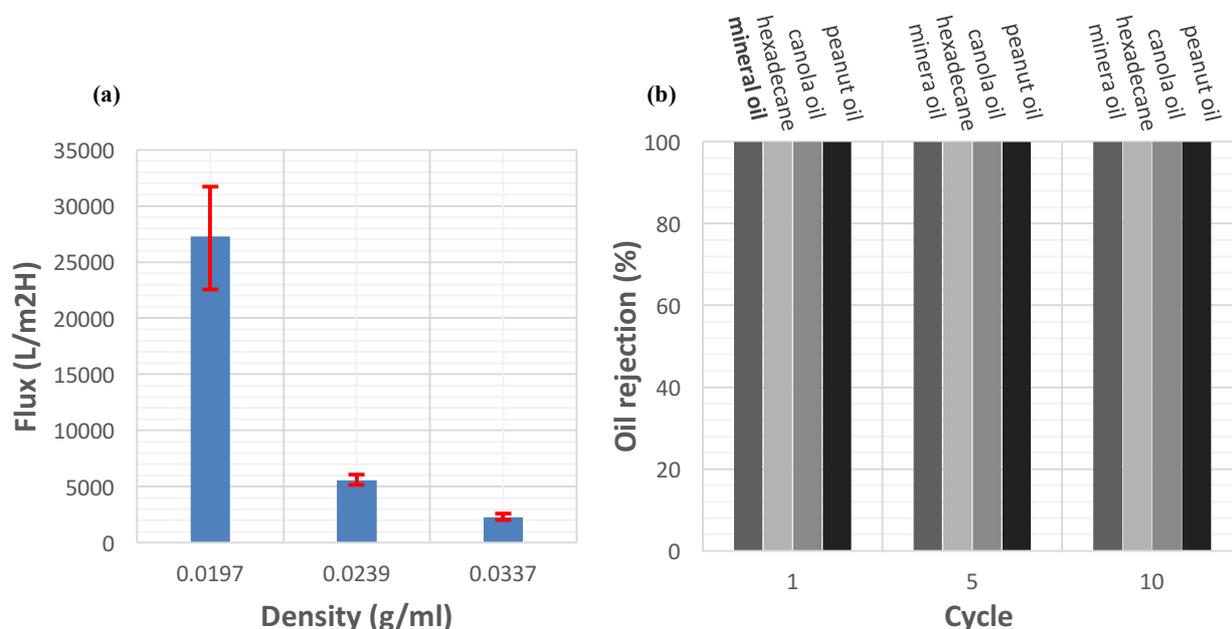


Figure 18 Water flux and separation efficiency for oil/water mixture separation

Using the method described previously, performance of the aerogel filter in term of flux and separation efficiency to oil water mixture was tested and quantified. Figure 17 shows the separation experiment with the oil-water mixture on the left and the result after the oil-water experiment on the right. Visually, oil (dyed in red) was retained on the top surface of the aerogel filter, while water was allowed to pass through freely. The quantitative results are shown in Figure 18. In terms of flux, the aerogel filter with a low density (0.0197 g/ml) yielded a large flux (about 27000 L/m²h) due to its more porous structure, while the one with a high density (0.0337 g/ml) resulted in a much lower flux (about 2200 L/m²h) as shown in Figure 18a. Note that the data plotted were average value, and error bars indicate real range of results from all experiments. The full set of raw data is given in Appendix

I. Four types of oil, namely mineral oil, hexadecane, canola oil and peanut oil were tested. All the prepared cellulose aerogels (with various density) could mostly achieve 100% rejection of all these oils, even after 10 cycles (Figure 18b). Due to the under-water oleophobicity, oil was supported by the water layer on the top surface of the pre-wetted aerogel and would not wet the surface; hence it was easy to be removed. After each washing in between cycles, the surface was visually checked for any observable staining from the red-dyed oil. No oil was ever observed. In addition, the video in the supplementary information in the published paper attached in Appendix I shows the washing process, where oil rolled straight off from the surface of the membrane due to its underwater-superoleophobicity. As compared to the pure water flux testing, the flux to oil/water mixture is slightly lower because the filtration pressure at the surface of aerogel was lower when filtering oil/water mixture than pure water. It is worth noting that due to the cross-linking by PAE, the cellulose aerogel possesses high wet strength and durability underwater and was readily able to be handled and cleaned without any noticeable issues.

3.3.4 Oil/water surfactant-free emulsion

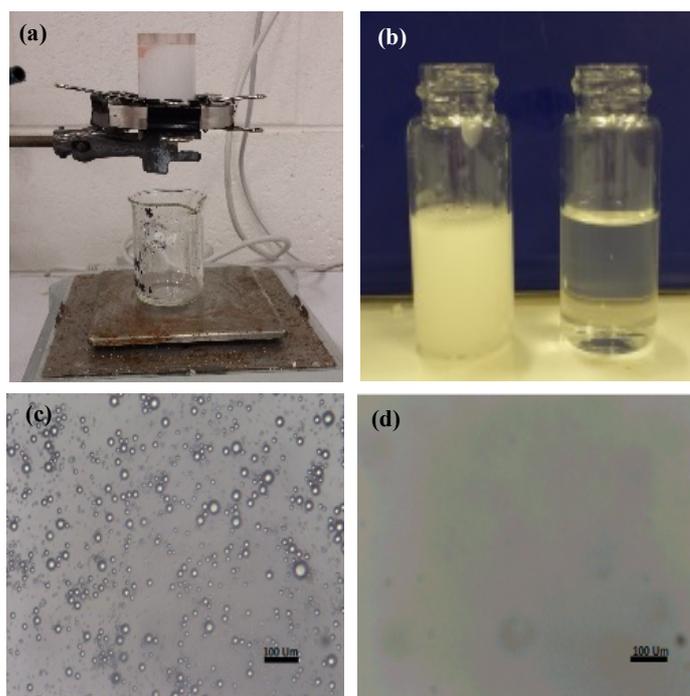


Figure 19 (a) Experimental set-up for oil/water separation testing. (b) Comparison between oil/water emulsion (left) and filtrate (right). (c) Microscopic image of emulsion. (d) Microscopic image of filtrate

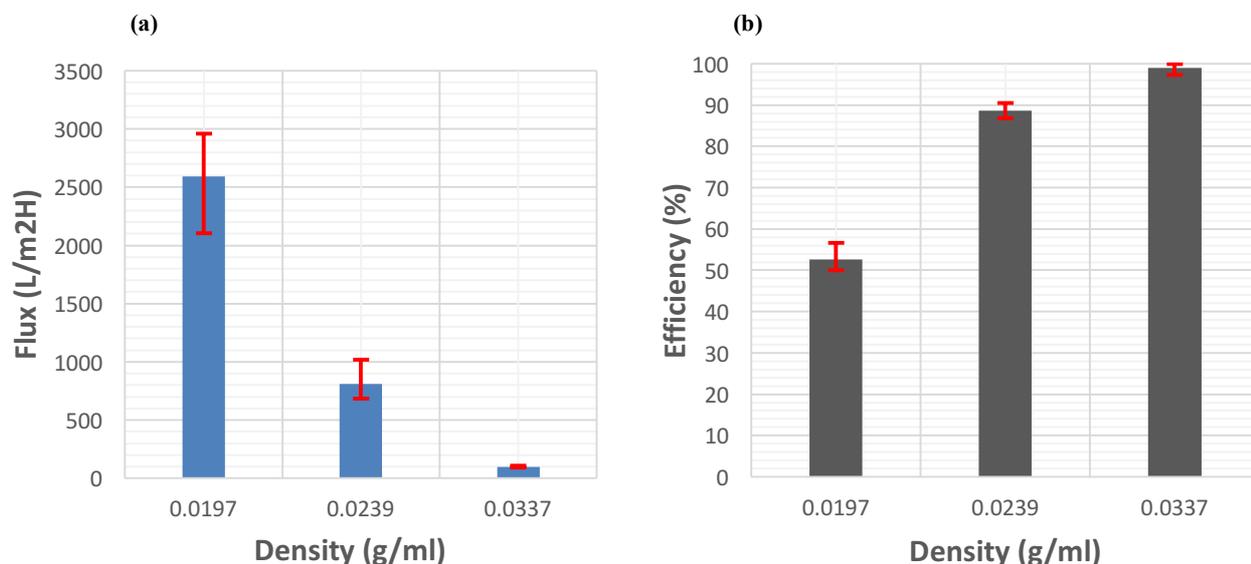


Figure 20 Water flux and separation efficiency for oil/water surfactant-free emulsion

The separation efficiency of the cellulose aerogel filter was further evaluated using oil/water surfactant-free emulsions. The experimental set-up of this testing was demonstrated in Figure 19a. Figure 19b shows the comparison between the oil/water emulsion (left) and the filtrate collected (right). The significant change in colour and light transmission between the two samples indicates the excellent separation efficiency. The microscope image shows that the oil/water emulsion contains a large amount of oil droplets of several microns in diameter (Figure 19c). In comparison, the filtrate collected barely contains any oil droplet (Figure 19 d). These results were obtained by carrying out experiments with aerogel samples of 0.0337 g/ml in density. The full set of raw data is given in Appendix I.

As shown in Figure 20, Aerogel with cellulose nanofiber concentration of 0.0197 g/ml achieved a flux of about 2500 L/m²h, but only an average of 52.9% oil rejection. This was due to its relatively loose pore structure. By contrast, the aerogel prepared with cellulose nanofiber concentration of 0.0337 g/ml had a much lower water flux (around 98 L/m²h), but an excellent oil rejection (98.7%) due to its more compact pore structure. Clearly, there is a trade-off between the flux and the oil rejection as the pore structure of the cellulose aerogel changes. Therefore, taking advantage of the tuneable pore structure, this type of cellulose aerogel can be tailored to separate oil droplets with various sizes from water while maximising fluid flux.

3.3.5 Oil/water surfactant-stabilised emulsion

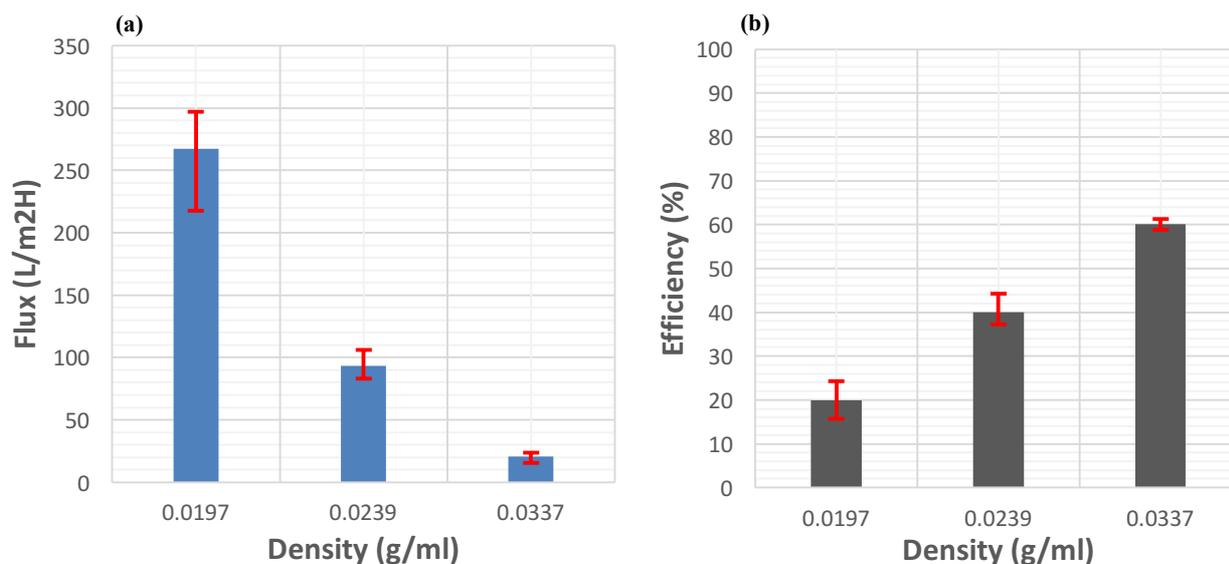


Figure 21 Water flux and separation efficiency for oil/water surfactant-stabilized emulsion

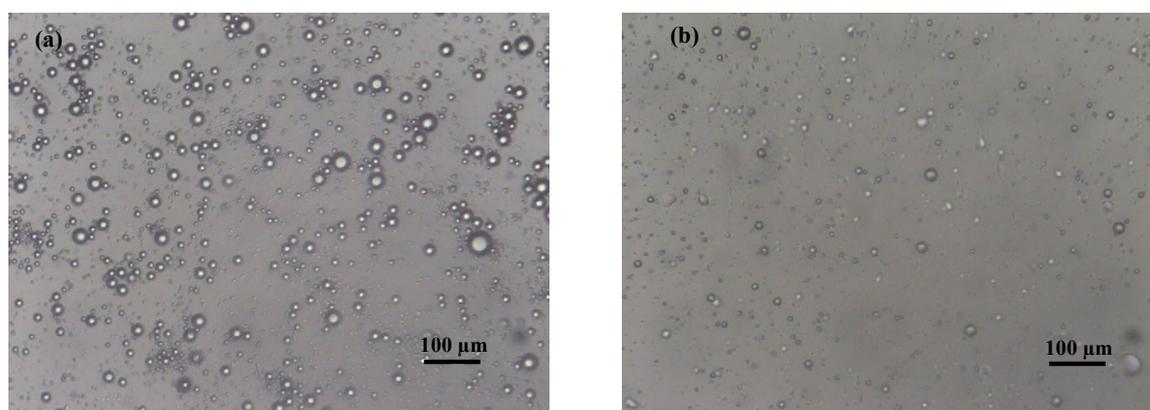


Figure 22 Comparison between oil droplets in surfactant-free emulsion (a) and surfactant-stabilized emulsion (b).

Similar testings were done on oil/water surfactant-stabilized emulsion. As it can be seen in Figure 21, the water flux for aerogel filter with 0.0197 was about 260 L/m²h, which was much lower than that (about 2500 L/m²h) when filtering oil/water the surfactant-free emulsion. On the other hand, similar trend can be observed for the separation efficiency; the highest efficiency value among the three samples was about 60%, which is also significantly lower than that (about 98%) when filtering the oil/water surfactant-free emulsion. These results suggested that the aerogel filter was much more prone to fouling with oil/water surfactant-stabilized emulsion, which has high stability and relatively strong interaction between oil droplets and smaller droplets. It was shown in Figure 22 that the majority of droplets in surfactant-stabilized emulsions have sizes only about a few microns, which is significantly smaller than those in surfactant-free emulsions. The flux has dropped dramatically (By around 85%) as compared to oil/water surfactant-free emulsion. Note that the data plotted were average value, and error bars indicate real range of results from all experiments. The full set of raw data is given in Appendix I.

3.3.6 Proposed mechanism of separation

Figure 23a shows the separation testing for oil/water emulsion after approximately half the original volume had been filtered. Surprisingly, the well-dispersed oil-in-water emulsion had developed a de-emulsified oil layer on top, as shown by light yellow colour appearing at the top. By contrast, the original emulsion remained stable and no separate layer was formed if left alone (Figure 23b) for equal amount of time. This indicates that the separation process by the aerogel filter de-emulsified the stable oil/water emulsion (Figure 23c). This may be attributed to the specific structure of the cellulose nanofibre aerogel. At the surface of the hydrated cellulose aerogel, small oil droplets do not wet the surface because of the hydration layer surrounding the nanofibres. Owing to the pothole-like surface structure of the cellulose aerogel (Figure 23d), the small oil droplets are trapped in the voids on the surface while the continuous phase (water) is passing through the walls of the voids. The flowing motion of the continuous phase eventually results in the accumulation of small oil droplets inside the void. The small droplets are then pulled together, coalescing to form a single droplet, large enough to rise out of the continuous phase (water) due to the increasing buoyancy force (Figure 23e). This mechanism is comparable to that of mechanical coalesces, in which small droplets are merged in to larger ones as they pass through several layers of filter media.

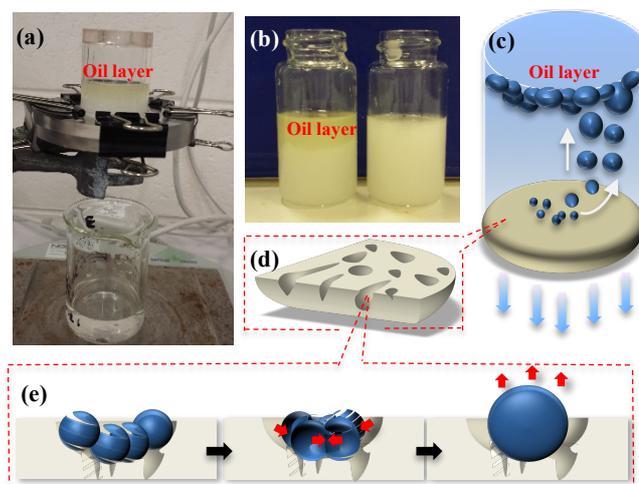


Figure 23 (a) Separation process running for 1.5 hrs since the beginning. Oil/water emulsion has turned into a layered mixture with the light yellow oil layer floating on top. (b) Comparison between two emulsions (both prepared at the same time); one was used for separation testing (left), while the other was left alone for equal amount of time (right). (c) Proposed schematic of the separation process. Droplets in blue are oil droplets. (d) Magnified version of a cellulose aerogel part. (e) Proposed schematic of small oil droplets coalescing in the void of the surface of the aerogel.

As it was suspected that the coalescence might be caused purely by surface contact, a small test was carried out where one side of the aerogel membrane was sealed, not allowing the emulsion to penetrate. The emulsion was agitated so that it had thorough contact with the membrane surface, and

it was found that the emulsion was not de-emulsified, which proved that the coalescence effect was not only a surface contact mechanism.

Based on the work by Burlutskiy (Burlutskiy and Turangan 2015) who performed a computational fluid dynamics study on oil-in-water dispersion in vertical pipe flows, small oil droplets experience a lift force perpendicular to the direction of the flow as shown in Figure 24. This shear lift originates from the inertia effects in the viscous flow around the droplets.

According to the study done by Ivanov, et al. (Ivanov, Danov et al. 1999), in an oil-in-water surfactant-free emulsion, two colliding oil droplets are kept apart by various interactions in between them. Many effects can contribute to the energy of interaction between these two droplets, such as Van der Waals interaction, electrostatic interaction, ionic correlation surface force, hydration repulsion, protrusion and steric interaction, and oscillatory structural force. The shear-lift force mentioned acts externally on both the droplets, counteracting these interactions. This results in the collision, hence the coalescence of the droplets.

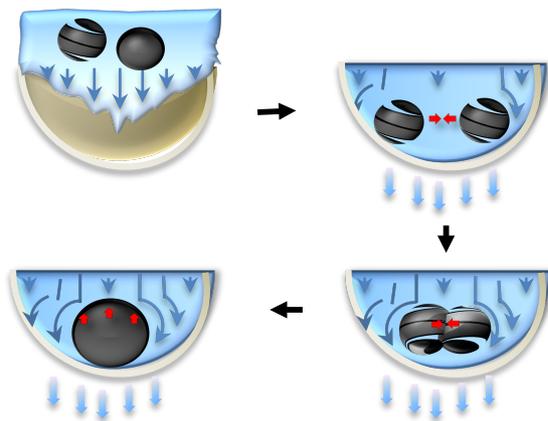


Figure 24 Scheme of the coalescence of oil droplets in the void of the aerogel filter surface

As described by Spicer (Pawar, Caggioni et al. 2012), the coalescence of two droplets is initiated when a liquid neck forms between them. The droplets being pulled together are then combined via flow of oil through the liquid neck. As the coalescence proceeds, the neck radius of the coalescing structure gradually increases, and the interfacial tension eventually drives it into a sphere droplet to achieve a minimization of the surface-to-volume ratio (Wu, Cubaud et al. 2004). The newly formed single droplet will have a larger diameter, which results in larger buoyancy force. Once the buoyancy force of the oil droplet is greater than the sum of drag and gravitational forces, the oil droplet will start floating upwards.

