Recovery of Oil from Palm Oil Mill Effluent using Polypropylene Micro/nanofiber

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Abstract

1. Introduction

In palm oil mill industry, oil losses during the milling process are unavoidable. The main sources of oil losses are through wastewater clarification, sterilizer condensate and hydro-cyclone, which affect the oil extraction rate, % (OER) and the oil extraction efficiency, % (OEE) of the mills [1], [2]. In palm oil milling process, palm oil mill effluent (POME) is the largest waste generated where 2.5 tons of POME are produced from the average in every ton of oil extracted and typical raw POME contains about 1% or range in 4,000 mg/L of oil and grease [3]–[5]. The presence of residual oil in POME may cause serious environmental pollution due to elevation of biological oxygen demand (BOD) and chemical oxygen demand (COD) values, which could detrimental to aquatic organisms and surrounding habitats if untreated [6]. High concentration of BOD and COD values means high presents of organic matter, thus high consumption of oxygen for the microorganisms to decompose the organic matter [7]. Therefore, against the oil layer could reduce the biological activity of conventional biological ponding system since the suspended

microbes are surrounded by oil layer. Hence, the presence of residual palm oil in the river ought to be regarded as hazardous material in order to safeguard the environment. In light of this, palm oil mills are typically required by the local authority to treat POME to meet stringent limits before the POME can be discharged into the environment.

Effective and efficient treatment of POME still remain a challenge for the palm oil millers because of the nature of the residual oil in the POME. The residual oil in POME can be classified into four measured size, such as free oil (>150 μm), dispersed oil mixture (20-150 μm), emulsified oil (5 – 20 μm) and soluble oil mixture (<5 μm) [8]. The free oil in POME could easily be removed by the conventional techniques, such as skimming or gravitational separation as it is readily floating to the surface [9]. However, the dispersed oil and other smaller oil in the water phase causing the oil not readily separable using conventional techniques, hence derived into oil losses.

The oil losses mean losing profit annually. The production of palm oil keeps in increasing globally due to the high demand in the food industry and consumer products. This causes an increase in the amount of POME. Often times, the approach is to breakdown the pollutants to achieve the allowable discharge limits set by the government regulations such as open ponding treatment [1], biological wastewater treatment [10], membrane filtration [3], a series of treatment process in aerobic and anaerobic digestion (i.e. sedimentation-coagulation-flocculation) [11], [12] and physiochemical treatment [13]. Recently, more efforts are done to recover the residual oil in the POME by using oil trap tank [14]. Recovering the residual oil gives double benefits which are reducing the organic loads in the POME and also increasing the OER.

Adsorption using sorbent is likely the most feasible and effective technique in recovery of residual oil in water [15]. The sorbent property such as hydrophobic and oleophilic, are the most important factor in oil-