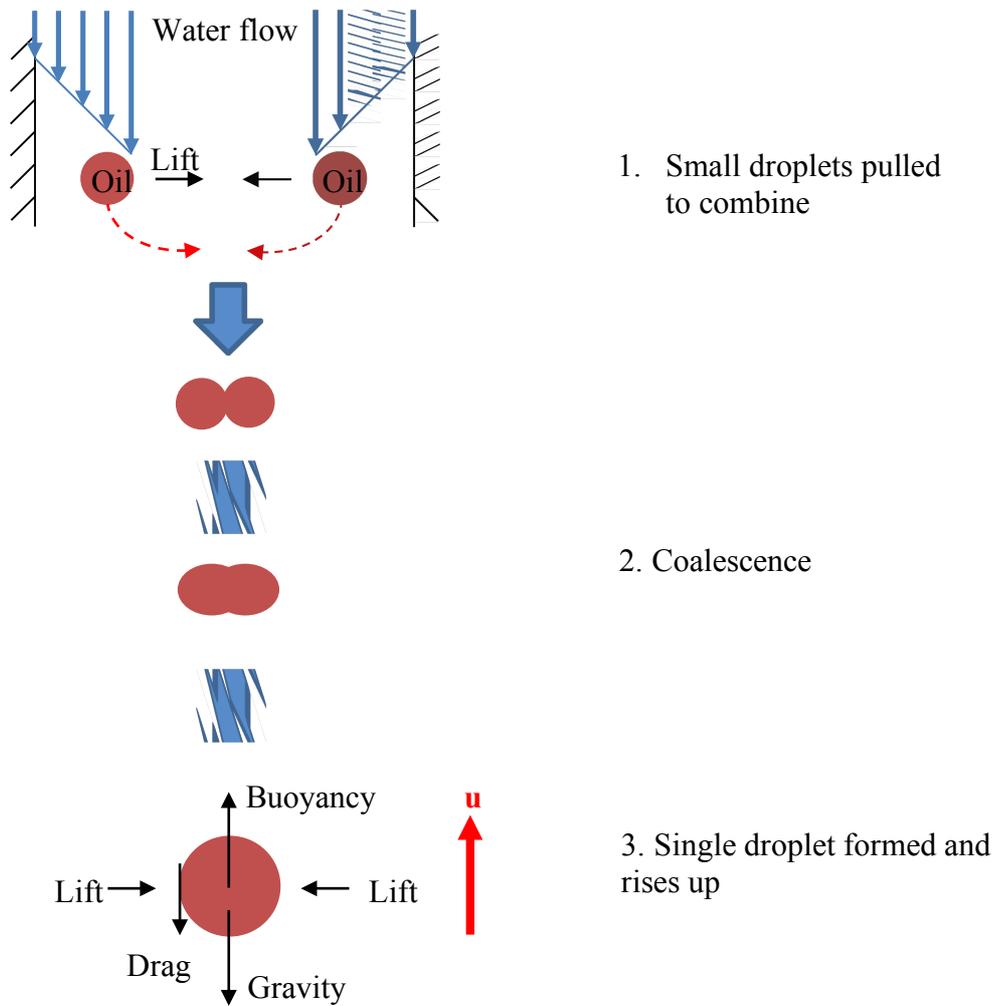


Figure 25 Proposed Mechanism

The mathematical model of the flow takes into account the aerodynamic drag, gravitational, buoyancy and shear-lift forces.

$$m_d \frac{d(U_d)}{dt} = F_{drag} + F_{grav} + F_{shear\ lift} \quad (2)$$

where m_d represents the individual oil droplet mass, t is time, U_d is the velocity of droplet, F_{drag} is the aerodynamic drag force, F_{grav} is gravitational/ buoyancy force and $F_{shear\ lift}$ is shear-lift force.

The experiment used DI water and canola oil, and their thermodynamic properties were: density equal to 998 kg/m^3 (water) and 920 kg/m^3 , viscosity equal to $0.993 \times 10^{-3} \text{ Pa s}$ (water, ρ) and $6.4 \times 10^{-2} \text{ Pa s}$ (canola oil, ρ_d). The oil-water interfacial tension is 20 mN/m . The velocity of fluid in vertical

direction U is 6.7×10^{-4} m/s (This is estimated from the initial flux in the surfactant-free emulsion flux testing with aerogel sample of 0.0337 g/ml in density).

Assumption:

1. The net shear-lift forces is 0, causing no horizontal movement of oil droplet.
2. Only forces in the vertical direction are considered
3. It is assumed that the droplet velocity $U_d = 0$; the coalesced oil droplet was static in the vertical direction before floating up

The drag force, F_{drag} can be defined as

$$F_{drag} = \frac{3}{4} \left(\frac{\rho}{\rho_d D_d} \right) m_d C_D (U - U_d) |U - U_d| \quad (3)$$

where ρ_d is dispersed phase density (oil droplets), D_d is the diameter of the droplet, C_D is the aerodynamic drag coefficient, the drag coefficient C_D is calculated by using the results provided in Clift, Grace and Weber (Clift, Grace et al. 2005).

*Calculation of drag coefficient C_D

$$Re = \frac{U D_H}{\nu} \quad (4)$$

Where D_H is the hydraulic diameter of the void, which is assumed to be a circular tube with a mean diameter of $180 \mu m$. ν is the kinematic viscosity of the fluid, which is $\nu = \mu/\rho$

$$Re = \frac{6.7 \times 10^{-4} \times 180 \times 10^{-6}}{0.993 \times 10^{-3} / 998} = 0.12$$

$$\text{For } 0.01 < Re < 20, C_D = \frac{24}{Re} [1 + 0.1315 Re^{(0.82 - 0.05w)}] \quad (5)$$

Where

$$w = \log_{10} Re$$

Therefore,

$$C_D = \frac{24}{0.12} [1 + 0.1315 \times 0.12^{(0.82 - 0.05 \times \log_{10} 0.12)}] = 204$$

Continue with Eq.10,

$$F_{drag} = \frac{3}{4} \left(\frac{998}{920D_d} \right) m_d \times 204 \times (6.7 \times 10^{-4})^2$$

The gravitational force is given by

$$F_{grav} = -m_d g \quad (6)$$

The buoyancy force is given by

$$F_{buoy} = -m_d g \frac{\rho}{\rho_d} \quad (7)$$

where g is the gravitational acceleration, which represents the buoyancy force impact into the flow.

$$F_{grav} + F_{buoy} = -m_d g \left(1 - \frac{\rho}{\rho_d} \right) = -m_d \times 9.81 \times \left(1 - \frac{998}{920} \right)$$

Therefore, $F_{grav} + F_{buoy} = F_{drag}$ is a critical point, where the coalesced oil droplet is about to rise because of the increasing buoyancy force as the droplet grows bigger via further coalescence. From Eq (6) (7), it could be calculated that $D_d = 89.6$ microns, when $F_{grav} = F_{drag}$. Hence, at a fluid velocity of 6.7×10^{-4} m/s, the minimum diameter required for a coalesced oil droplet to float upwards is about 89 microns.

Therefore, the minimum diameter required for a coalesced oil droplet to float upwards is about 89 μm . This means that coalescence of a number of the original droplets are needed to form oil droplets with large enough diameter to float.

3.3.7 Conclusion

In summary, we reported an aerogel filter made of bio-derived, renewable and environmental friendly cellulose nanofibres for an oil/water separation process. The aerogel can be easily fabricated on a large scale by freeze-drying cellulose suspension, followed by cross-linking with PAE. With the super-hydrophilic and underwater super-oleophobic properties, excellent wet strength and pothole-like surface structure, it allows excellent oil/water separation efficiency to not only oil/water mixture (100%, even after 10 cycles), but also oil/water surfactant-free emulsion (98.7% with the aerogel sample of 0.0337 g/ml in density). We also demonstrated that the pore structure of this aerogel could be easily engineered to fulfil the need of separating oil-in-water emulsion with various droplet sizes while achieving an optimal fluid flux. The aerogel filter also caused the transformation of stable oil/water emulsion to a de-emulsified mixture, which makes oil recovery easier. In addition, the separation was solely driven by gravitational force without any external power or additional facilities.

Based on the observation that an oil layer appeared on top of the emulsion over the course of the separation, a possible mechanism is proposed, showing that the 'pothole' surface structure causes small oil droplets to coalesce and form a bigger one large enough to float due to the increasing buoyancy force. Despite all the success, it was found that the aerogel filter could achieve a separation efficiency of only about 60% to oil/water surfactant-stabilized emulsion. This is likely due to the relative large pores in the aerogel structure, relatively small droplets size and strong bonds between the droplets. Modification needs to be made to further improve the selectivity of this aerogel filter. This will be discussed in the next chapter.

Chapter 4

4 Research Part 2: Cellulose sponge filter with double layers

4.1 Introduction

The under-water superoleophobic property of hydrophilic materials is due to the air or water trapped between the oil droplet and the solid surface (Hejazi and Nosonovsky 2011), the aerogel surface in this case. Like the aerogel filter we described in the previous chapter, underwater-superoleophobic materials cannot be wetted by oil once they are pre-wetted with water. Figure 26 (Wang, He et al. 2015) reveals the two schemes after the water phase permeated the sponge (pre-wetted): an oil layer supported by a thin water layer stored by the hydrophilic materials (Figure 26b); the oil layer cannot wet the hydrophilic materials and is supported by the air trapped in the holes (Figure 26a). According to Wang's research (Wang, He et al. 2015), under the effect of gravity, the breakthrough pressure of a membrane will decrease when the water is replaced by the air to the thin membrane with a low water retention rate, as shown Figure 26b.

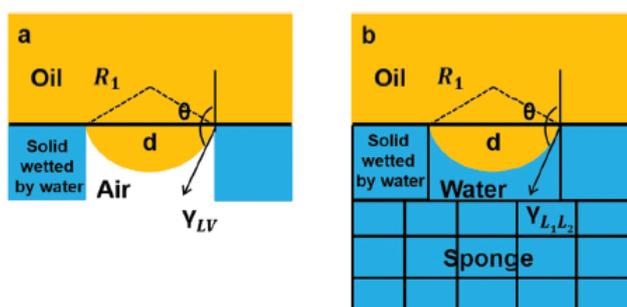


Figure 26 The two schemes of oil supported by air or water (a) the oil layer supported by an air layer. (b) the oil layer supported by a water layer (Wang, He et al. 2015).

The scheme in Figure 26b can be achieved by constructing a double-layer aerogel filter with a denser layer on top and a relatively loose structure as the base. When pre-wetting the aerogel filter, water absorbed in the base rises up, climbing the wall of the small voids in the top layer due to the capillary effect. Wang's group (Wang, He et al. 2015) has developed a nanocellulose aerogel with a double layer structure following this direction and showed promising results. However, the fabrication process was slightly complicated requiring a pore forming agent and reinforced fibre.

In this chapter, we aimed to develop a double-layer aerogel filter by filtering dilute MFC suspension through a single layer aerogel filter.

4.2 Methodology

4.2.1 Aerogel filter fabrication

Firstly, 15 g of wet MFC was weighed (MFC has water content of 75%). A measured amount of PAE (15% wt) was then weighed (0.05 g/g dry weight MFC) and dissolved into 50 mL of water. The MFC and PAE were mixed together with water to make up to 1.5 L because the minimum volume required in the disintegrator is 1.5 L. The mixture was then mixed thoroughly with a disintegrator (Messmer Disintegrator MK3C) for 15000 revolutions. After mixing, the mixtures were poured into 50 mL containers, forming suspensions that weight 15 g each to ensure a consistent size of sponge final products. These suspensions were then placed in an oven at 50 °C for 3 hours. This step was to shrink the pores in the structure of the product aerogel filter so that it would be suitable for the filtration of dilute MFC suspension when making the double-layer structure in the later steps. Note that this single layer membrane was different from the one fabricated in Chapter 3 due to the additional step. The containers were allowed to freeze in the freezer for 24 hours at -25 °C to maintain their porous structure. Lastly, they were freeze-dried in a freeze dryer for another 24 hours to remove all moisture in the sponges while maintaining their porous structure. The freeze-dried samples were then place in the oven for 3 hours at 120°C to promote crosslinking between MFC and PAE.

4.2.2 Second layer of aerogel fabrication

A series of experiments were conducted with different suspension concentrations and total fibre mass. Note that gsm, namely grammage is the mass per unit area. In our case, it refers to the amount of MFC in the dilute suspension per unit area of the filtration area (g/m²). The solids content or concentration, refers to the amount of MFC in the dilute suspension per unit mass of the whole suspension (g/g, or wt%). The solids content of MFC in the dilute suspension used in different experiments ranged from 0.027wt% to 0.432wt%, while the total mass of MFC was varied between 10 and 60 gsm where gsm stands for grams per square meter of the effective filter area, which was measured to have a diameter of 3.8 cm and an area of 1.134 x 10⁻³m². The full list of experiments completed is shown in Table 2.

Table 2 List of experiments

Experiment No.	Solids Content (wt%)	Grammage (gsm)
1	0.027	10
2	0.027	20
3	0.027	30
4	0.054	30
5	0.108	30

6	0.216	30
7	0.432	40
8	0.108	60
9	0.216	60

For each experiment, the required amount of MFC was weighed (MFC has water content of 75%) to achieve a certain solids content (solids content: weight of dry MFC added/total weight of the suspension). Then, the measured amount of PAE was weighed (0.05 g/g dry weight MFC) and added into 50ml of water. The MFC and PAE were mixed together with water to make up to 1.5 L because the minimum volume required in the disintegrator is 1.5 L. The mixture is then mixed in a disintegrator for 15000 revolutions. The aerogel was sandwiched within the filtration device as shown in Figure 27 below and pre-wetted before filtration to form the second layer.



Figure 27 Experiment Set-up for filtration procedure to form the second layer

To achieve the desired grammage, the amount of diluted MFC needed was determined by calculating the weight percentage of MFC needed for the desired gsm layer (MFC needed/total MFC added). For example, if $\frac{1}{4}$ of the total amount of MFC added was needed to form a 60 gsm layer, then $\frac{1}{4}$ of the total suspension (1.5 L) was used for the filtration. The weighted amount of diluted MFC suspension was poured onto the aerogel, being filtrated with the help of vacuum. The double layer aerogel was formed and was then placed in the freezer at $-26\text{ }^{\circ}\text{C}$ for 24 hours. Next, the samples were freeze-dried for another 24 hours. As a final step, the dry samples were then placed in the oven for 3 hours at $120\text{ }^{\circ}\text{C}$ to promote crosslinking between the MFC and PAE.

4.2.3 Performance testing

a. Flux testing

Same as Chapter 3, flux data was measured when using sample to filter pure DI water, oil/water mixture, oil/water surfactant-free emulsion and oil/water surfactant-stabilised emulsion, respectively. The procedures of fabricating mixtures and emulsions, and flux measurements are the same as those described in section 3.2.3. Except that the timeframe for this measurement is from 10 minutes to 20 minutes instead. Please refer to Appendix I for the raw data.

b. Separation efficiency

The procedures of measuring separation efficiency are the same as those described in section 3.2.3.

4.3 Results & Discussions

4.3.1 Characterization

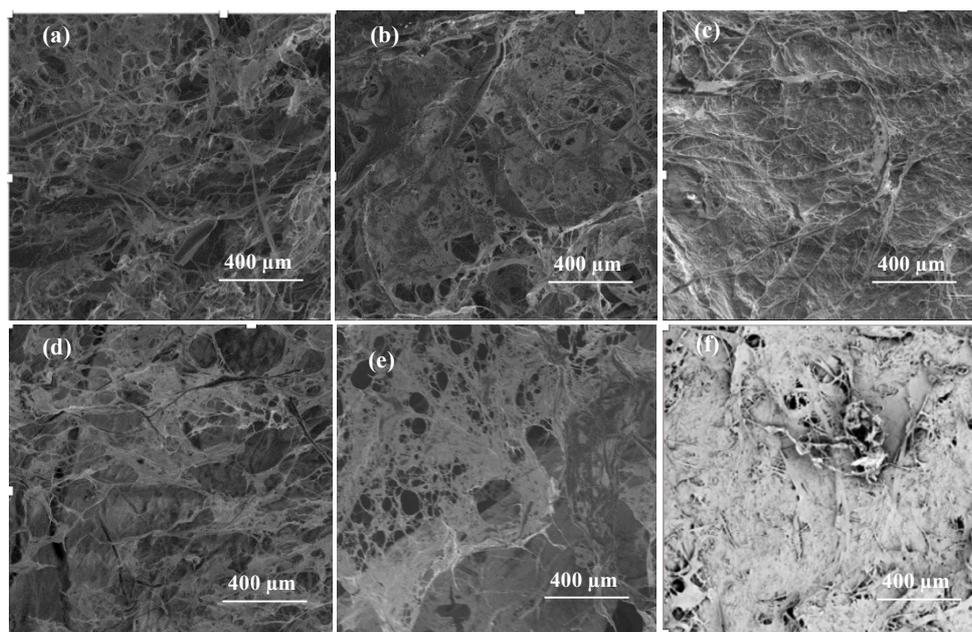


Figure 28 (a) SEM image of the single layer aerogel filter. (b) SEM image of the filter with a 10 gsm second layer (Ex.1). (c) SEM image of the filter with a 20 gsm second layer (Ex.2). (d) SEM image of the filter with a 30 gsm second layer (Ex.3). (e) SEM image of the filter with a 40 gsm second layer (Ex.7). (f) SEM image of the filter with a 60 gsm second layer (Ex.9). *' Ex.' Stands for experiment No. which are displayed in table 2.

As seen in Figure 28, the structure becomes denser with an increasing grammage of the second layer. As expected, compared to the single layer, the double-layer ones appeared to have an extra layer on top. However, this extra layer of samples with grammage ranging from 10 to 40 appeared to be quite loose with large pores. It may be due to that the MFC fibre used for filtration initially

penetrated the voids of the base layer until it is saturated. The remaining MFC fibres loosely deposit on top, forming a second layer with large pores.

Interestingly, the 60 gsm second layer appeared to be quite different as compared to the ones with lower grammage. The second layer had been tightly packed and filled in the voids of the base layer, making a much more compact structure. Following the logic above, with larger amount of MFC fibres used for the filtration, this may be due to that after filling the base layer, the remaining MFC fibres formed a denser layer instead of a loose layer on the surface. It was interesting to find out how these differences in structure would affect the flux and separation efficiency of the double layer aerogel, and whether it would be able to improve the separation efficiency to oil/water surfactant-stabilised emulsions.

4.3.2 Solids content on Water flux

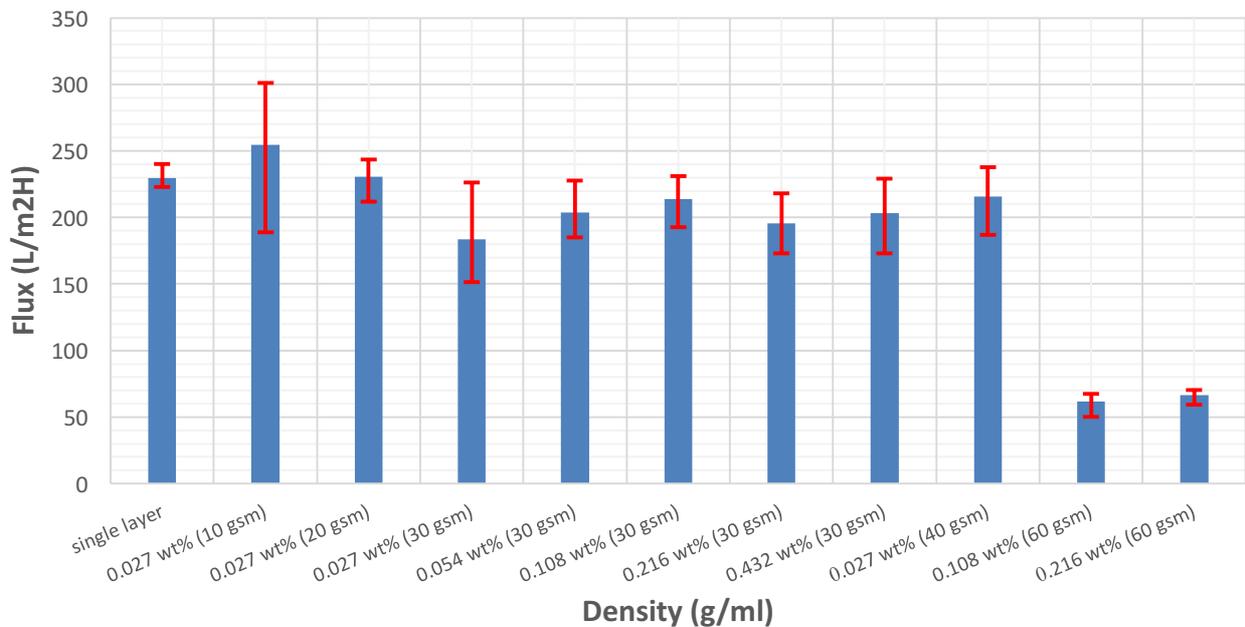


Figure 29 Flux of sponges with varied solids content and grammage when filtering DI water

Figure 29 shows the effect of concentration of the cellulose suspension for second layer on the water flux of the double layer aerogel sponge. Note that the data plotted were average value, and error bars indicate real range of results from all experiments. The full set of raw data is given in Appendix I. The concentration mentioned was changed by altering the water content in the cellulose suspension used to form the second layer via filtration. A set of 30 gsm samples with increasing concentration ranging from 0.027 wt% to 0.432 wt% are included as well as samples with different grammage formed at 0.27 wt% and two 60 gsm samples formed at consistencies of 0.108 and 0.216 wt%. It was observed that the flux of all these samples, except the two 60 gsm samples were averaging about 210

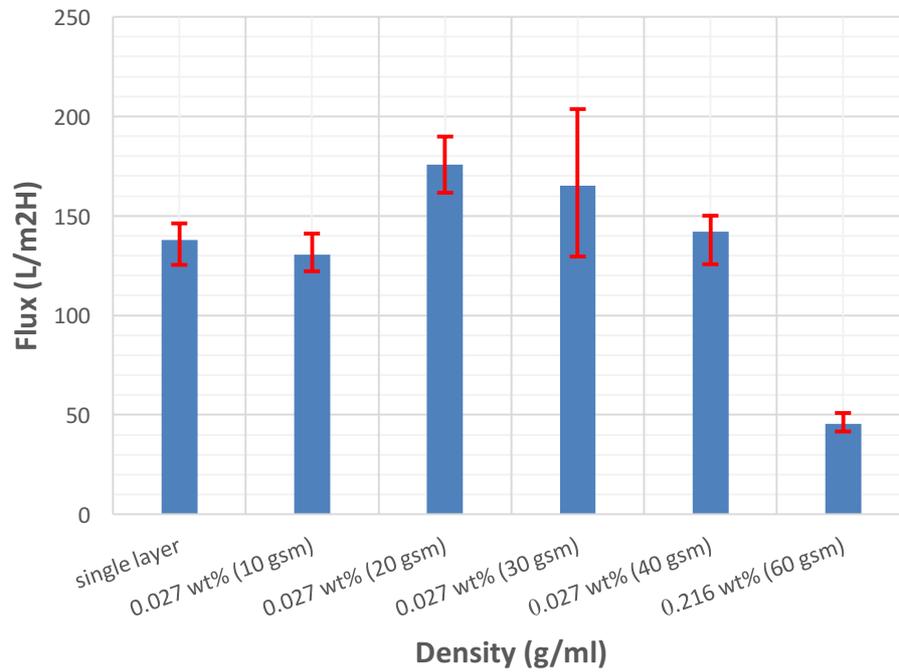
Lm^2h and this is similar to the single layer sample (left most data set in Figure 29). This means that, the flux performance was not affected significantly by the variation in solids content of the cellulose suspension that constructs the second layer, except when the second layer grammage reached 60 gsm. Furthermore, the variation of flux for second layer ranging from 10 to 40 gsm is therefore a result of inconsistency of structures in the base layer. This inconsistency was induced from the manufacturing process of hand-made base layer at lab-scale.

It had been expected that changing the solids content would have changed the performance by forming a denser second layer on the surface. According to Varanasi's research (Varanasi, He et al. 2013), the gel-point, the lowest solids content at which the fibres form a continuous network, of this MFC sample was approximately 0.25wt%. However, no change in performance was observed when solids content was increased above this gel point. This could be due to the fibre network not being retained on the surface because of the relatively large surface pores. The nanofibres have possibly adhered to the aerogel walls or even passing through.

On the other hand, the increase in grammage up to 40gsm of the second layer too has little effect on the water flux. Only when the grammage was increased to 60 gsm, there was a change in water flux observed. For 60 gsm second layer coated samples with concentration in both 0.108 wt% and 0.216 wt%, the water flux dropped more than 70% of that of other samples with lower grammages, averaging around $63 \text{ Lm}^2\text{h}$. This meets the expectation that 60 gsm would result in a significant drop in water flux due to much more compact surface pore structures, which was an observation from the SEM images shown previously in Figure 28.

4.3.3 Oil/water mixture & Oil/water surfactant-free emulsion

(a)



(b)

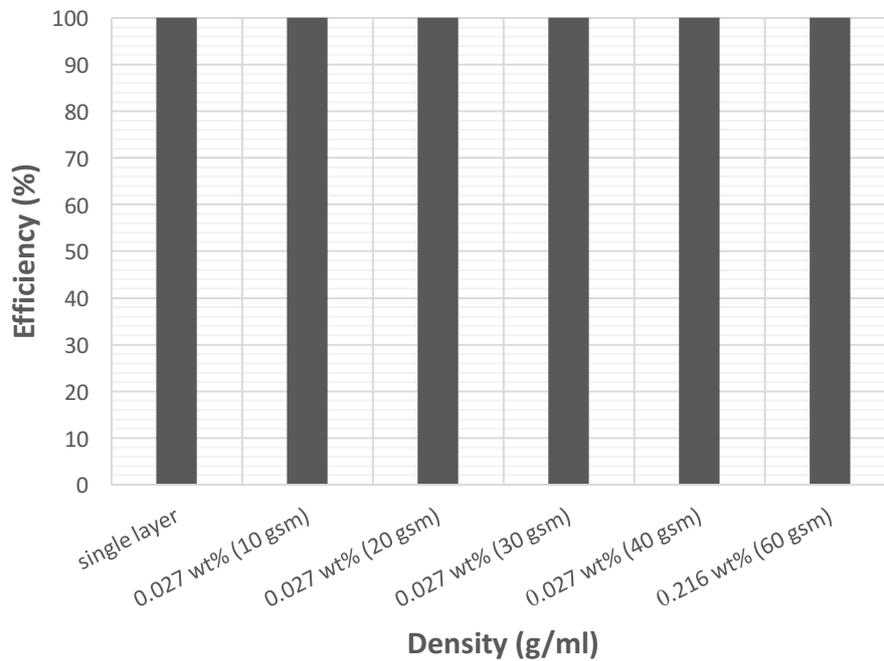


Figure 30 Water flux and separation efficiency for separating oil/water mixture

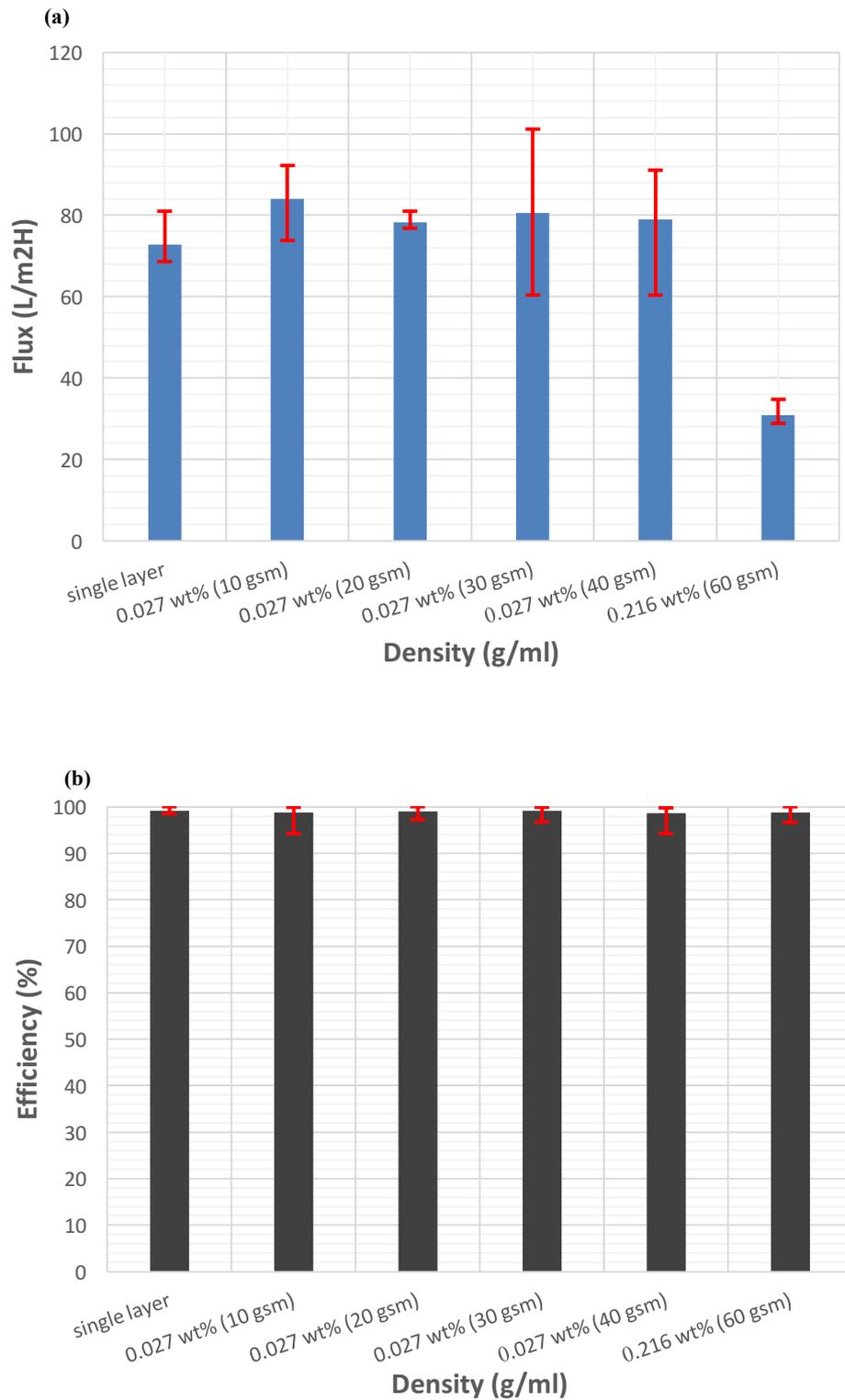


Figure 31 Water flux and separation efficiency for oil/water surfactant-free emulsion

Figure 30 shows the measurements of water flux and separation efficiency when separating oil/water mixture by aerogel samples with increasing gammage (ranging from 0 gsm to 60 gsm) in the second layer. Figure 31 shows the measurements of water flux and separation efficiency when

separating oil/water surfactant-free emulsion by aerogel samples with increasing grammage (ranging from 0 gsm to 60 gsm) in the second layer. The full set of raw data is given in Appendix I.

The results in Figure 30 & Figure 31 suggested that the increasing grammage in the second layer (from 10 gsm to 40 gsm) did not result in a lower flux nor higher efficiency in both oil/water surfactant-free mixture and oil/water emulsion separation. The flux over the course of oil/water mixture separation was roughly about 150 L/m²h for all the samples, regardless of the addition of second layer. Similar trend could be observed for oil/water surfactant-free emulsion with an average flux estimated about 78 L/m²h. It was found that the water flux has dropped by about 60% when separating oil/water surfactant-free emulsion as compared to that for pure water shown in Figure 29. This was because that oil droplets in the emulsion tended to coagulate in the voids of the aerogel surface, limiting access for water to pass through. In addition, there was minimal effect with the addition of the second layer on the already high separation efficiency.

Interestingly, a significant drop in water flux was observed on samples with 60 gsm in the second layer. It dropped from 150 L/m²h to 45 L/m²h for oil/water mixture, and similarly from 78 L/m²h to 30 L/m²h for oil/water surfactant-free emulsion. This indicated that 60 gsm in the second layer greatly minimised the surface pore size of the aerogel, and hence resulted in a potentially higher selectivity.

In summary, the results shown in the separation of both oil/water mixture and oil/water surfactant-free emulsion indicates that the addition second layer did not meet the expectation; the second layer was expected to create a dense layer (surface with smaller pores) on top of the single layer sponge, improving its selectivity against smaller oil droplets. This result aligns with the observation in SEM images shown in Figure 28. The second layer of samples with grammage ranging from 10 to 40 appeared to be quite loose with large pores. It may be due to that the MFC in the dilute suspension form a loose structure on top of the base layer, which would not help improve the selectivity of the aerogel filter. The ultimate goal was to use this second layer sponge to separate oil/water surfactant-stabilized emulsion. Therefore, the second layer with grammage ranging from 10 g/m² to 40 g/m² did not seem promising. On the other hand, second layer with 60 gsm showed great potential as it resulted in a large drop in water flux, making it more likely to separate surfactant-stabilized emulsion.

4.3.4 Oil/water surfactant-stabilized emulsion

Samples with 60 gsm second layer have demonstrated low water flux, indicating potentially improved selectivity in separating oil/water surfactant-stabilized emulsion as compared to the single layer aerogel as well as the double-layer aerogels with second layer of low grammage. Therefore,

this section shows a comparison between 60 gm second layer and 30 gm second layer on the separation of oil/water surfactant-stabilized emulsion.

a. Separation efficiency (60 gm VS 30 gm)

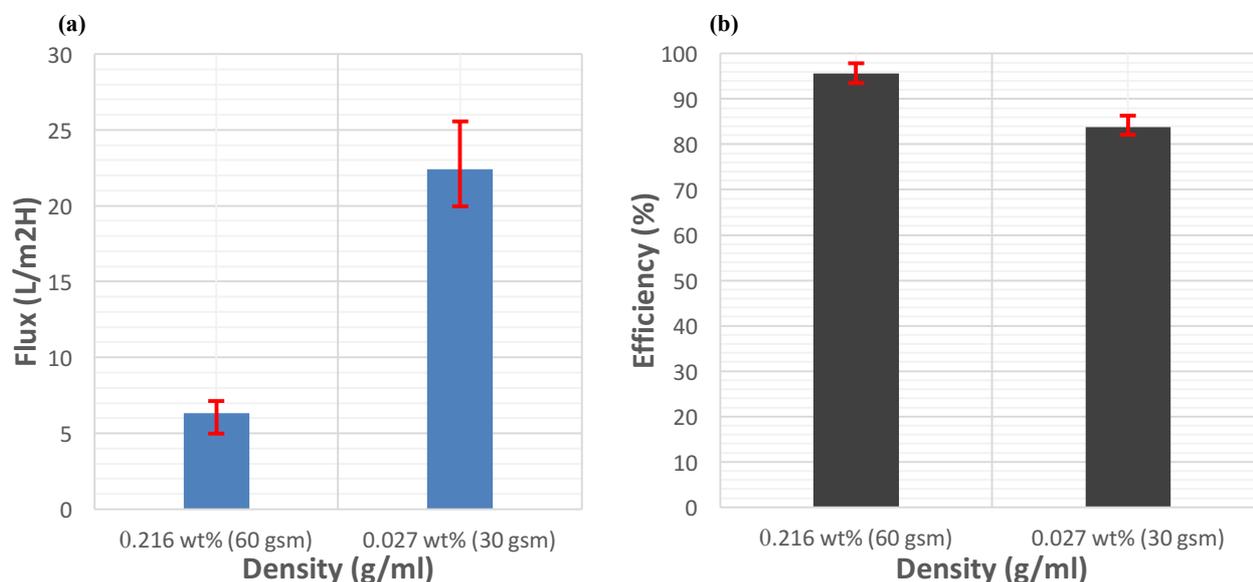


Figure 32 Performance comparison between 60 gm and 30 gm in terms of flux and separation efficiency for oil/water surfactant-stabilized emulsion

Results in Figure 32 show that with a 60 GSM second layer, the double-layer aerogel was able to achieve an improved separation efficiency of ~96%. The separation efficiency value is comparable to reports of above 99% using membranes made of cellulose, however, the flux is much lower (6.3 L/m²h) compared to those reported ones (89 L/m²h and 91 L/m²h)(Rohrbach, Li et al. 2014, Wang, He et al. 2015). In addition, these results are consistent with the SEM images shown in Figure 28 and the water, oil-water mixture and surfactant free flux data shown in Figure 29, Figure 30 and Figure 31, respectively. These figures show that only the 60 gm extra layer has substantially consolidated the sheet surface, reducing the pore size and therefore decreasing the flux. It is clear that only by reducing the pore size has it then been possible to increase the separation efficiency. As mentioned previously in Figure 22, droplet size in surfactant-stabilized emulsion (a few microns) is smaller than that in surfactant-free emulsion (8-40 microns). Smaller pores in the aerogel structures would restrict the penetration of oil droplets more effectively; hence result in a higher separation efficiency.

b. Flux recovery (60 gsm VS 30 gsm)

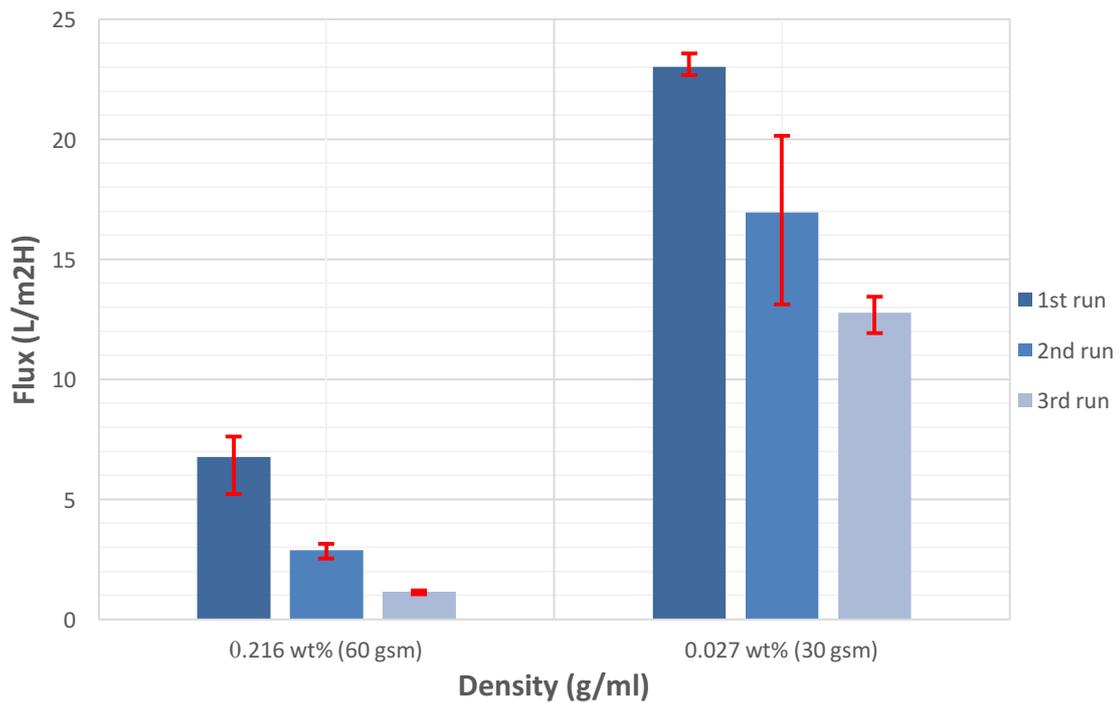


Figure 33 Comparison between 60 gsm and 30 gsm in recyclability in flux

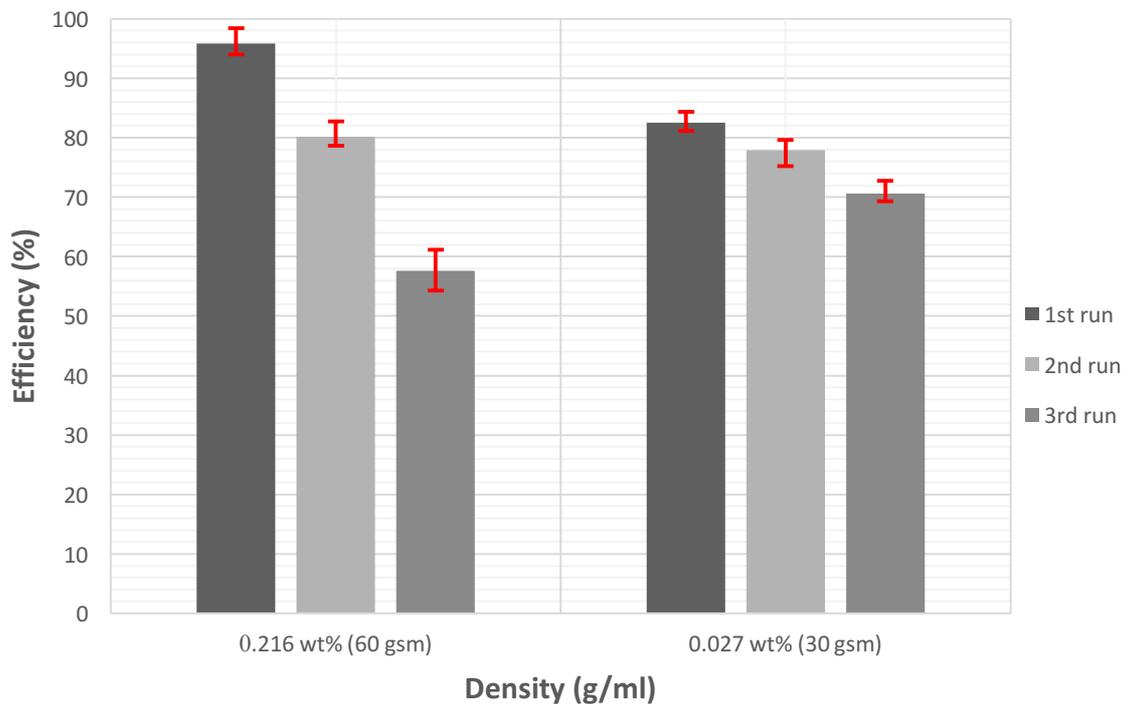


Figure 34 Comparison between 60 gsm and 30 gsm in recyclability in separation efficiency

The flex recovery data in Figure 33 & Figure 34 show that while the addition of the 60 gsm second layer has improved the separation efficiency in the first cycle, this has been at the expense of the performance in subsequent cycles as flux decreased from 6.8 L/m²h to 1 L/m²h after two cycles,

which was more than 80% drop. Similarly, its separation efficiency decreases dramatically, dropping from 96% down to 58%. The full set of raw data is given in Appendix I. This poorer performance resulted from the fact that second layer of 60 gsm is much more prone to clogging due to its smaller surface pore size.

As mentioned in the previous chapter, oil droplets in surfactant-stabilized emulsion have strong interaction between them, resisting external force that break them apart or cause them to coalesce. Over the course of separation, unlike oil/water surfactant-free emulsion, there was no oil layer separated out and floated on top for oil/water surfactant-stabilized emulsion. It was suspected that small oil droplets clogged up the surface pore structures of the double-layer cellulose aerogel, the bond between droplets were not broken and still sticking together. Water was pushed (because water has a lower breakthrough pressure than oil) through the gaps in the voids filled with oil droplets due to the filtration pressure at the surface.

The cellulose double layer sponge developed by Wang's group (Wang, He et al. 2015) could reportedly achieve a water flux of 91 L/m²h when separating oil/water surfactant-stabilized emulsion with a separation efficiency of 99.4%. Whereas the cellulose aerogel developed in our research could only achieve a water flux of 6.7 L/m²h and a separation efficiency of 96% under similar experimental conditions. This could be resulted from the inconsistency in manufacturing the aerogel samples, which do not have desirably uniform surface structure and pore sizes. In Wang's research, pore-forming agent was distributed uniformly in the starting suspension when fabricating the second layers, which would likely to result in more uniform pore structures.

4.3.5 Conclusion

A second layer was coated onto the single layer cellulose aerogel by filtration to produce a double-layer aerogel in order to achieve the separation of oil/water surfactant-stabilized emulsion. A series of experiments was conducted to examine the effect on the aerogel by varying two key parameters: the grammage of the second layer and concentration in the cellulose suspension used for the second layer formation. For the two-layer structure, the flux only decreased and separation increased when the grammage of the second layer was increased to 60 gsm while those samples with second layer grammage ranging from 10 to 40 gsm had the same performance as the single layer aerogel. For the conditions tested here, the concentration in cellulose suspension for the second layer formation was found to have no impact on improving the single layer aerogel. While the samples with a second layer grammage of 60 gsm showed significant improvement in terms of separating oil/water surfactant-stabilized emulsion (96%), for the first cycle, the separation efficiency and flux deteriorated rapidly with subsequent cycles. This was likely due to its relatively narrower pore size, which resulted in higher tendency of clogging. With only a slight improvement in terms of separation

efficiency and a significant sacrifice in flux, it was concluded that the addition of a second layer to the original aerogel was not a feasible method to improve the performance in separating surfactant stabilised oil-water emulsions. Therefore, alternatives should be considered; such as plasma surface modification or grafting.

Chapter 5

5 Conclusion

This research project aimed to develop a novel filter membrane for oil/water separation application. The choice of conducting research in membrane technology was due to its advantages such as high-energy efficiency, low cost, etc. over other existing technologies. More importantly, this research also aimed to address some of the issues such as use of harmful chemicals, difficulty in separating emulsion and secondary pollution during disposal, which are associated with the current research advances in membrane technology for this application.

We have successfully developed a cellulose nanofibre aerogel filter with tuneable pore structure exhibiting super-hydrophilic and underwater-super-oleophobic behaviours. This was synthesised by freeze-drying a suspension of cellulose nanofibres mixed with polyamideamine-epichlorohydrin (PAE), followed by heating to product cross-linking between cellulose fibres and the PAE. The prepared aerogel filter showed excellent oil/water separation efficiency for both oil/water mixtures (100%, even after 10 cycles), and oil/water surfactant-free emulsion (98.6%), driven solely by gravity. In addition, the specific structure can de-emulsify oil/water surfactant-free emulsion.

However, the aerogel filter was still faced with difficulties in separating oil/water surfactant-stabilized emulsion due to its relatively large pores within and on the surface of the structure. Therefore, a modification was needed to address this difficulty. A second layer was coated onto the single layer cellulose aerogel by filtration to produce a double-layer aerogel filter in order to achieve the separation of oil/water surfactant-stabilized emulsion. Diluted nanocellulose suspension was filtered through the single layer aerogel membrane filter. This was to create a relatively dense top layer, which could improve its selectivity to oil/water surfactant-stabilized and to achieve better oleophobicity by drawing water from the loose layer at the bottom due to capillary effect.

As compared to the single-layer aerogel, this double-layer aerogel demonstrated improved performance due to its higher selectivity, achieving a 96% separation efficiency in separating oil/water stabilized emulsion. Although the double layer nanocellulose aerogel showed improvement in terms of separation efficiency, it also showed a significant sacrifice in flux and recyclability due to clogging of the surface pores. Therefore, alternative surface modification treatment to achieve oleophobicity should be considered and explored.

Chapter 6

6 *Future work*

The single layer cellulose aerogel could separate oil/water mixture and oil/water surfactant-free emulsion with a high efficiency, and however, a relatively low flux as compared to some of the cellulosic membrane materials (Rohrbach, Li et al. 2014, Fan, Song et al. 2015, Wang, He et al. 2015) developed in other recent studies due to the high thickness. It is a trade-off not only between flux and thickness, but also between strength and thickness. Therefore, more studies should be conducted to optimize this aerogel to achieve a better overall performance. In addition, the wet strength was not quantified. It would be useful to prove the improved wet strength by the crosslinking between the MFC and PAE in a scientific way. It is also important to consider the possibility to scale up the aerogel for larger industrial applications. In the current production process at lab-scale, the method used to remove water when fabricating the aerogel to maintain its porous structure was freeze-drying, which would be costly for a large-scale production. A more cost-effective alternative should be considered to make this aerogel more competitive economically such as solvent exchange method.

The double layer cellulose aerogel with 60 gsm second layer coating showed improvement in terms of separation efficiency for the surfactant stabilized emulsion but a significant sacrifice in flux and recyclability due to clogging. Therefore, an alternative surface modification treatment to achieve oleophobicity should be considered and explored. Bio-inspired superoleophobic materials such as chitosan (Zhang, Lu et al. 2013, Yang, Song et al. 2014) could be potentially used for the second layer coating to improve the oleophobicity of this aerogel. In addition, construction of macrottextures on the surface could help induce superoleophobic behaviour with the two most common structure: overhang structure (Herminghaus 2000, Cao, Cao et al. 2008) and re-entrant structure (Tuteja, Choi et al. 2008).

Lastly, the oil used in this research is pure oil, which is very different from the oily wastewater produced from industries in the real situation. In such cases, the viscosity and high density of the oil would weaken the separation ability and efficiency of the surfaces substantially. The fouling of the filter membrane by these heavy oils can also be a serious problem, since it can easily damage the pore structure of the membrane, including its substrate and nanotexture of the coating. Therefore, future studies may aim towards the development of mechanically stable filter membrane that not only can separate pure oil/water emulsion, but also true oily wastewater from the industries, especially those with heavy oils.

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Acknowledgements

I offer my sincere gratitude and appreciation to my both of supervisors Dr. Warren Batchelor and Dr. Xiwang Zhang for their insightful and patient guidance during my entire candidature. They encouraged me to develop as an independent researcher with critical thinking and strong problem solving skills. They often helped me to realise my own mistakes and improve by learning from these mistakes. I cannot thank them enough for being a strong support behind me throughout this whole journey, which would have been a tough one.

I would like to acknowledge the use of facilities in Monash Centre for Electron Microscopy (MCEM). We would like to acknowledge financial support from the Australian Research Council, Australian Paper, Carter Holt Harvey, Circa, Norske Skog and Visy through the Industry Transformation Research Hub grant IH130100016. Zhiyong He would like to acknowledge MGS and FEIPRS scholarships from Monash University.

It has been a privilege working at Australia Paper and Pulp Institute (APPI), Department of Chemical Engineering. I would like to thank my colleagues Scot Sharman, Jielong Su, Praveena Raj, Uthpala Garusinghe, Rosiana Lestiani, Thilina Gunawardhana, Llyza Mendoza, Azadeh Nilqaz, Natasha Yeow, Whuilyn Then, Janette Lehaney, Heather McIlesh. Their help and support along the way has made this journey smooth and enjoyable. I would like to acknowledge the support of the administrative staff and the technical staff in Department of Chemical Engineering, particularly Kim Phu, Lilyanne Price, Jill Crisfield, Harry Bouwmeester.

I am grateful for the financial support of Monash University through APA scholarship and Engineering Faculty for FIPRS scholarship.

Lastly, I would like to thank my family. They have been supportive, standing by my side through all the ups and downs. I could not have finish this milestone without them.

Appendix I

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Single layer

Water flux (DI water)

0.0197 g/ml

1st batch

Time (s)		1.00	2.00	3.00	4.00	5.00
Weight (g)	#1	8.01	14.77	20.42	25.71	29.87
	#2	7.98	14.32	20.66	26.88	29.92
	#3	5.56	13.98	20.31	25.92	29.84
Average (g)		7.18	14.36	20.46	26.17	29.88
<u>2nd batch</u>						
Time (s)	-	1.00	2.00	3.00	4.00	5.00
Weight (g)	#1	6.24	13.25	19.24	24.22	29.16
	#2	6.84	14.12	20.21	25.34	29.56
	#3	5.42	12.33	18.81	24.32	29.03
Average (g)		6.17	13.23	19.42	24.63	29.25
<u>3rd batch</u>						
Time (s)	-	1.00	2.00	3.00	4.00	5.00
Weight (g)	#1	7.21	13.65	19.23	25.03	29.13
	#2	5.69	12.24	18.50	24.51	29.04
	#3	5.19	10.42	16.89	21.81	28.01
Average (g)		6.03	12.10	18.21	23.78	28.73

0.0239g/ml

1st batch

Time (s)		5.00	10.00	15.00	20.00	25.00	30.00	35.00	40.00	45.00	50.00
Weight (g)	#1	6.95	13.34	17.55	21.40	24.03	26.01	27.71	28.34	29.02	29.34
	#2	6.11	12.98	16.34	19.78	23.77	24.98	26.35	27.80	28.34	29.14
	#3	6.53	13.12	17.80	21.00	23.83	25.98	27.98	28.66	29.39	29.06
Average (g)		6.53	13.15	17.23	20.73	23.88	25.66	27.35	28.27	28.92	29.18
<u>2nd batch</u>	-										
Time (s)		5.00	10.00	15.00	20.00	25.00	30.00	35.00	40.00	45.00	50.00
Weight (g)	#1	6.01	12.68	16.34	20.45	23.29	24.56	26.12	27.54	28.50	29.63
	#2	5.99	11.02	15.30	19.95	22.95	24.12	25.97	27.04	28.40	29.29
	#3	6.38	13.33	16.55	19.02	23.97	25.86	27.30	28.66	29.29	29.71
Average (g)		6.13	12.34	16.06	19.81	23.40	24.85	26.46	27.75	28.73	29.54
<u>3rd batch</u>	-										
Time (s)		5.00	10.00	15.00	20.00	25.00	30.00	35.00	40.00	45.00	50.00
Weight (g)	#1	6.88	13.19	17.42	20.79	23.80	25.71	27.04	28.81	28.95	29.71
	#2	7.01	14.01	16.24	20.55	23.12	24.60	26.82	28.01	28.77	29.56
	#3	5.98	12.87	16.30	18.21	22.89	24.47	26.18	27.51	28.41	29.26
Average (g)		6.62	13.36	16.65	19.85	23.27	24.93	26.68	28.11	28.71	29.51

0.0337 g/ml

1st batch

Time (s)		10.00	20.00	30.00	40.00	50.00	60.00	70.00	80.00	90.00	100.00
Weight (g)	#1	5.10	10.94	16.03	20.12	23.34	25.48	26.67	27.42	28.33	29.02
	#2	5.56	11.04	16.13	21.07	23.31	25.07	27.61	28.19	29.66	29.77
	#3	6.01	11.12	16.10	21.08	24.91	26.02	27.08	28.39	29.01	29.03
Average (g)		5.56	11.03	16.09	20.76	23.85	25.52	27.12	28.00	29.00	29.27
<u>2nd batch</u>	-										
Time (s)		10.00	20.00	30.00	40.00	50.00	60.00	70.00	80.00	90.00	100.00
Weight (g)	#1	4.85	9.94	14.60	19.44	23.23	24.96	26.65	27.91	28.61	29.84
	#2	5.00	10.20	14.76	19.87	23.01	24.78	26.41	27.99	28.70	29.30
	#3	5.33	10.27	15.45	20.06	23.14	25.66	26.77	28.91	29.06	29.77
Average (g)		5.06	10.14	14.94	19.79	23.13	25.13	26.61	28.27	28.79	29.64
<u>3rd batch</u>	-										
Time (s)		10.00	20.00	30.00	40.00	50.00	60.00	70.00	80.00	90.00	100.00
Weight (g)	#1	5.50	10.56	16.03	20.22	24.59	26.38	28.50	29.29	29.89	29.93
	#2	5.89	11.34	15.53	21.71	24.06	27.01	28.58	29.05	29.30	30.03
	#3	4.70	9.91	15.03	19.85	23.91	25.80	26.91	28.46	29.15	29.46
Average (g)		5.36	10.60	15.53	20.59	24.19	26.40	28.00	28.93	29.45	29.81

Water flux (Oil/water mixture)

0.0197 g/ml

1st batch

Time (s)		1.00	2.00	3.00
Weight (g)	#1	7.31	14.20	14.92
	#2	6.57	13.66	14.90
	#3	7.55	14.81	14.85
Average (g)		7.14	14.22	14.89
<u>2nd batch</u>				
Time (s)		1.00	2.00	3.00
Weight (g)	#1	6.39	12.33	14.23
	#2	6.45	13.67	14.89
	#3	5.70	11.03	14.95
Average (g)		6.18	12.34	14.69
<u>3rd batch</u>				
Time (s)		1.00	2.00	3.00
Weight (g)	#1	5.20	11.01	14.96
	#2	5.04	10.02	14.90
	#3	4.98	9.31	14.98
Average (g)		5.07	10.11	14.95

0.0239g/ml

1st batch

Time (s)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00	11.00	12.00	13.00	14.00	15.00
Weight (g)	#1	0.98	2.01	3.25	4.67	5.26	6.35	7.99	8.81	10.08	11.24	12.32	13.06	13.56	13.82	14.00
	#2	1.17	2.21	3.14	4.25	5.46	7.01	8.06	9.12	10.23	11.12	12.01	12.55	13.02	13.23	13.55
	#3	1.36	2.77	3.51	4.13	5.95	7.13	8.12	9.55	11.01	12.04	13.04	13.99	14.12	14.30	14.38
Average (g)		1.17	2.33	3.30	4.35	5.56	6.83	8.06	9.16	10.44	11.47	12.46	13.20	13.57	13.78	13.98
<u>2nd batch</u>	-															
Time (s)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00	11.00	12.00	13.00	14.00	15.00
Weight (g)	#1	1.02	2.05	3.56	4.34	5.18	6.29	7.20	8.23	9.26	10.24	11.30	12.12	13.24	14.00	14.12
	#2	2.01	3.10	4.19	5.28	6.10	7.32	8.10	9.21	10.01	10.52	11.68	12.88	13.26	13.50	14.00
	#3	1.01	2.50	3.78	5.20	6.59	7.97	9.36	10.74	11.33	12.32	13.01	13.55	13.58	13.91	13.99
Average (g)		1.35	2.55	3.84	4.94	5.96	7.19	8.22	9.39	10.20	11.03	12.00	12.85	13.36	13.80	14.04
<u>3rd batch</u>	-															
Time (s)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00	11.00	12.00	13.00	14.00	15.00
Weight (g)	#1	1.02	2.29	3.63	4.67	5.83	7.04	8.15	9.26	10.26	11.18	11.97	12.59	13.18	13.50	13.66
	#2	1.98	3.04	4.02	5.12	5.91	6.78	8.34	9.51	11.01	11.23	12.06	13.16	13.68	14.03	14.21
	#3	1.05	2.78	3.89	5.48	7.01	9.02	9.81	10.38	11.34	12.56	13.13	13.78	13.90	13.98	14.01
Average (g)		1.35	2.70	3.85	5.09	6.25	7.61	8.77	9.72	10.87	11.66	12.39	13.18	13.59	13.84	13.96

0.0337 g/ml

1st batch

Time (s)		5.00	10.00	15.00	20.00	30.00
Weight (g)	#1	3.01	5.31	7.61	9.90	12.10
	#2	1.98	5.21	8.22	11.00	13.49
	#3	2.05	5.31	8.33	10.82	13.46
Average (g)		2.35	5.28	8.05	10.57	13.02
<u>2nd batch</u>						
Time (s)		5.00	10.00	15.00	20.00	30.00
Weight (g)	#1	2.14	4.79	7.44	10.09	12.70
	#2	2.06	4.37	6.66	8.93	11.19
	#3	2.21	4.55	6.89	9.23	11.53
Average (g)		2.14	4.57	7.00	9.42	11.81
<u>3rd batch</u>						
Time (s)		5.00	10.00	15.00	20.00	30.00
Weight (g)	#1	2.15	4.98	7.80	10.62	13.40
	#2	1.89	3.89	5.85	7.80	9.73
	#3	2.16	4.23	6.22	8.19	10.13
Average (g)		2.07	4.37	6.62	8.87	11.09

Separation efficiency (Oil/water mixture)

0.0197 g/ml								
	Mineral oil		Hexadecane		Canola oil		peanut oil	
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8
Empty Bottle	14.542	14.630	14.644	14.510	14.665	14.721	14.630	14.542
Empty Bottle + Filtrate	29.391	29.461	29.325	28.571	29.484	29.500	29.420	29.341
After Evaporation	14.542	14.630	14.644	14.519	14.665	14.721	14.636	14.542
After Evaporation - Empty	0.000	0.000	0.000	0.009	0.000	0.000	0.006	0.000
Total Filtrate Weight	14.849	14.831	14.681	14.061	14.819	14.779	14.790	14.799
C2	0.0000	0.0000	0.0000	0.0006	0.0000	0.0000	0.0004	0.0000
efficiency	100.0	100.0	100.0	99.9	100.0	100.0	99.9	100.0

0.0239 g/ml								
	Mineral oil		Hexadecane		Canola oil		peanut oil	
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8
Empty Bottle	14.530	14.328	14.584	14.568	14.665	14.635	14.645	14.645
Empty Bottle + Filtrate	28.511	27.839	28.942	28.668	28.611	28.558	28.253	28.822
After Evaporation	14.530	14.328	14.584	14.580	14.665	14.641	14.645	14.645
After Evaporation - Empty	0.000	0.000	0.000	0.012	0.000	0.006	0.000	0.000
Total Filtrate Weight	13.981	13.511	14.358	14.100	13.946	13.923	13.608	14.177
C2	0.0000	0.0000	0.0000	0.0009	0.0000	0.0004	0.0000	0.0000
efficiency	100.0	100.0	100.0	99.8	100.0	99.9	100.0	100.0

0.0337 g/ml

	Mineral oil		Hexadecane		Canola oil		peanut oil	
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8
Empty Bottle	14.237	14.327	14.584	14.720	14.575	14.556	14.720	14.573
Empty Bottle + Filtrate	27.198	26.984	28.031	24.141	26.036	26.838	25.141	23.870
After Evaporation	14.237	14.331	14.584	14.720	14.575	14.556	14.720	14.573
After Evaporation - Empty	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.000
Total Filtrate Weight	12.961	12.657	13.447	9.421	11.461	12.282	10.421	9.297
C2	0.0000	0.0003	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
efficiency	100.0	99.9	100.0	100.0	100.0	100.0	100.0	100.0

Water flux (Oil/water surfactant-free emulsion)

0.0197 g/ml				
<u>1st batch</u>				
Time (s)		5.00	10.00	15.00
Weight (g)	#1	3.23	6.53	9.10
	#2	2.22	4.98	8.01
	#3	3.01	6.01	8.45
Average (g)		2.82	5.84	8.52
<u>2nd batch</u>				
Time (s)	-	5.00	10.00	15.00
Weight (g)	#1	3.78	6.56	9.01
	#2	2.26	6.01	8.17
	#3	3.62	7.01	8.71
Average (g)		3.22	6.53	8.63
<u>3rd batch</u>				
Time (s)	-	5.00	10.00	15.00
Weight (g)	#1	2.01	4.86	7.40
	#2	2.92	5.01	6.19
	#3	2.11	4.23	7.02
Average (g)		2.35	4.70	6.87

0.0239g/ml

1st batch

Time (s)		10.00	20.00	30.00	40.00	50.00	60.00
Weight (g)	#1	1.56	3.24	4.92	6.23	7.12	8.01
	#2	1.34	2.89	4.31	5.56	6.82	7.12
	#3	0.98	2.67	4.26	5.45	6.41	7.01
Average (g)		1.29	2.93	4.50	5.75	6.78	7.38
<u>2nd batch</u>	-						
Time (s)		10.00	20.00	30.00	40.00	50.00	60.00
Weight (g)	#1	2.02	4.12	6.21	7.52	8.13	8.32
	#2	2.61	5.32	7.12	8.12	8.31	8.41
	#3	1.99	4.02	6.06	7.01	7.92	8.06
Average (g)		2.21	4.49	6.46	7.55	8.12	8.26
<u>3rd batch</u>	-						
Time (s)		10.00	20.00	30.00	40.00	50.00	60.00
Weight (g)	#1	1.34	2.78	4.22	5.32	6.63	7.13
	#2	0.99	1.91	2.83	3.75	4.67	5.30
	#3	1.10	3.31	4.92	6.82	7.23	8.00
Average (g)		1.14	2.67	3.99	5.30	6.18	6.81

0.0337 g/ml

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00
Weight (g)	#1	0.99	2.01	2.98	3.62	4.52	5.41	6.14	7.02
	#2	1.03	3.05	5.07	6.02	6.58	7.10	7.36	7.47
	#3	0.95	1.62	2.29	2.96	3.63	4.30	4.97	5.64
Average (g)		0.99	2.23	3.45	4.20	4.91	5.60	6.16	6.71
<u>2nd batch</u>	-								
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00
Weight (g)	#1	1.49	3.12	4.75	6.20	6.79	7.23	7.45	7.68
	#2	1.20	2.67	4.14	5.61	6.80	7.33	7.82	8.01
	#3	1.73	3.06	4.39	5.72	7.01	7.82	8.00	8.31
Average (g)		1.47	2.95	4.43	5.84	6.87	7.46	7.76	8.00
<u>3rd batch</u>	-								
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00
Weight (g)	#1	1.30	2.53	3.76	4.99	6.22	7.45	8.68	9.91
	#2	2.01	3.01	4.01	4.99	5.92	6.87	7.16	7.25
	#3	1.01	2.01	3.01	4.01	4.99	5.83	7.01	7.33
Average (g)		1.44	2.52	3.59	4.66	5.71	6.72	7.62	8.16

Separation efficiency (Oil/water surfactant-free emulsion)

0.0197 g/ml									
	1st Batch			2nd Batch			3rd Batch		
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8	#9
Empty Bottle	14.575	14.575	14.556	14.540	14.720	14.665	14.531	14.546	14.645
Empty Bottle + Filtrate	23.660	22.576	22.990	23.540	22.790	23.358	22.010	20.690	21.590
After Evaporation	14.972	14.950	14.921	14.943	15.090	15.046	14.935	14.821	14.952
After Evaporation - Empty	0.397	0.375	0.365	0.403	0.370	0.381	0.404	0.275	0.307
Total Filtrate Weight	9.085	8.001	8.434	9.000	8.070	8.693	7.479	6.144	6.945
C2	0.0437	0.0469	0.0433	0.0448	0.0458	0.0438	0.0540	0.0448	0.0442
efficiency	53.3	50.0	53.8	52.2	51.0	53.2	42.3	52.2	52.8

0.0239 g/ml									
	1st Batch			2nd Batch			3rd Batch		
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8	#9
Empty Bottle	14.542	14.721	14.665	14.665	14.635	14.546	14.721	14.665	14.644
Empty Botle + Filtrate	22.544	21.791	21.594	22.891	22.993	22.592	21.780	19.875	22.580
After Evaporation	14.641	14.801	14.740	14.740	14.710	14.625	14.800	14.721	14.720
After Evaporation - Empty	0.099	0.080	0.075	0.075	0.075	0.079	0.079	0.056	0.076
Total Filtrate Weight	8.002	7.070	6.929	8.226	8.358	8.046	7.059	5.210	7.936
C2	0.0124	0.0113	0.0108	0.0091	0.0090	0.0098	0.0112	0.0107	0.0096
efficiency	86.8	87.9	88.4	90.3	90.4	89.5	88.1	88.5	89.8

0.0337 g/ml									
	1st Batch			2nd Batch			3rd Batch		
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8	#9
Empty Bottle	14.542	14.721	14.665	14.630	14.546	14.644	14.531	14.510	14.641
Empty Botle + Filtrate	21.482	22.090	20.243	22.271	22.483	22.884	24.384	21.591	21.780
After Evaporation	14.552	14.740	14.681	14.634	14.552	14.663	14.533	14.522	14.642
After Evaporation - Empty	0.010	0.019	0.016	0.004	0.006	0.019	0.002	0.012	0.001
Total Filtrate Weight	6.940	7.369	5.578	7.641	7.937	8.240	9.853	7.081	7.139
C2	0.0014	0.0026	0.0029	0.0005	0.0008	0.0023	0.0002	0.0017	0.0001
efficiency	98.5	97.2	96.9	99.4	99.2	97.5	99.8	98.2	99.9

Water flux (Oil/water surfactant-stabilised emulsion)

0.0197 g/ml

1st batch						
Time (s)		10.00	30.00	50.00	70.00	90.00
Weight (g)	#1	1.10	2.23	3.15	4.22	4.99
	#2	1.42	3.13	4.25	5.86	7.21
	#3	1.01	2.01	3.01	3.71	4.50
Average (g)		1.18	2.46	3.47	4.60	5.57
2nd batch						
	-					
Time (s)		10.00	30.00	50.00	70.00	90.00
Weight (g)	#1	1.02	2.50	3.45	4.12	4.66
	#2	0.97	2.45	3.91	5.33	6.00
	#3	1.31	2.33	3.35	4.23	5.03
Average (g)		1.10	2.43	3.57	4.56	5.23
3rd batch						
	-					
Time (s)		10.00	30.00	50.00	70.00	90.00
Weight (g)	#1	0.99	1.90	2.72	3.42	4.01
	#2	1.12	2.03	2.71	3.35	3.97
	#3	1.07	2.17	3.20	4.30	5.25
Average (g)		1.06	2.03	2.88	3.69	4.41

0.0239g/ml

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00
Weight (g)	#1	1.21	2.40	3.55	4.56	5.31	6.02
	#2	1.16	2.31	3.45	4.59	5.55	5.91
	#3	1.05	2.98	4.00	4.97	5.41	5.98
Average (g)		1.14	2.56	3.67	4.71	5.42	5.97
<u>2nd batch</u>	-						
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00
Weight (g)	#1	1.25	2.70	3.61	4.52	5.31	6.02
	#2	1.42	2.51	3.66	4.65	5.38	5.81
	#3	0.77	1.89	2.99	3.41	4.21	5.01
Average (g)		1.15	2.37	3.42	4.19	4.97	5.61
<u>3rd batch</u>	-						
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00
Weight (g)	#1	1.01	1.97	2.76	3.62	4.30	4.89
	#2	1.26	2.33	3.54	4.02	4.69	5.02
	#3	0.78	2.08	2.67	3.59	4.57	5.23
Average (g)		1.02	2.13	2.99	3.74	4.52	5.05

0.0337 g/ml

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	0.29	0.60	0.91	1.22	1.51	1.80	2.05	2.33	2.62	2.79
	#2	0.38	0.73	1.08	1.43	1.78	2.13	2.46	2.83	3.18	3.33
	#3	0.28	0.57	0.86	1.15	1.44	1.73	2.02	2.30	2.60	2.77
Average (g)		0.32	0.63	0.95	1.27	1.58	1.89	2.18	2.49	2.80	2.96
<u>2nd batch</u>	-										
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	0.31	0.52	0.73	0.94	1.15	1.36	1.57	1.78	1.99	2.17
	#2	0.21	0.36	0.51	0.66	0.79	0.89	1.02	1.15	1.33	1.40
	#3	0.24	0.81	1.38	1.95	2.52	3.09	3.66	4.21	4.64	4.89
Average (g)		0.25	0.56	0.87	1.18	1.49	1.78	2.08	2.38	2.65	2.82
<u>3rd batch</u>	-										
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	0.20	0.43	0.66	0.89	1.12	1.35	1.58	1.79	2.02	2.26
	#2	0.11	0.31	0.51	0.71	0.91	1.11	1.31	1.49	1.68	1.82
	#3	0.24	0.44	0.64	0.84	1.04	1.24	1.44	1.61	1.82	1.98
Average (g)		0.18	0.39	0.60	0.81	1.02	1.23	1.44	1.63	1.84	2.02

Separation efficiency (Oil/water surfactant-stabilised emulsion)

0.0197 g/ml									
	1st Batch			2nd Batch			3rd Batch		
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8	#9
Empty Bottle	14.263	14.685	14.237	14.327	14.520	14.530	14.584	14.558	14.854
Empty Botle + Filtrate	19.140	21.784	18.626	18.880	20.342	19.490	18.540	18.489	20.090
After Evaporation	14.630	15.230	14.560	14.650	14.980	14.901	14.880	14.850	15.250
After Evaporation - Empty	0.367	0.545	0.323	0.323	0.460	0.371	0.296	0.292	0.396
Total Filtrate Weight	4.877	7.099	4.389	4.553	5.822	4.960	3.956	3.931	5.236
C2	0.0753	0.0768	0.0736	0.0709	0.0790	0.0748	0.0748	0.0743	0.0756
efficiency	19.7	18.0	21.4	24.3	15.6	20.1	20.1	20.7	19.2

0.0239 g/ml									
	1st Batch			2nd Batch			3rd Batch		
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8	#9
Empty Bottle	14.273	14.629	14.157	14.573	14.529	14.582	14.561	14.329	14.512
Empty Botle + Filtrate	20.250	20.510	20.137	20.498	20.293	19.570	19.432	19.298	19.689
After Evaporation	14.612	14.936	14.498	14.921	14.844	14.868	14.843	14.598	14.809
After Evaporation - Empty	0.339	0.307	0.341	0.348	0.316	0.286	0.282	0.269	0.297
Total Filtrate Weight	5.977	5.881	5.980	5.925	5.765	4.988	4.871	4.969	5.177
C2	0.0567	0.0522	0.0570	0.0587	0.0547	0.0574	0.0579	0.0541	0.0574
efficiency	39.4	44.3	39.1	37.3	41.6	38.7	38.1	42.2	38.7

0.0337 g/ml									
	1st Batch			2nd Batch			3rd Batch		
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8	#9
Empty Bottle	14.558	14.530	13.140	14.237	14.328	14.584	14.558	14.272	14.568
Empty Botle + Filtrate	17.311	17.842	15.889	16.389	15.700	19.453	16.798	16.054	16.487
After Evaporation	14.661	14.650	13.240	14.320	14.380	14.762	14.642	14.340	14.640
After Evaporation - Empty	0.103	0.120	0.100	0.083	0.052	0.178	0.084	0.068	0.072
Total Filtrate Weight	2.753	3.312	2.749	2.152	1.372	4.869	2.240	1.782	1.919
C2	0.0374	0.0362	0.0364	0.0386	0.0379	0.0366	0.0375	0.0382	0.0375
efficiency	60.1	61.3	61.2	58.8	59.5	61.0	60.0	59.3	59.9

Double layer

Water flux (DI water)

single layer											
<u>1st batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	2.33	5.40	8.28	11.31	12.99	15.31	17.07	18.74	19.61	21.36
	#2	2.94	6.01	8.83	11.23	13.47	15.55	17.43	19.03	20.48	21.90
	#3	2.23	5.15	7.53	9.70	12.05	14.25	15.88	17.15	18.64	20.12
Average (g)		2.50	5.52	8.21	10.75	12.84	15.04	16.79	18.31	19.58	21.13
<u>2nd batch</u>											
	-										
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	3.21	6.78	10.00	13.12	15.97	18.38	20.28	21.99	23.37	24.73
	#2	2.40	5.47	8.45	11.18	13.70	15.85	17.63	19.23	20.64	22.02
	#3	2.41	5.42	8.09	10.46	12.51	14.50	16.15	17.72	19.27	20.58
Average (g)		2.67	5.89	8.85	11.59	14.06	16.24	18.02	19.65	21.09	22.44
<u>3rd batch</u>											
	-										
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	2.31	5.12	8.37	11.40	14.43	17.46	19.01	20.56	21.70	23.11
	#2	3.14	6.02	8.90	11.78	14.66	17.54	18.76	19.79	20.95	22.07
	#3	2.01	5.29	8.57	11.85	15.10	18.24	19.25	20.31	21.06	22.00
Average (g)		2.49	5.48	8.61	11.68	14.73	17.75	19.01	20.22	21.24	22.40

11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
22.37	23.20	24.10	25.43	26.33	26.43	27.69	27.79	29.01	29.11
23.24	24.31	25.22	26.16	27.09	27.88	28.63	29.35	29.96	30.52
21.22	22.50	23.48	24.34	25.26	26.18	27.04	27.82	28.46	29.04
22.28	23.34	24.27	25.31	26.23	26.83	27.79	28.32	29.14	29.56
11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
25.80	26.90	27.85	28.64	29.35	30.05	30.69	31.24	31.70	32.18
23.21	24.31	25.25	26.19	26.97	27.75	28.45	29.07	29.60	30.14
21.72	22.77	23.81	24.73	25.64	26.44	27.15	27.83	28.47	29.00
23.58	24.66	25.64	26.52	27.32	28.08	28.76	29.38	29.92	30.44
11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
24.46	25.80	27.15	28.49	29.12	29.40	29.54	29.78	29.99	30.01
23.20	23.97	24.56	25.78	26.01	27.43	28.02	28.99	29.19	29.70
22.88	23.56	24.60	25.64	26.54	27.45	28.35	28.95	29.23	29.56
23.51	24.44	25.44	26.64	27.22	28.09	28.64	29.24	29.47	29.76

0.027 wt% (10 gsm)

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	3.420	6.320	8.302	10.284	12.266	14.100	15.934	17.000	18.066	19.132
	#2	1.232	3.316	3.425	4.886	6.063	7.520	8.591	9.630	10.735	11.865
	#3	2.010	4.610	7.130	9.650	12.000	14.350	15.880	17.410	18.230	19.050
Average (g)		2.22	4.75	6.29	8.27	10.11	11.99	13.47	14.68	15.68	16.68
<u>2nd batch</u>	-										
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	5.350	9.755	13.359	16.352	18.948	21.087	23.027	24.700	26.098	27.250
	#2	3.524	7.788	10.997	13.656	16.550	18.134	20.261	21.885	23.367	24.798
	#3	3.783	7.222	10.204	12.819	15.202	17.245	19.066	20.725	22.243	23.526
Average (g)		4.22	8.26	11.52	14.28	16.90	18.82	20.78	22.44	23.90	25.19
<u>3rd batch</u>	-										
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	3.744	7.398	10.183	13.825	15.113	17.263	19.890	21.018	23.002	24.297
	#2	3.652	7.961	11.763	14.281	16.676	18.614	21.026	22.708	24.146	25.352
	#3	3.065	6.144	9.261	12.033	14.596	16.806	18.527	20.066	21.482	22.760
Average (g)		3.49	7.17	10.40	13.38	15.46	17.56	19.81	21.26	22.88	24.14

11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
20.010	20.888	21.300	21.712	22.124	22.600	23.076	23.400	23.724	24.000
12.981	14.092	15.120	16.143	17.702	18.102	18.987	19.870	20.755	21.460
19.800	20.550	21.100	21.650	22.000	22.350	22.600	22.850	23.010	23.170
17.60	18.51	19.17	19.84	20.61	21.02	21.55	22.04	22.50	22.88
11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
28.406	29.296	30.182	30.762	31.420	31.950	32.230	32.444	32.444	32.437
25.651	27.028	28.052	28.803	29.581	30.319	31.018	31.655	31.892	32.131
24.724	25.914	26.788	27.750	28.492	29.321	29.869	30.469	31.000	31.564
26.26	27.41	28.34	29.11	29.83	30.53	31.04	31.52	31.78	32.04
11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
25.907	26.886	27.654	28.364	29.012	29.881	30.023	30.987	31.167	31.598
26.282	27.263	28.381	29.108	29.891	30.491	31.045	31.546	31.955	32.252
23.877	24.874	25.829	26.646	27.459	28.175	28.806	29.398	30.026	30.459
25.36	26.34	27.29	28.04	28.79	29.52	29.96	30.64	31.05	31.44

0.027 wt% (20 gsm)

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	3.61	7.23	11.32	14.20	16.21	17.98	19.35	20.99	22.34	24.11
	#2	3.45	6.59	9.73	12.70	15.67	18.31	20.95	23.30	25.65	26.61
	#3	2.98	6.02	9.06	12.01	14.96	17.73	20.50	21.89	23.28	24.51
Average (g)		3.35	6.61	10.04	12.97	15.61	18.01	20.27	22.06	23.76	25.08
<u>2nd batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	2.71	6.82	9.42	11.71	14.00	16.29	18.41	20.53	22.65	24.30
	#2	2.63	5.30	7.97	10.61	13.20	15.79	18.38	20.92	22.31	23.70
	#3	2.20	4.91	6.04	7.17	8.21	9.25	10.29	11.30	12.31	13.32
Average (g)		2.51	5.68	7.81	9.83	11.80	13.78	15.69	17.58	19.09	20.44
<u>3rd batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	3.21	6.54	8.02	9.45	10.85	12.25	13.61	14.97	16.30	17.63
	#2	2.58	5.12	7.63	10.10	11.89	13.64	15.30	16.91	18.48	19.68
	#3	2.36	5.01								
Average (g)		2.72	5.56	7.83	9.78	11.37	12.95	14.46	15.94	17.39	18.66

11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
25.70	26.41	27.36	28.25	29.17	30.01	30.85	31.69	31.88	32.02
27.57	28.01	28.45	28.89	29.20	29.51	29.70	29.89	30.03	30.17
25.74	26.71	27.68	28.40	29.12	29.50	29.88	30.21	30.54	30.62
26.34	27.04	27.83	28.51	29.16	29.67	30.14	30.60	30.82	30.94
11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
25.95	26.47	26.99	27.51	28.01	28.51	29.01	29.51	29.77	30.03
25.00	26.30	27.01	27.72	28.21	28.70	29.01	29.32	29.40	29.48
14.03	14.74	15.45	16.11	16.77	17.40	18.03	18.66	19.23	19.80
21.66	22.50	23.15	23.78	24.33	24.87	25.35	25.83	26.13	26.44
11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
18.92	20.21	21.50	22.73	23.92	25.01	26.10	27.02	27.91	28.44
20.73	21.62	22.51	23.36	24.21	25.04	25.87	26.52	27.17	27.66
19.83	20.92	22.01	23.05	24.07	25.03	25.99	26.77	27.54	28.05

0.027 wt% (30 gsm)

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	3.48	6.12	8.76	11.10	13.44	15.65	17.86	20.00	21.02	22.04
	#2	2.67	5.87	8.96	11.65	14.04	15.97	17.95	19.51	21.09	22.37
	#3	2.77	6.03	9.12	11.78	14.15	16.19	17.92	19.51	21.01	22.42
Average (g)		2.97	6.01	8.95	11.51	13.88	15.94	17.91	19.67	21.04	22.28
<u>2nd batch</u>	-										
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	3.118	6.040	8.524	10.830	12.814	14.716	16.293	17.872	19.337	20.492
	#2	2.582	4.933	7.355	9.497	11.394	13.302	14.803	16.274	17.779	18.990
	#3	2.200	3.023	4.575	6.666	8.195	9.891	11.179	12.510	13.885	14.769
Average (g)		2.63	4.67	6.82	9.00	10.80	12.64	14.09	15.55	17.00	18.08
<u>3rd batch</u>	-										
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	2.161	5.007	7.130	9.203	11.282	12.621	14.141	15.791	17.095	18.276
	#2	1.871	4.080	6.049	7.900	9.627	11.211	12.760	14.077	15.392	16.721
	#3	2.223	4.131	5.946	7.710	9.338	10.777	12.215	13.734	14.836	15.986
Average (g)		2.09	4.41	6.38	8.27	10.08	11.54	13.04	14.53	15.77	16.99

11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
23.06	24.00	24.94	25.88	26.78	27.63	28.48	29.33	30.18	30.56
22.37	23.57	24.75	25.65	26.58	27.39	28.13	28.81	29.43	29.86
23.63	24.70	25.72	26.64	27.40	28.09	28.84	29.52	30.09	30.69
23.02	24.09	25.14	26.06	26.92	27.70	28.48	29.22	29.90	30.37
11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
21.653	22.752	23.704	24.673	25.578	26.293	27.004	27.674	28.220	28.793
20.215	21.349	22.255	23.117	24.207	24.932	25.796	26.428	27.120	27.714
15.604	16.452	17.279	18.169	19.222	20.230	20.350	21.372	22.337	22.550
19.16	20.18	21.08	21.99	23.00	23.82	24.38	25.16	25.89	26.35
11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
19.296	20.326	21.454	22.290	22.986	23.890	24.420	25.099	25.883	26.470
17.706	19.687	20.594	21.175	21.793	22.328	23.077	23.807	24.494	25.086
17.074	18.034	19.090	19.990	20.859	21.726	22.464	23.213	23.834	24.517
18.03	19.35	20.38	21.15	21.88	22.65	23.32	24.04	24.74	25.36

0.054 wt% (30 gsm)

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	3.01	6.10	9.19	10.87	13.91	16.00	18.09	20.18	21.02	21.86
	#2	3.43	7.01	9.67	12.33	14.50	16.67	18.25	19.83	21.41	22.30
	#3	2.75	5.23	7.71	10.00	12.29	14.23	16.17	18.03	19.89	21.28
Average (g)		3.06	6.11	8.86	11.07	13.57	15.63	17.50	19.35	20.77	21.81
<u>2nd batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	2.91	5.78	8.51	10.56	12.30	13.89	15.48	17.07	18.31	19.55
	#2	2.31	4.52	6.73	8.94	11.00	13.06	15.12	17.18	19.01	20.84
	#3	3.12	6.04	8.96	11.30	12.99	14.68	16.37	17.51	18.65	19.79
Average (g)		2.78	5.45	8.07	10.27	12.10	13.88	15.66	17.25	18.66	20.06
<u>3rd batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	2.39	4.88	7.32	9.76	12.00	14.24	16.20	18.16	20.00	21.30
	#2	2.71	5.24	7.77	9.55	11.33	13.00	14.67	16.34	17.52	18.70
	#3	2.61	5.02	7.43	9.41	11.39	13.20	15.01	16.39	17.77	19.15
Average (g)		2.57	5.05	7.51	9.57	11.57	13.48	15.29	16.96	18.43	19.72

11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
22.70	23.30	24.06	24.30	25.01	25.72	26.43	27.00	27.57	27.88
23.88	25.00	26.12	27.02	27.92	28.34	28.76	29.18	29.35	29.52
22.10	22.92	23.58	24.24	24.74	25.24	25.60	26.05	26.48	26.71
22.89	23.74	24.59	25.19	25.89	26.43	26.93	27.41	27.80	28.04
11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
20.27	20.99	21.49	21.99	22.41	22.83	23.08	23.33	23.58	23.83
21.02	21.20	21.38	21.44	21.50	21.56	21.50	21.44	21.38	21.32
20.93	22.07	23.05	24.03	25.00	25.97	26.18	26.39	26.48	26.57
20.74	21.42	21.97	22.49	22.97	23.45	23.59	23.72	23.81	23.91
11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
22.60	23.17	23.74	24.21	24.68	25.03	25.38	25.73	26.08	26.22
19.88	20.82	21.76	22.70	23.30	23.90	24.02	24.14	24.26	24.21
19.99	20.83	21.67	22.36	23.05	23.51	23.97	24.43	24.89	25.35
20.82	21.61	22.39	23.09	23.68	24.15	24.46	24.77	25.08	25.26

0.108 wt% (30 gsm)

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	2.87	5.94	8.88	11.31	12.80	14.29	15.69	17.09	18.20	19.31
	#2	2.61	5.12	7.60	10.08	12.50	14.92	16.83	18.69	20.55	22.30
	#3	3.31	6.47	8.24	9.92	11.60	13.24	14.88	16.49	18.10	19.30
Average (g)		2.93	5.84	8.24	10.44	12.30	14.15	15.80	17.42	18.95	20.30
<u>2nd batch</u>	-										
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	3.01	6.08	9.10	11.68	14.10	15.98	18.05	19.50	20.59	21.31
	#2	2.51	4.98	7.45	9.70	11.95	14.10	16.25	18.20	20.15	22.01
	#3	2.91	5.12	7.33	9.24	11.10	12.41	13.69	14.73	15.77	16.53
Average (g)		2.81	5.39	7.96	10.21	12.38	14.16	16.00	17.48	18.84	19.95
<u>3rd batch</u>	-										
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	2.90	5.91	8.14	9.87	11.60	13.33	14.79	16.25	17.30	18.30
	#2	3.07	6.14	9.11	11.05	12.96	14.50	16.04	17.55	18.89	20.23
	#3	3.19	6.40	8.50	10.60	12.10	13.40	14.70	16.00	17.09	18.18
Average (g)		3.05	6.15	8.58	10.51	12.22	13.74	15.18	16.60	17.76	18.90

11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
20.21	21.11	22.01	22.51	23.01	23.20	23.32	23.44	23.56	23.70
24.05	25.61	27.17	28.30	29.43	29.88	30.00	30.12	30.24	30.30
20.25	21.20	22.09	22.98	23.87	24.21	24.55	24.89	25.20	25.51
21.50	22.64	23.76	24.60	25.44	25.76	25.96	26.15	26.33	26.50
11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
22.03	22.79	23.55	24.29	25.03	25.62	26.21	26.79	27.37	27.52
23.87	25.40	26.81	28.21	29.10	29.45	29.73	29.96	30.19	30.34
17.29	18.00	18.71	19.41	20.11	20.77	21.43	22.09	22.72	23.31
21.06	22.06	23.02	23.97	24.75	25.28	25.79	26.28	26.76	27.06
11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
19.30	20.10	20.91	21.72	22.53	23.30	24.07	24.78	25.49	26.04
21.50	22.77	24.01	25.25	26.40	27.55	28.20	28.85	29.06	29.16
19.20	20.22	21.21	22.20	23.07	23.94	24.61	25.28	25.95	26.20
20.00	21.03	22.04	23.06	24.00	24.93	25.63	26.30	26.83	27.13

0.216 wt% (30 gsm)

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	2.36	4.78	6.52	8.20	9.34	10.48	11.51	12.54	13.57	14.60
	#2	2.73	5.68	8.60	10.02	11.44	12.80	14.16	15.48	16.80	18.12
	#3	2.51	5.01	7.51	10.01	11.87	13.03	14.04	15.05	15.98	16.91
Average (g)		2.53	5.16	7.54	9.41	10.88	12.10	13.24	14.36	15.45	16.54
<u>2nd batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	2.03	4.93	6.42	7.91	9.25	10.59	11.61	12.63	13.49	14.35
	#2	1.68	3.24	4.80	6.36	7.50	8.64	9.78	10.80	11.82	12.84
	#3	2.21	4.71	6.30	7.89	9.20	10.51	11.23	11.95	12.67	13.31
Average (g)		1.97	4.29	5.84	7.39	8.65	9.91	10.87	11.79	12.66	13.50
<u>3rd batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	2.41	5.77	8.34	10.78	13.22	15.42	17.62	19.20	20.78	22.01
	#2	3.00	6.02	9.00	10.98	12.96	14.90	16.84	18.70	20.56	22.42
	#3	2.52	4.91	7.30	9.60	11.90	14.20	16.44	18.68	20.05	21.42
Average (g)		2.64	5.57	8.21	10.45	12.69	14.84	16.97	18.86	20.46	21.95

11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
15.60	16.60	17.60	18.52	19.44	20.35	21.26	22.16	23.06	23.54
19.39	20.66	21.93	23.03	24.13	25.14	26.15	27.10	28.05	28.79
17.81	18.58	19.35	19.95	20.55	21.15	21.70	22.25	22.74	23.23
17.60	18.61	19.63	20.50	21.37	22.21	23.04	23.84	24.62	25.19
11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
15.26	16.17	17.08	17.94	18.80	19.66	20.44	21.22	21.89	22.33
13.86	14.32	14.78	15.24	15.52	15.80	16.00	16.36	16.72	17.00
13.95	14.59	15.23	15.87	16.58	17.23	17.88	18.53	19.14	19.62
14.36	15.03	15.70	16.35	16.97	17.56	18.11	18.70	19.25	19.65
11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
23.24	24.31	25.38	26.35	27.32	28.15	28.98	29.20	29.42	29.60
24.01	25.60	27.19	28.05	28.91	29.35	29.79	30.00	30.21	30.30
22.79	24.01	25.23	26.40	27.57	28.62	29.00	29.38	29.70	30.00
23.35	24.64	25.93	26.93	27.93	28.71	29.26	29.53	29.78	29.97

0.432 wt% (30 gsm)

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	3.32	6.48	9.23	10.99	12.75	14.51	16.26	18.01	19.74	21.47
	#2	2.31	4.12	5.92	7.72	9.50	11.28	13.00	14.70	16.40	17.94
	#3	2.51	4.49	6.47	8.40	10.20	12.00	13.73	15.46	17.10	18.74
Average (g)		2.71	5.03	7.21	9.04	10.82	12.60	14.33	16.06	17.75	19.38
<u>2nd batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	2.63	5.32	8.01	10.50	12.95	15.40	17.72	20.04	22.28	24.52
	#2	2.74	5.42	8.10	10.71	13.32	15.72	18.09	20.41	22.70	24.88
	#3	3.01	6.01	8.71	10.82	12.72	14.52	16.32	18.10	19.88	21.60
Average (g)		2.79	5.58	8.27	10.68	13.00	15.21	17.38	19.52	21.62	23.67
<u>3rd batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	1.85	3.65	5.40	7.15	8.72	10.29	11.86	13.40	14.94	16.42
	#2	2.62	6.81	9.52	11.56	13.25	14.72	16.13	17.54	18.90	20.20
	#3	2.81	6.03	9.20	11.24	13.20	15.16	17.12	19.00	20.36	21.72
Average (g)		2.43	5.50	8.04	9.98	11.72	13.39	15.04	16.65	18.07	19.45

11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
23.00	24.53	26.00	27.47	28.88	29.23	29.58	29.90	30.20	30.50
19.48	21.00	22.52	23.98	25.44	26.82	28.00	29.10	30.00	30.90
20.30	21.86	23.39	24.92	26.40	27.21	28.02	28.40	28.78	29.00
20.93	22.46	23.97	25.46	26.91	27.75	28.53	29.13	29.66	30.13
11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
25.72	26.03	26.34	26.63	26.92	27.19	27.46	27.70	27.94	28.12
26.42	27.90	28.41	28.89	29.23	29.57	29.88	30.00	30.12	30.20
23.36	25.00	26.64	28.03	28.30	28.57	28.80	29.03	29.20	29.37
25.17	26.31	27.13	27.85	28.15	28.44	28.71	28.91	29.09	29.23
11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
17.90	19.38	20.82	22.26	23.62	24.98	26.26	27.54	28.50	29.06
21.62	22.60	23.58	24.50	25.42	26.34	27.21	28.08	28.90	29.62
23.01	24.27	25.53	26.79	28.02	29.04	29.77	30.10	30.43	30.47
20.84	22.08	23.31	24.52	25.69	26.79	27.75	28.57	29.28	29.72

0.027 wt% (40 gsm)

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	2.120	5.600	7.577	9.732	11.643	13.391	14.914	16.405	17.798	19.024
	#2	1.260	3.410	4.467	6.610	8.056	9.577	11.177	12.705	14.130	15.483
	#3	1.320	3.200	4.789	6.442	7.992	9.592	11.188	12.572	13.888	15.171
Average (g)		1.57	4.07	5.61	7.59	9.23	10.85	12.43	13.89	15.27	16.56
<u>2nd batch</u>	-										
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	3.700	6.020	8.340	10.660	12.920	15.180	17.440	19.510	21.000	22.490
	#2	3.670	7.528	10.634	13.517	15.994	18.328	20.450	22.180	23.852	25.214
	#3	3.220	5.999	9.853	13.046	15.237	17.578	19.637	21.353	23.087	24.519
Average (g)		3.53	6.52	9.61	12.41	14.72	17.03	19.18	21.01	22.65	24.07
<u>3rd batch</u>	-										
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	3.560	7.220	9.040	10.860	12.560	14.260	15.990	17.720	19.400	21.080
	#2	3.050	6.150	8.530	10.910	13.000	14.890	16.780	18.670	20.330	21.990
	#3	2.500	5.300	7.620	9.940	12.020	14.100	16.050	18.000	19.730	21.460
Average (g)		3.04	6.22	8.40	10.57	12.53	14.42	16.27	18.13	19.82	21.51

11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
20.114	21.251	22.214	23.089	23.962	24.882	25.661	26.273	26.972	27.581
16.941	18.138	19.308	20.500	21.738	22.737	23.639	24.434	25.067	25.796
16.452	17.787	18.854	19.960	20.786	21.615	22.392	23.158	23.882	24.533
17.84	19.06	20.13	21.18	22.16	23.08	23.90	24.62	25.31	25.97
11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
23.980	25.000	26.020	27.040	28.060	29.058	30.000	30.942	31.884	32.826
26.685	27.903	29.124	29.809	30.493	31.280	31.965	32.099	32.232	32.232
25.950	27.396	28.113	28.687	29.561	30.275	30.990	31.566	31.861	32.018
25.54	26.77	27.75	28.51	29.37	30.20	30.99	31.54	31.99	32.36
11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
22.500	23.920	25.000	26.080	27.000	27.920	28.840	29.500	30.160	30.820
23.650	25.010	26.370	27.050	27.730	28.330	28.930	29.760	30.590	31.140
23.010	24.560	25.920	27.280	28.330	29.380	30.030	30.680	31.330	31.780
23.05	24.50	25.76	26.80	27.69	28.54	29.27	29.98	30.69	31.25

0.108 wt% (60 gsm)

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	1.07	2.00	3.13	4.10	5.01	5.92	6.60	7.23	7.86	8.42
	#2	1.03	2.01	2.99	3.97	4.93	5.89	6.30	6.71	7.10	7.49
	#3	0.99	1.78	2.57	3.33	4.09	4.83	5.57	6.28	6.99	7.32
Average (g)		1.03	1.93	2.90	3.80	4.68	5.55	6.16	6.74	7.32	7.74
<u>2nd batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	0.50	0.98	1.43	1.88	2.31	2.74	3.15	3.56	3.94	4.32
	#2	1.40	2.67	3.94	4.78	5.62	6.31	7.00	7.64	8.28	8.90
	#3	1.01	1.98	2.95	3.92	4.80	5.64	6.48	7.22	7.96	8.52
Average (g)		0.97	1.88	2.77	3.53	4.24	4.90	5.54	6.14	6.73	7.25
<u>3rd batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	0.65	1.23	1.81	2.39	2.94	3.49	4.00	4.51	5.00	5.49
	#2	1.08	2.12	3.16	4.18	5.20	6.21	7.22	8.19	9.16	10.10
	#3	0.48	0.88	1.28	1.65	2.02	2.39	2.74	3.09	3.41	3.73
Average (g)		0.74	1.41	2.08	2.74	3.39	4.03	4.65	5.26	5.86	6.44

11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
8.98	9.50	10.02	10.48	10.92	11.36	11.80	12.19	12.54	12.78
7.85	8.21	8.57	8.90	9.23	9.51	9.79	10.07	10.32	10.51
7.65	7.94	8.23	8.50	8.77	9.00	9.23	9.41	9.58	9.74
8.16	8.55	8.94	9.29	9.64	9.96	10.27	10.56	10.81	11.01
11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
4.68	5.04	5.37	5.70	6.02	6.34	6.63	6.92	7.20	7.44
9.52	10.10	10.68	11.22	11.76	12.20	12.61	13.01	13.41	13.66
9.08	9.60	10.12	10.52	10.73	10.94	11.15	11.34	11.53	11.67
7.76	8.25	8.72	9.15	9.50	9.83	10.13	10.42	10.71	10.92
11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
5.98	6.47	6.91	7.35	7.79	8.20	8.61	9.02	9.40	9.66
11.04	11.78	12.52	13.10	13.30	13.50	13.62	13.74	13.86	13.98
4.03	4.33	4.61	4.89	5.13	5.35	5.57	5.79	6.00	6.11
7.02	7.53	8.01	8.45	8.74	9.02	9.27	9.52	9.75	9.92

0.216 wt% (60 gsm)

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	0.56	1.30	2.04	2.74	3.44	4.10	4.76	5.40	6.04	6.68
	#2	1.01	2.10	3.13	4.10	5.02	5.94	6.50	7.06	7.60	8.11
	#3	0.43	0.99	1.55	2.10	2.62	3.14	3.60	4.06	4.42	4.78
Average (g)		0.67	1.46	2.24	2.98	3.69	4.39	4.95	5.51	6.02	6.52
<u>2nd batch</u>	-										
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	1.00	1.94	2.88	3.80	4.72	5.58	6.22	6.86	7.39	7.92
	#2	0.98	2.02	3.02	4.01	4.89	5.77	6.62	7.47	8.32	9.14
	#3	0.94	1.79	2.64	3.45	4.26	5.03	5.80	6.53	7.26	7.78
Average (g)		0.97	1.92	2.85	3.75	4.62	5.46	6.21	6.95	7.66	8.28
<u>3rd batch</u>	-										
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	1.01	2.03	3.02	4.01	4.87	5.73	6.54	7.35	8.10	8.80
	#2	1.30	2.41	3.47	4.53	5.42	6.31	7.11	7.91	8.25	8.59
	#3	1.02	1.71	2.40	3.09	3.73	4.37	4.97	5.57	6.14	6.71
Average (g)		1.11	2.05	2.96	3.88	4.67	5.47	6.21	6.94	7.50	8.03

11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
7.30	7.92	8.51	9.10	9.69	10.22	10.75	11.28	11.80	12.32
8.60	9.08	9.56	10.00	10.44	10.83	11.22	11.61	11.99	12.34
5.10	5.42	5.70	5.98	6.26	6.50	6.74	6.98	7.20	7.42
7.00	7.47	7.92	8.36	8.80	9.18	9.57	9.96	10.33	10.69
11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
8.38	8.84	9.19	9.54	9.85	10.16	10.42	10.68	10.94	11.20
9.96	10.31	10.66	11.00	11.21	11.42	11.60	11.78	11.94	12.10
8.30	8.80	9.30	9.78	10.26	10.72	11.18	11.61	12.04	12.33
8.88	9.32	9.72	10.11	10.44	10.77	11.07	11.36	11.64	11.88
11.00	12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
9.48	10.16	10.80	11.44	12.05	12.66	13.20	13.74	14.22	14.50
8.90	9.21	9.50	9.79	10.02	10.25	10.40	10.55	10.61	10.65
7.25	7.79	8.30	8.81	9.27	9.70	10.13	10.40	10.67	10.90
8.54	9.05	9.53	10.01	10.45	10.87	11.24	11.56	11.83	12.02

Water flux (Oil/water mixture)

single layer											
<u>1st batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	1.49	3.26	5.24	7.08	8.96	10.83	12.71	13.41	14.05	14.27
	#2	2.09	4.01	6.02	7.96	9.92	11.25	12.58	13.65	14.77	15.68
	#3	2.34	4.36	6.13	7.67	9.12	10.50	11.85	13.13	14.41	15.60
Average (g)		1.97	3.88	5.80	7.57	9.33	10.86	12.38	13.40	14.41	15.18
<u>2nd batch</u>											
Time (min)	-	1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	2.04	4.05	6.02	7.83	9.64	11.21	12.41	13.32	14.23	15.00
	#2	2.21	4.21	5.34	7.05	8.54	10.00	11.44	12.78	13.54	14.20
	#3	2.04	3.91	5.03	6.65	8.10	9.50	11.01	12.20	13.22	13.78
Average (g)		2.10	4.06	5.46	7.18	8.76	10.24	11.62	12.77	13.66	14.33
<u>3rd batch</u>											
Time (min)	-	1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	2.05	4.11	6.02	7.22	8.41	9.32	10.23	11.14	12.00	12.55
	#2	1.05	2.03	3.02	4.00	4.73	5.46	6.02	6.34	6.66	6.56
	#3	2.67	4.67	6.67	8.54	10.22	11.23	12.24	13.00	13.44	13.65
Average (g)		1.92	3.60	5.24	6.59	7.79	8.67	9.50	10.16	10.70	10.92

0.027 wt% (10 gsm)

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	1.98	3.89	5.67	7.54	9.32	11.12	12.34	12.89	13.40	13.82
	#2	2.03	4.02	6.00	7.51	9.02	10.50	11.62	12.74	13.80	14.77
	#3	1.85	3.62	5.39	7.10	8.81	10.52	12.20	13.88	15.50	17.02
Average (g)		1.95	3.84	5.69	7.38	9.05	10.71	12.05	13.17	14.23	15.20
<u>2nd batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	1.86	3.78	5.70	7.62	8.20	8.73	9.26	9.60	10.10	10.26
	#2	1.31	2.56	3.81	5.06	5.98	6.90	7.82	8.74	9.66	10.58
	#3	2.00	4.01	6.02	8.03	9.43	10.83	12.23	13.22	14.23	15.01
Average (g)		1.72	3.45	5.18	6.90	7.87	8.82	9.77	10.52	11.33	11.95
<u>3rd batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	1.34	2.85	3.78	4.71	5.64	6.57	7.54	8.40	9.36	10.00
	#2	1.67	3.01	4.89	5.79	6.35	7.08	7.81	8.54	9.27	9.95
	#3	1.71	3.77	4.65	5.53	6.41	7.11	7.87	8.72	9.41	9.67
Average (g)		1.57	3.21	4.44	5.34	6.13	6.92	7.74	8.55	9.35	9.87

0.027 wt% (20 gsm)

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	2.67	4.36	6.05	7.04	8.03	9.00	9.97	10.50	11.03	11.56
	#2	1.21	3.29	5.37	7.20	9.03	10.23	11.04	11.85	12.31	12.77
	#3	2.33	5.06	7.25	9.18	10.98	12.23	13.25	14.16	15.00	15.84
Average (g)		2.07	4.24	6.22	7.81	9.35	10.49	11.42	12.17	12.78	13.39
<u>2nd batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	3.13	5.21	7.29	9.30	11.31	13.24	14.20	15.01	15.82	16.63
	#2	2.79	4.87	9.54	11.93	14.09	15.97	16.50	16.50	16.55	16.57
	#3	3.05	5.95	8.33	10.55	11.75	12.45	13.14	13.80	14.43	15.03
Average (g)		2.99	5.34	8.39	10.59	12.38	13.89	14.61	15.10	15.60	16.08
<u>3rd batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	2.38	5.02	7.78	9.82	11.85	13.51	15.08	16.31	16.44	16.44
	#2	1.58	3.81	6.01	7.89	9.77	11.43	12.68	13.56	13.84	14.14
	#3	2.22	4.98	7.08	8.98	10.76	12.38	13.90	15.13	15.56	15.56
Average (g)		2.06	4.60	6.95	8.90	10.79	12.44	13.88	15.00	15.28	15.38

0.027 wt% (30 gsm)

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	3.51	6.01	8.07	9.11	10.75	12.03	13.98	15.55	17.69	17.74
	#2	2.69	5.34	7.12	9.63	11.84	14.06	14.58	15.12	15.82	16.01
	#3	2.83	5.87	8.05	10.07	11.77	13.55	14.24	15.02	15.23	16.04
Average (g)		3.01	5.74	7.75	9.60	11.45	13.21	14.27	15.23	16.25	16.60
<u>2nd batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	2.88	4.57	7.11	8.56	9.02	10.59	11.78	12.51	13.21	13.98
	#2	2.24	5.03	7.12	8.20	9.34	10.34	12.01	12.33	13.03	13.43
	#3	1.72	3.78	5.76	7.74	9.72	10.98	11.77	12.55	13.07	13.24
Average (g)		2.28	4.46	6.66	8.17	9.36	10.64	11.85	12.46	13.10	13.55
<u>3rd batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	2.87	5.11	7.00	8.58	9.92	11.10	12.19	13.13	13.97	14.76
	#2	1.67	3.14	4.59	6.00	7.41	8.75	10.00	11.25	12.34	13.00
	#3	1.52	3.02	4.23	5.63	6.99	8.03	9.07	9.93	11.35	12.05
Average (g)		2.02	3.76	5.27	6.74	8.11	9.29	10.42	11.44	12.55	13.27

0.027 wt% (40 gsm)

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	1.76	4.11	5.99	7.87	9.54	11.12	12.26	13.80	14.23	14.36
	#2	1.93	4.31	6.68	8.77	10.86	12.23	13.25	14.27	15.02	15.44
	#3	1.93	3.52	5.02	6.52	7.98	9.44	10.84	12.24	13.43	14.60
Average (g)		1.88	3.98	5.90	7.72	9.46	10.93	12.12	13.44	14.23	14.80
<u>2nd batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	2.34	4.78	7.52	9.87	11.87	13.30	14.51	14.44	14.66	14.86
	#2	1.23	2.78	4.13	5.44	6.75	8.00	9.25	10.34	11.40	12.43
	#3	2.17	4.22	6.96	9.31	11.52	13.83	14.61	15.36	16.02	16.27
Average (g)		1.91	3.92	6.20	8.21	10.05	11.71	12.79	13.38	14.03	14.52
<u>3rd batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	2.10	4.10	6.10	8.10	9.56	10.34	11.27	11.92	12.12	12.88
	#2	1.67	2.56	3.45	4.34	5.23	6.01	6.98	7.90	8.79	9.68
	#3	2.10	4.27	6.40	8.25	10.10	11.20	12.30	13.11	13.92	14.44
Average (g)		1.96	3.64	5.32	6.90	8.30	9.18	10.18	10.98	11.61	12.33

0.216 wt% (60 gsm)

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	0.62	1.30	1.98	2.66	3.30	3.97	4.63	5.01	5.34	5.56
	#2	0.45	1.12	1.56	2.00	2.35	2.70	3.01	3.32	3.64	3.96
	#3	0.73	1.43	2.13	2.83	3.53	4.12	4.53	4.93	5.31	5.26
Average (g)		0.60	1.28	1.89	2.50	3.06	3.60	4.06	4.42	4.76	4.93
<u>2nd batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	0.52	1.10	1.52	2.12	2.60	3.05	3.52	4.01	4.22	4.35
	#2	0.62	1.29	1.93	2.55	3.17	3.75	4.22	4.86	5.45	5.78
	#3	0.44	0.95	1.46	1.95	2.44	2.89	3.34	3.75	4.16	4.46
Average (g)		0.53	1.11	1.64	2.21	2.74	3.23	3.69	4.21	4.61	4.86
<u>3rd batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	0.51	1.03	1.45	2.10	2.55	3.10	3.54	4.03	4.31	4.54
	#2	0.62	1.32	2.02	2.70	3.42	4.12	4.44	4.75	5.06	5.34
	#3	0.33	0.79	1.57	2.02	2.47	2.92	3.37	3.82	4.16	4.26
Average (g)		0.49	1.05	1.68	2.27	2.81	3.38	3.78	4.20	4.51	4.71

Separation efficiency (Oil/water mixture)

single layer									
	1st Batch			2nd Batch			3rd Batch		
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8	#9
Empty Bottle	14.575	14.556	14.524	14.526	14.571	14.558	14.526	14.531	14.579
Empty Botle + Filtrate	28.202	29.565	29.471	28.863	28.116	27.664	26.322	20.419	27.451
After Evaporation	14.575	14.556	14.524	14.526	14.571	14.558	14.526	14.531	14.579
After Evaporation - Empty	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Total Filtrate Weight	13.627	15.009	14.947	14.337	13.545	13.106	11.796	5.888	12.872
C2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
efficiency	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

0.027 wt% (10 gsm)									
	1st Batch			2nd Batch			3rd Batch		
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8	#9
Empty Bottle	14.524	14.526	14.511	14.571	13.180	14.575	14.575	14.573	14.558
Empty Botle + Filtrate	28.010	28.973	31.188	24.411	23.439	29.240	24.213	24.183	23.804
After Evaporation	14.524	14.526	14.511	14.571	13.180	14.575	14.575	14.573	14.558
After Evaporation - Empty	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Total Filtrate Weight	13.486	14.447	16.677	9.840	10.259	14.665	9.638	9.611	9.246
C2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
efficiency	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

0.027 wt% (20 gsm)

	1st Batch			2nd Batch			3rd Batch		
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8	#9
Empty Bottle	13.137	13.180	14.526	14.508	14.641	14.540	14.526	14.511	14.642
Empty Botle + Filtrate	24.462	25.713	30.134	30.917	30.978	29.344	30.745	28.422	29.966
After Evaporation	13.137	13.180	14.526	14.508	14.641	14.540	14.526	14.511	14.642
After Evaporation - Empty	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Total Filtrate Weight	11.325	12.533	15.608	16.409	16.337	14.804	16.219	13.911	15.324
C2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
efficiency	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

0.027 wt% (30 gsm)

	1st Batch			2nd Batch			3rd Batch		
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8	#9
Empty Bottle	14.508	14.546	14.585	14.573	14.558	14.531	14.529	14.582	14.561
Empty Botle + Filtrate	31.973	30.291	30.366	28.302	27.726	27.508	29.016	27.292	26.342
After Evaporation	14.508	14.546	14.585	14.573	14.558	14.531	14.529	14.582	14.561
After Evaporation - Empty	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Total Filtrate Weight	17.465	15.745	15.781	13.730	13.168	12.977	14.488	12.710	11.781
C2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
efficiency	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

0.027 wt% (40 gsm)

	1st Batch			2nd Batch			3rd Batch		
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8	#9
Empty Bottle	14.526	14.508	14.641	14.540	14.720	14.665	14.635	14.546	14.645
Empty Botle + Filtrate	28.661	29.754	29.018	29.195	26.942	30.737	27.290	23.924	28.803
After Evaporation	14.526	14.508	14.641	14.540	14.720	14.665	14.635	14.546	14.645
After Evaporation - Empty	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Total Filtrate Weight	14.135	15.246	14.377	14.655	12.222	16.072	12.655	9.378	14.158
C2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
efficiency	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

0.216 wt% (60 gsm)

	1st Batch			2nd Batch			3rd Batch		
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8	#9
Empty Bottle	14.526	14.579	14.573	14.558	14.552	14.522	14.641	14.546	14.642
Empty Botle + Filtrate	19.956	18.409	19.703	18.778	20.202	18.852	19.051	19.756	18.772
After Evaporation	14.526	14.579	14.573	14.558	14.552	14.522	14.641	14.546	14.642
After Evaporation - Empty	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Total Filtrate Weight	5.430	3.830	5.130	4.220	5.650	4.330	4.410	5.210	4.130
C2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
efficiency	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Water flux (Oil/water surfactant-free emulsion)

0.027 wt% (10 gsm)											
<u>1st batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	1.22	3.45	5.33	7.00	7.35	7.83	8.21	8.47	8.73	8.80
	#2	0.74	1.60	2.46	3.32	4.01	4.70	5.20	5.70	6.20	5.96
	#3	0.37	0.99	1.58	2.17	2.73	3.29	3.84	4.39	4.92	5.56
Average (g)		0.78	2.01	3.12	4.16	4.70	5.27	5.75	6.19	6.62	6.77
<u>2nd batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	1.00	2.04	3.08	4.12	5.10	6.00	6.90	7.33	7.76	8.00
	#2	1.60	3.13	4.23	5.20	6.17	7.03	7.50	7.97	8.33	8.69
	#3	1.03	1.92	2.81	3.70	4.59	5.32	6.05	6.44	6.83	7.03
Average (g)		1.21	2.36	3.37	4.34	5.29	6.12	6.82	7.25	7.64	7.91
<u>3rd batch</u>											
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	1.17	2.32	3.47	4.61	5.75	6.51	7.27	8.03	8.30	8.57
	#2	0.78	1.50	2.22	2.88	3.54	4.11	4.68	5.20	5.70	6.15
	#3	1.31	2.41	3.44	4.20	4.96	5.48	6.00	6.30	6.60	6.88
Average (g)		1.09	2.08	3.04	3.90	4.75	5.37	5.98	6.51	6.87	7.20

single layer

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	1.90	2.78	3.66	4.42	5.18	5.87	6.56	7.01	7.46	7.88
	#2	1.13	2.23	3.31	4.39	5.40	6.41	7.35	8.01	8.67	9.04
	#3	1.53	2.31	3.09	3.52	3.95	4.32	4.69	5.00	5.31	5.60
Average (g)		1.52	2.44	3.35	4.11	4.84	5.53	6.20	6.67	7.15	7.51
<u>2nd batch</u>											
Time (min)	-	1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	0.56	0.98	1.40	1.82	2.20	2.58	2.91	3.22	3.53	3.81
	#2	1.01	1.97	2.93	3.62	4.28	4.94	5.42	5.90	6.11	6.30
	#3	1.50	2.88	4.20	5.52	6.45	7.13	7.80	8.20	8.60	8.82
Average (g)		1.02	1.94	2.84	3.65	4.31	4.88	5.38	5.77	6.08	6.31
<u>3rd batch</u>											
Time (min)	-	1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	0.60	1.06	1.52	1.77	2.02	2.21	2.40	2.53	2.66	2.76
	#2	1.51	2.80	4.09	5.35	6.29	7.02	7.52	7.93	8.34	8.70
	#3	1.61	3.12	4.41	5.45	6.40	7.35	8.02	8.20	8.38	8.53
Average (g)		1.24	2.33	3.34	4.19	4.90	5.53	5.98	6.22	6.46	6.66

0.027 wt% (20 gsm)

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	1.02	2.01	3.00	3.99	4.62	5.25	5.85	6.41	6.97	7.43
	#2	1.04	2.34	3.64	4.82	5.86	6.45	7.04	7.60	8.13	8.56
	#3	1.12	2.09	3.06	4.01	4.96	5.91	6.41	6.91	7.34	7.79
Average (g)		1.06	2.15	3.23	4.27	5.15	5.87	6.43	6.97	7.48	7.93
<u>2nd batch</u>	-										
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	0.99	1.98	2.97	3.92	4.87	5.62	6.37	7.02	7.67	8.25
	#2	1.05	2.15	3.25	4.24	5.23	6.01	6.79	7.50	8.21	8.45
	#3	1.07	2.07	3.07	4.07	5.04	6.01	6.82	7.40	7.98	8.53
Average (g)		1.04	2.07	3.10	4.08	5.05	5.88	6.66	7.31	7.95	8.41
<u>3rd batch</u>	-										
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	0.82	1.76	2.70	3.60	4.50	5.35	6.20	7.00	7.75	8.34
	#2	0.91	1.56	2.20	2.84	3.40	3.96	4.46	4.96	5.40	5.84
	#3	1.05	2.56	3.51	4.42	5.33	6.21	7.05	7.66	8.20	8.72
Average (g)		0.93	1.96	2.80	3.62	4.41	5.17	5.90	6.54	7.12	7.63

0.027 wt% (30 gsm)

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	1.47	2.59	3.54	4.38	5.10	5.74	6.37	6.97	7.41	7.82
	#2	0.37	0.97	1.48	2.12	2.71	3.23	3.74	4.26	4.77	5.21
	#3	0.22	0.92	1.55	2.01	2.54	2.96	3.31	3.63	4.10	4.48
Average (g)		0.68	1.49	2.19	2.84	3.45	3.97	4.47	4.95	5.43	5.84
<u>2nd batch</u>	-										
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	1.84	3.73	5.19	6.12	7.05	7.32	7.59	7.83	8.07	8.27
	#2	0.29	0.84	1.49	2.26	2.99	3.72	4.38	5.04	5.70	6.28
	#3	0.48	1.26	2.08	2.67	3.12	3.63	4.08	4.53	4.99	5.45
Average (g)		0.87	1.94	2.92	3.68	4.38	4.89	5.35	5.80	6.25	6.66
<u>3rd batch</u>	-										
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	1.95	3.86	5.33	6.13	6.50	6.87	7.11	7.30	7.49	7.63
	#2	1.01	2.12	3.21	4.30	5.39	6.43	7.20	7.97	8.70	9.10
	#3	0.99	2.04	3.03	3.99	4.95	5.67	6.33	6.99	7.61	8.23
Average (g)		1.32	2.67	3.86	4.81	5.61	6.32	6.88	7.42	7.93	8.32

0.027 wt% (40 gsm)

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	1.47	2.59	3.54	4.38	5.10	5.74	6.37	6.97	7.41	7.82
	#2	0.37	0.97	1.48	2.12	2.71	3.23	3.74	4.26	4.77	5.21
	#3	0.22	0.92	1.55	2.01	2.54	2.96	3.31	3.63	4.10	4.48
Average (g)		0.68	1.49	2.19	2.84	3.45	3.97	4.47	4.95	5.43	5.84
<u>2nd batch</u>	-										
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	1.84	3.73	5.19	6.15	6.59	7.03	7.48	7.92	8.30	8.61
	#2	0.29	0.84	1.49	2.26	2.99	3.72	4.38	5.04	5.70	6.28
	#3	1.34	2.34	3.34	4.32	5.31	6.10	6.89	7.36	7.83	8.12
Average (g)		1.16	2.30	3.34	4.24	4.96	5.62	6.25	6.77	7.27	7.67
<u>3rd batch</u>	-										
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	1.74	3.43	5.03	6.01	6.39	6.77	7.10	7.43	7.71	7.93
	#2	0.61	1.23	1.85	2.33	2.81	3.27	3.73	4.16	4.59	5.02
	#3	1.20	2.55	3.78	5.01	6.23	7.01	7.79	8.33	8.61	8.89
Average (g)		1.18	2.40	3.55	4.45	5.14	5.68	6.21	6.64	6.97	7.28

0.216 wt% (60 gsm)

1st batch

Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	0.47	0.89	1.31	1.70	2.09	2.45	2.77	3.09	3.33	3.50
	#2	0.51	0.92	1.33	1.71	2.06	2.41	2.74	3.07	3.39	3.65
	#3	0.44	0.77	1.10	1.41	1.72	2.00	2.25	2.50	2.75	2.99
Average (g)		0.47	0.86	1.25	1.61	1.96	2.29	2.59	2.89	3.16	3.38
<u>2nd batch</u>	-										
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	0.52	0.98	1.44	1.88	2.32	2.73	3.14	3.44	3.74	4.01
	#2	0.48	0.92	1.36	1.77	2.18	2.53	2.88	3.20	3.52	3.83
	#3	0.36	0.62	0.88	1.14	1.38	1.62	1.80	1.96	2.12	2.20
Average (g)		0.45	0.84	1.23	1.60	1.96	2.29	2.61	2.87	3.13	3.35
<u>3rd batch</u>	-										
Time (min)		1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
Weight (g)	#1	0.45	0.87	1.29	1.71	2.11	2.46	2.80	3.13	3.46	3.77
	#2	0.51	1.03	1.53	2.03	2.53	3.01	3.49	3.94	4.35	4.66
	#3	0.56	1.02	1.47	1.92	2.20	2.40	2.58	2.74	2.90	3.04
Average (g)		0.51	0.97	1.43	1.89	2.28	2.62	2.96	3.27	3.57	3.82

Separation efficiency (Oil/water surfactant-free emulsion)

0.027 wt% (10 gsm)									
	1st Batch			2nd Batch			3rd Batch		
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8	#9
Empty Bottle	13.139	13.181	14.579	14.571	14.558	14.526	14.531	14.584	14.559
Empty Botle + Filtrate	21.929	19.139	20.139	22.568	23.231	21.546	23.090	20.700	21.421
After Evaporation	13.146	13.187	14.587	14.579	14.565	14.535	14.533	14.584	14.560
After Evaporation - Empty	0.007	0.006	0.008	0.008	0.007	0.009	0.002	0.000	0.001
Total Filtrate Weight	8.790	5.958	5.560	7.997	8.673	7.020	8.559	6.116	6.862
C2	0.0008	0.0010	0.0014	0.0010	0.0008	0.0013	0.0002	0.0000	0.0001
efficiency	99.1	98.9	98.5	98.9	99.1	98.6	99.8	100.0	99.8

single layer									
	1st Batch			2nd Batch			3rd Batch		
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8	#9
Empty Bottle	14.530	14.584	14.558	14.573	14.558	14.530	13.140	13.183	14.580
Empty Botle + Filtrate	22.399	23.584	20.057	18.387	20.858	23.342	15.831	21.793	23.015
After Evaporation	14.531	14.586	14.559	14.579	14.559	14.578	13.142	13.196	14.582
After Evaporation - Empty	0.001	0.002	0.001	0.006	0.001	0.048	0.002	0.013	0.002
Total Filtrate Weight	7.869	9.000	5.499	3.814	6.300	8.812	2.691	8.610	8.435
C2	0.0001	0.0002	0.0002	0.0016	0.0002	0.0054	0.0007	0.0015	0.0002
efficiency	99.9	99.8	99.8	98.3	99.8	94.2	99.2	98.4	99.7

0.027 wt% (20 gsm)									
	1st Batch			2nd Batch			3rd Batch		
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8	#9
Empty Bottle	13.137	13.180	14.575	14.575	14.556	14.524	14.526	14.511	14.642
Empty Botle + Filtrate	20.487	21.686	22.275	22.765	23.000	23.004	22.766	20.231	22.890
After Evaporation	13.156	13.182	14.577	14.584	14.557	14.526	14.547	14.511	14.656
After Evaporation - Empty	0.019	0.002	0.002	0.009	0.001	0.002	0.021	0.000	0.014
Total Filtrate Weight	7.350	8.506	7.700	8.190	8.444	8.480	8.240	5.720	8.248
C2	0.0026	0.0002	0.0003	0.0011	0.0001	0.0002	0.0025	0.0000	0.0017
efficiency	97.2	99.7	99.7	98.8	99.9	99.7	97.3	100.0	98.2

0.027 wt% (30 gsm)									
	1st Batch			2nd Batch			3rd Batch		
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8	#9
Empty Bottle	13.140	13.184	14.585	14.573	14.558	14.531	14.529	14.582	14.561
Empty Botle + Filtrate	20.872	18.290	19.023	22.743	20.699	19.980	22.090	23.435	22.680
After Evaporation	13.163	13.185	14.589	14.577	14.567	14.531	14.529	14.583	14.564
After Evaporation - Empty	0.023	0.001	0.004	0.005	0.009	0.001	0.001	0.001	0.003
Total Filtrate Weight	7.732	5.106	4.439	8.170	6.141	5.449	7.561	8.853	8.119
C2	0.0030	0.0002	0.0010	0.0006	0.0014	0.0001	0.0001	0.0001	0.0004
efficiency	96.8	99.8	98.9	99.4	98.5	99.9	99.9	99.8	99.6

0.027 wt% (40 gsm)									
	1st Batch			2nd Batch			3rd Batch		
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8	#9
Empty Bottle	14.526	14.508	14.641	14.540	14.720	14.665	14.635	14.546	14.645
Empty Botle + Filtrate	22.113	19.506	19.032	23.022	20.597	22.523	22.432	19.366	23.202
After Evaporation	14.529	14.510	14.665	14.541	14.727	14.672	14.639	14.558	14.647
After Evaporation - Empty	0.003	0.002	0.024	0.001	0.007	0.007	0.004	0.012	0.002
Total Filtrate Weight	7.587	4.998	4.391	8.482	5.877	7.858	7.797	4.820	8.557
C2	0.0004	0.0004	0.0055	0.0001	0.0012	0.0009	0.0005	0.0025	0.0002
efficiency	99.6	99.6	94.2	99.9	98.7	99.0	99.5	97.3	99.8

0.216 wt% (60 gsm)									
	1st Batch			2nd Batch			3rd Batch		
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8	#9
Empty Bottle	13.133	13.179	14.577	14.568	14.552	14.522	14.526	14.579	14.553
Empty Botle + Filtrate	16.456	16.679	17.427	18.374	18.213	16.401	18.203	19.104	17.204
After Evaporation	13.137	13.182	14.581	14.571	14.552	14.528	14.527	14.581	14.558
After Evaporation - Empty	0.004	0.003	0.004	0.003	0.000	0.006	0.001	0.002	0.005
Total Filtrate Weight	3.323	3.500	2.850	3.806	3.661	1.879	3.677	4.525	2.651
C2	0.0012	0.0009	0.0014	0.0008	0.0000	0.0032	0.0003	0.0004	0.0019
efficiency	98.7	99.1	98.5	99.2	100.0	96.6	99.7	99.5	98.0

Water flux (Oil/water surfactant-stabilised emulsion)

0.216 wt% (60 gsm)

1st batch

Time (min)		5.00	10.00	15.00	20.00
Weight (g)	#1	0.50	0.90	1.25	1.58
	#2	0.40	0.75	0.98	1.23
	#3	0.36	0.61	0.83	1.10
Average (g)		0.42	0.75	1.02	1.30
<u>2nd batch</u>					
Time (min)	-				
Time (min)		5.00	10.00	15.00	20.00
Weight (g)	#1	0.32	0.75	1.14	1.54
	#2	0.48	0.84	1.12	1.33
	#3	0.70	1.34	1.79	2.05
Average (g)		0.50	0.98	1.35	1.64
<u>3rd batch</u>					
Time (min)	-				
Time (min)		5.00	10.00	15.00	20.00
Weight (g)	#1	0.41	0.86	1.24	1.67
	#2	0.32	0.74	1.10	1.51
	#3	0.63	1.14	1.52	1.66
Average (g)		0.45	0.91	1.29	1.61

0.027 wt% (30 gsm)

1st batch

Time (min)		5.00	10.00	15.00	20.00
Weight (g)	#1	1.11	2.35	3.55	4.60
	#2	1.03	2.44	3.85	4.98
	#3	1.20	2.42	3.62	4.80
Average (g)		1.11	2.40	3.67	4.79
<u>2nd batch</u>					
Time (min)		5.00	10.00	15.00	20.00
Weight (g)	#1	1.46	3.10	4.50	5.72
	#2	1.92	3.56	5.20	5.70
	#3	1.17	2.89	4.57	6.21
Average (g)		1.52	3.18	4.76	5.88
<u>3rd batch</u>					
Time (min)		5.00	10.00	15.00	20.00
Weight (g)	#1	1.02	2.31	3.30	4.03
	#2	1.05	2.46	3.87	5.05
	#3	1.10	3.05	4.87	6.35
Average (g)		1.06	2.61	4.01	5.14

0.216 wt% (60 gsm)

1st batch

Time (min)		5.00	10.00	15.00	20.00
Weight (g)	First time	0.62	1.12	1.60	2.05
	Second time	0.21	0.42	0.60	0.75
	Third time	0.13	0.21	0.29	0.35
<u>2nd batch</u>	-				
Time (min)		5.00	10.00	15.00	20.00
Weight (g)	First time	0.49	1.00	1.49	1.94
	Second time	0.19	0.36	0.53	0.62
	Third time	0.08	0.15	0.20	0.22
<u>3rd batch</u>	-				
Time (min)		5.00	10.00	15.00	20.00
Weight (g)	First time	0.37	0.72	1.07	1.41
	Second time	0.21	0.41	0.61	0.76
	Third time	0.09	0.17	0.22	0.25

0.027 wt% (30 gsm)

1st batch

Time (min)		5.00	10.00	15.00	20.00
Weight (g)	First time	1.72	3.30	4.87	6.42
	Second time	1.84	2.72	3.52	4.32
	Third time	0.86	1.66	2.46	3.22
<u>2nd batch</u>	-				
Time (min)		5.00	10.00	15.00	20.00
Weight (g)	First time	1.56	3.08	4.42	5.74
	Second time	1.31	2.49	3.63	4.72
	Third time	0.93	1.80	2.65	3.46
<u>3rd batch</u>	-				
Time (min)		5.00	10.00	15.00	20.00
Weight (g)	First time	1.60	3.13	4.62	6.10
	Second time	1.32	2.67	4.01	5.32
	Third time	1.01	1.91	2.80	3.65

Separation efficiency (Oil/water surfactant-stabilised emulsion)

0.216 wt% (60 gsm)									
	1st Batch			2nd Batch			3rd Batch		
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8	#9
Empty Bottle	13.183	14.578	14.568	14.528	14.530	14.640	14.528	14.530	14.640
Empty Botle + Filtrate	14.525	15.706	15.468	16.000	15.760	16.490	16.088	16.000	16.134
After Evaporation	13.190	14.582	14.570	14.534	14.536	14.651	14.532	14.539	14.643
After Evaporation - Empty	0.007	0.004	0.002	0.006	0.006	0.011	0.004	0.009	0.003
Total Filtrate Weight	1.342	1.128	0.900	1.472	1.230	1.850	1.560	1.470	1.494
C2	0.0052	0.0035	0.0022	0.0041	0.0049	0.0059	0.0026	0.0061	0.0020
efficiency	94.4	96.2	97.6	95.6	94.8	93.7	97.3	93.5	97.9

0.027 wt% (30 gsm)									
	1st Batch			2nd Batch			3rd Batch		
Weight (g)	#1	#2	#3	#4	#5	#6	#7	#8	#9
Empty Bottle	14.582	14.559	13.139	14.522	14.526	14.579	14.721	14.546	14.510
Empty Botle + Filtrate	18.678	18.433	17.122	20.111	20.202	18.623	18.520	19.498	18.634
After Evaporation	14.637	14.618	13.203	14.611	14.621	14.642	14.783	14.617	14.563
After Evaporation - Empty	0.055	0.059	0.064	0.089	0.095	0.063	0.062	0.071	0.053
Total Filtrate Weight	4.096	3.874	3.983	5.589	5.676	4.044	3.799	4.952	4.124
C2	0.0134	0.0152	0.0161	0.0159	0.0167	0.0156	0.0163	0.0143	0.0129
efficiency	85.7	83.7	82.8	83.0	82.1	83.4	82.6	84.7	86.3

0.216 wt% (60 gsm)									
	1st Batch			2nd Batch			3rd Batch		
Weight (g)	First time	Second time	Third time	First time	Second time	Third time	First time	Second time	Third time
Empty Bottle	14.528	14.530	14.640	14.529	14.721	14.540	14.642	14.559	13.139
Empty Botle + Filtrate	16.494	15.282	14.991	16.269	15.342	14.763	16.021	15.318	13.389
After Evaporation	14.539	14.545	14.655	14.537	14.731	14.548	14.644	14.574	13.149
After Evaporation - Empty	0.011	0.015	0.015	0.008	0.010	0.008	0.002	0.015	0.010
Total Filtrate Weight	1.966	0.752	0.351	1.740	0.621	0.223	1.379	0.759	0.250
C2	0.0056	0.0199	0.0427	0.0046	0.0161	0.0359	0.0015	0.0198	0.0400
efficiency	94.0	78.7	54.4	95.1	82.8	61.7	98.5	78.9	57.3

0.027 wt% (30 gsm)									
	1st Batch			2nd Batch			3rd Batch		
Weight (g)	First time	Second time	Third time	First time	Second time	Third time	First time	Second time	Third time
Empty Bottle	13.179	14.568	14.579	14.573	14.531	14.582	14.578	14.529	14.553
Empty Botle + Filtrate	19.342	18.874	17.799	20.263	19.251	18.042	20.572	19.823	18.203
After Evaporation	13.288	14.650	14.670	14.667	14.640	14.681	14.666	14.634	14.646
After Evaporation - Empty	0.109	0.082	0.091	0.095	0.110	0.099	0.088	0.105	0.093
Total Filtrate Weight	6.163	4.306	3.220	5.691	4.720	3.460	5.994	5.294	3.650
C2	0.0177	0.0190	0.0283	0.0166	0.0232	0.0287	0.0147	0.0198	0.0255
efficiency	81.1	79.7	69.8	82.3	75.2	69.4	84.3	78.8	72.8

Appendix II

Please note that there was a minor difference in terms of experiment in the published paper as compared to the relevant sections in this thesis: 31L of fluid, instead of 34 L, was used for all the flux and separation tests. This led to slight differences in measurement in flux and separation efficiency.



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Cite this: *RSC Adv.*, 2016, 6, 21435

Received 22nd December 2015
Accepted 12th February 2016

DOI: 10.1039/c5ra27413c

www.rsc.org/advances

Cellulose nanofibre aerogel filter with tuneable pore structure for oil/water separation and recovery†

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A cellulose nanofibre aerogel filter with tuneable pore structure exhibiting super-hydrophilic and underwater-super-oleophobic behaviours is synthesized by a facile method of cross-linking between cellulose nanofibres and polyamideamine-epichlorohydrin (PAE). The prepared aerogel filter showed excellent oil/water separation efficiency for both oil/water mixtures (100%, even after 10 cycles), and oil/water surfactant-free emulsion (98.6%), which is driven solely by gravity. In addition, the specific structure can de-emulsify oil/water emulsion. The results showed that the cellulose aerogel filter can be used for oil/water separation and recovery.

With the rapid industrial growth, a large amount of oily wastewater is generated daily in many industries such as oil and gas, petrochemical, pharmaceutical, metallurgical and food processing industries.¹ Traditional techniques for oil/water separation including flotation,^{2–4} biological treatment^{5,6} and coagulation,^{7–9} are either energy or chemical-intensive or not applicable to the separation of oil/water emulsions.^{10,11} Recently, increasing attention has been paid to hydrophobic/oleophilic materials for oil/water separation particularly *via* absorption.^{12–14} However, they are still faced with some challenges.^{14–16} Firstly, they absorb both water and oil during separation, limiting both selectivity and efficiency. Second, they are restricted by the oil fouling and clogging in the pore structures, reducing absorption capacity and fluid flux. Moreover, these materials can easily cause secondary pollution as the absorbed oils, especially those with high viscosity are hard to clear during post-treatments.¹⁷ Furthermore, the recovery of the oil absorbed in these materials is still difficult.¹⁸ Consequently, these factors are slowly moving researchers' interest away from hydrophobic/oleophilic materials towards hydrophilic/oleophobic materials in oil/water separation.¹⁹ Many existing hydrophilic/oleophobic materials are fabricated using petroleum-derived materials, and

modified using harmful chemicals such as those with fluoride groups to gain oleophobic properties.^{20–22} Therefore, there is still large room for improvement to minimize their environmental impact.

Cellulose is a bio-derived material that is abundant, environmentally friendly and renewable.²³ With the preponderance of hydroxyl functional groups, cellulose possesses a strong affinity to water.²⁴ Along with the advantages mentioned above, the hydrophilic nature of cellulose makes it attractive for the design of materials with underwater super-oleophobic properties. In this paper, we demonstrate an aerogel filter, which was fabricated using cellulose nanofibres, with existing applications in ultrafiltration.²⁵ The prepared aerogel shows excellent super-hydrophilicity and underwater super-oleophobicity leading to excellent performance in the separation of both oil/water layered mixture and oil-in-water emulsion. Fig. 1 shows the synthesis procedure of the cellulose aerogel. Cellulose nanofibres were first mixed with polyamideamine-epichlorohydrin

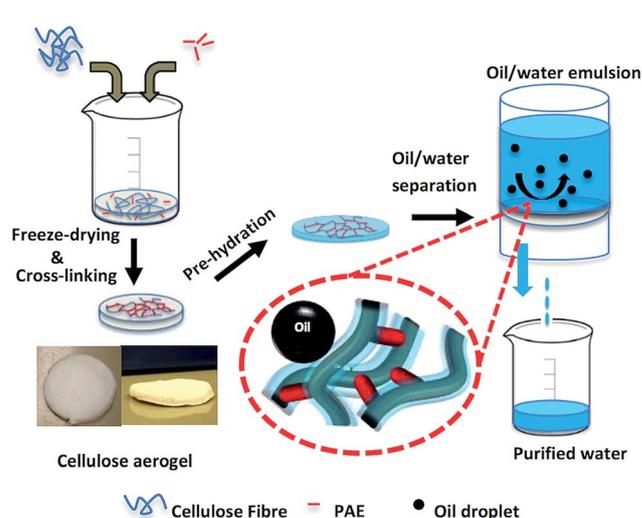


Fig. 1 Schematic of fabrication process of the cellulose aerogel filter and its application in oil/water separation.

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† Electronic supplementary information (ESI) available: Experimental details, characterization, mechanism analysis. See DOI: 10.1039/c5ra27413c

(PAE) forming a well-dispersed suspension. The cellulose nanofibre/PAE suspension was then freeze-dried, followed by heating at 120 °C to promote cross-linking between cellulose nanofibres and PAE (refer to S2† for more details). The reaction mechanism between azetidinium groups of PAE and carboxyl group of cellulose nanofibres reinforces the cellulose aerogel. More importantly, the formation of the water-insoluble PAE networks prevent the fibre-bond detachment of PAE-cross-linked cellulose aerogel re-wetted in water. These lead to wet-strength development of the cellulose aerogel filter, making it suitable material to be used underwater.²⁶ The pore structure of the aerogels can be easily tailored by altering the initial solids content in the cellulose suspension before freeze-drying.

The cross-sectional morphology and structure of the cellulose aerogel were characterized using scanning electron microscopy (SEM) and mercury porosimetry, as shown in Fig. 2a and b, respectively. The structure is composed of many nanofibre layers, in between which, there are pores with sizes ranging from 0 up to 300 μm, as shown in Fig. 2b. The wettability of water and oil on the cellulose aerogel was also characterized. The oil contact angle (155.6 °C ± 2.5 °C) on the cellulose aerogel indicates high oleophobicity. It was measured by placing 3 μl of oil on the surface of the cellulose aerogel underwater (Fig. 2c). The cellulose aerogel also exhibits super-hydrophilicity with a contact angle of almost 0 °C for water in air (Fig. 2d).

The separation efficiency of the cellulose aerogel filter for oil/water driven only by gravity was tested in the set up shown in Fig. 3b and S2.† For separation of oil/water-layered mixture, four types of oil, namely mineral oil, hexadecane, canola oil and peanut oil were tested (Movie S1†). The prepared cellulose aerogel can achieve almost 100% rejection of all these oils, even after 10 cycles (Fig. 3a, also refer to S4 and Movie S2† for recovery or aerogel between cycles). It is worth noting that due to the cross-linking by PAE, the cellulose aerogel possesses high wet strength (S7†) and durability underwater. The separation efficiency of the cellulose aerogel filter was further evaluated using

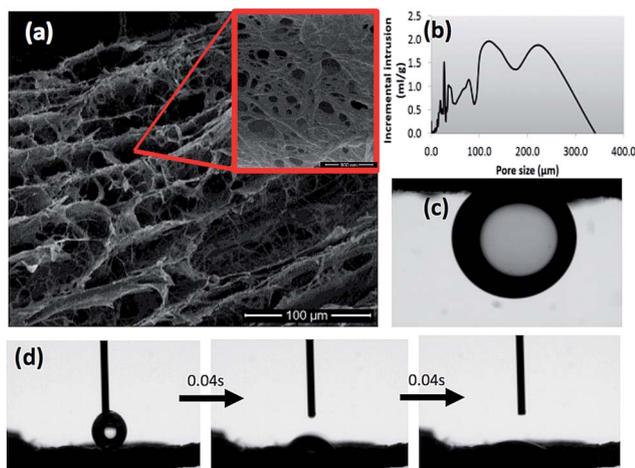


Fig. 2 (a) Cross-section SEM image of the cellulose aerogel. (b) Pore sizes and distribution of the cellulose aerogel. (c) Oil contact angle (>150 °C) on the cellulose aerogel underwater. (d) Water contact angle on the cellulose aerogel in air.

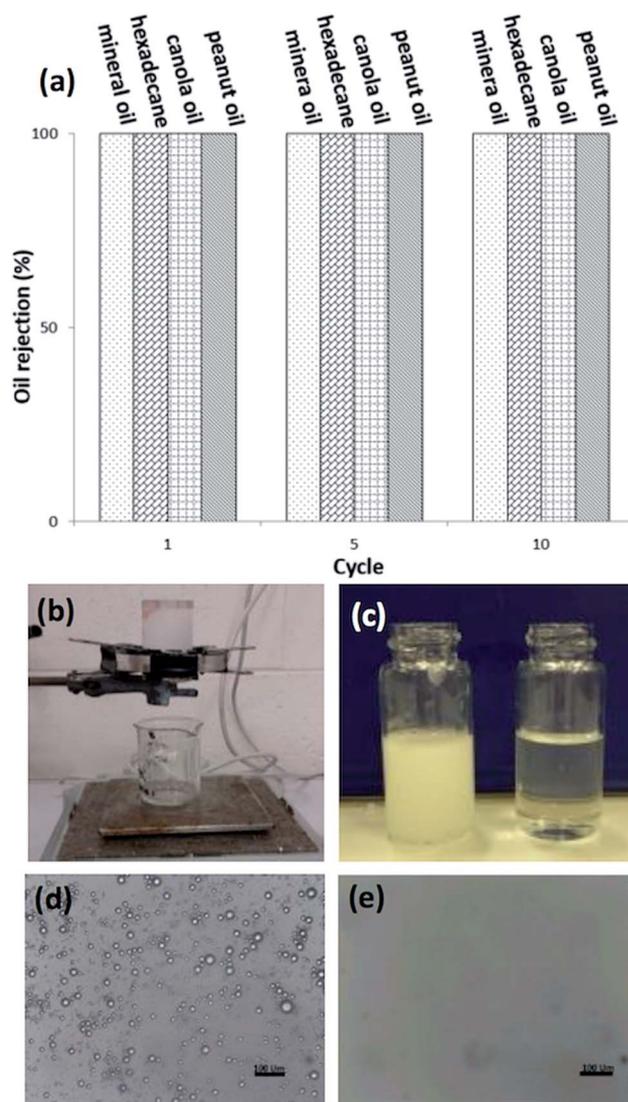


Fig. 3 (a) Separation efficiency of the cellulose aerogel to various oil/water layered mixture. (b) Experimental set-up for oil/water separation testing. (c) Comparison between oil/water emulsion (left) and filtrate (right). (d) & (e) Microscopic images of emulsion and filtrate, respectively.

oil/water emulsion (Movie S3†). Fig. 3c shows the comparison between the oil/water emulsion (left) and the filtrate collected (right).

The significant change in colour and light transmission between the two samples indicates the excellent separation efficiency. The microscope image shows that the oil/water emulsion contains a large amount of oil droplets of several microns in diameter (Fig. 3d). In comparison, the filtrate collected barely contains any oil droplet (Fig. 3e).

In addition, gravimetric analysis was also used to quantify the oil rejection. The oil rejection ($R\%$) was calculated as follows:

$$R(\%) = (1 - C_f/C_0) \times 100 \quad (1)$$

where C_0 and C_f are the concentrations of oil in the emulsion and filtrate, respectively. An oil rejection of 98.6% from the oil-in-water

emulsion was achieved by the aerogel filter prepared using a cellulose nanofibre concentration of 0.0337 g ml^{-1} (S5†).

The pore structures of the cellulose aerogels can be controlled by altering the solids content in the cellulose suspension before freeze-drying. As shown in Fig. S5,† higher solids content in cellulose suspension results in a more compact pore structure. The effect of pore structures on deionized (DI) water flux (S3†) and oil rejection to oil-in-water emulsion were also evaluated. Aerogel with cellulose nanofiber concentration of 0.0197 g ml^{-1} had a DI water flux of 27 022 LMH, but only 56.3% oil rejection, due to its relatively loose pore structure. By contrast, the aerogel prepared with cellulose nanofiber concentration of 0.0337 g ml^{-1} had a much lower DI water flux (2405 LMH), but excellent oil rejection (98.6%) due to its more compact pore structure (S5†). Clearly, there is a trade-off between flux and oil rejection as the pore structure of the cellulose aerogel changes. Therefore, taking advantage of the tuneable pore structure, this type of cellulose aerogel can be tailored to separate oil droplets with various sizes from water while achieving an optimal fluid flux.

Fig. 4a shows the separation testing for oil/water emulsion after approximately half the original volume had been filtered. Surprisingly, the well-dispersed oil-in-water emulsion had developed a de-emulsified oil layer on top, as shown by light yellow colour appearing at the top. By contrast, the original emulsion remained stable and no separate layer was formed if left alone (Fig. 4b) for equal amount of time. This indicates that the separation process by the aerogel filter de-emulsified the stable oil/water emulsion (Fig. 4c). This may be attributed to the specific structure of the cellulose nanofibre aerogel. At the surface of the hydrated cellulose aerogel, small oil droplets do

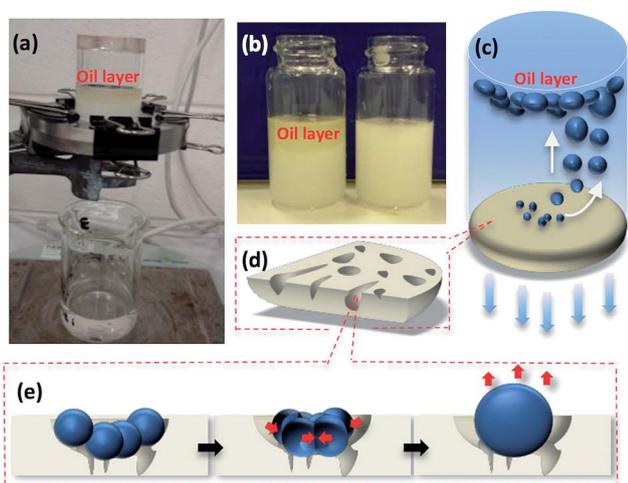


Fig. 4 (a) Separation process running for 1.5 h since the beginning. Oil/water emulsion has turned into a layered mixture with the light yellow oil layer floating on top. (b) Comparison between two emulsions (both prepared at the same time); one was used for separation testing (left), while the other was left alone for equal amount of time (right). (c) Proposed schematic of the separation process. Droplets in blue are oil droplets. (d) Magnified version of a cellulose aerogel part. (e) Proposed schematic of small oil droplets coalescing in the void of the surface of the aerogel.

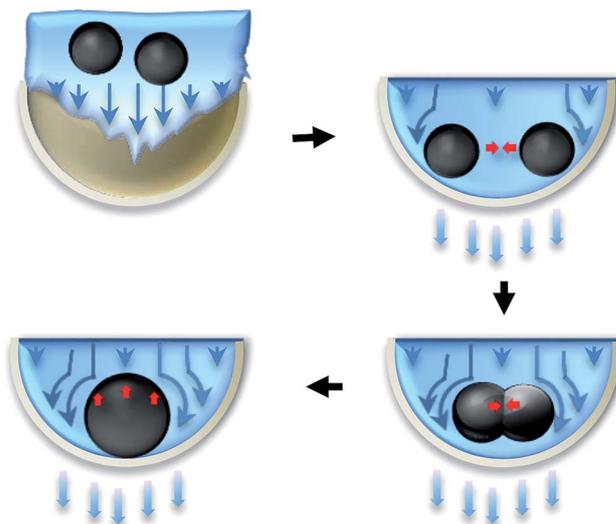


Fig. 5 Scheme of the coalescence of oil droplets in the void of the aerogel filter surface.

not wet the surface because of the hydration layer surrounding the nanofibres. Owing to the pothole-like surface structure of the cellulose aerogel (Fig. 4d, also refer to S1† for SEM images), the small oil droplets are trapped in the voids on the surface while the continuous phase (water) is passing through the walls of the voids. The flowing motion of the continuous phase eventually results in the accumulation of small oil droplets inside the void. The small droplets are then pulled together, coalescing to form a single droplet, large enough to rise out of the continuous phase (water) due to the increasing buoyancy force (Fig. 4e).

Over the course of this process, two colliding oil droplets are initially kept apart by various interactions in between them.²⁷ The inertia effects in the viscous flow around the droplets originate a shear-lift force perpendicular to the direction of the flow,²⁸ as shown in Fig. 5. This shear-lift force acts externally on both droplets, counteracting these interactions. This results in the collision, hence the coalescence of the droplets.

As described by Spicer,²⁹ the coalescence of two droplets is initiated when a liquid neck forms between them. The droplets being pulled together are then combined *via* flow of oil through the liquid neck. As the coalescence proceeds, the neck radius of the coalescing structure gradually increases, and the interfacial tension eventually drives it into a sphere droplet to achieve a minimization of the surface-to-volume ratio.³⁰ The newly formed single droplet will have a larger diameter, which results in larger buoyancy force. Once the buoyancy force of the oil droplet is greater than the sum of drag and gravitational forces, the oil droplet will start floating upwards. We estimated that at a fluid velocity of $6.7 \times 10^{-4} \text{ m s}^{-1}$, the minimum diameter required for a coalesced oil droplet to float upwards is about 89 μm (refer to S6† for detailed calculations). This means that coalescence of a number of the original droplets are needed to form oil droplets with large enough diameter to float.

Conclusions

In summary, we reported an aerogel filter made of bio-derived, renewable and environmental friendly cellulose nanofibres for an oil/water separation process. The aerogel can be easily fabricated on a large scale by freeze-drying cellulose suspension, followed by cross-linking with PAE. With the super-hydrophilic and underwater super-oleophobic properties, excellent wet strength and pothole-like surface structure, it allows excellent oil/water separation efficiency to not only oil/water mixture (100%, even after 10 cycles), but also oil/water surfactant-free emulsion (98.6%). We also demonstrated that the pore structure of this aerogel could be easily engineered to fulfil the need of separating oil-in-water emulsion with various droplet sizes while achieving an optimal fluid flux. The aerogel filter also caused the transformation of stable oil/water emulsion to a de-emulsified mixture, which makes oil recovery easier. In addition, the separation was solely driven by gravitational force without any external power or additional facilities.

Acknowledgements

The authors acknowledged the use of facilities in Monash Centre for Electron Microscopy (MCEM). We would like to acknowledge financial support from the Australian Research Council, Australian Paper, Carter Holt Harvey, Circa, Norske Skog and Visy through the Industry Transformation Research Hub grant IH130100016. Zhiyong He would like to acknowledge MGS and FEIPRS scholarships from Monash University.

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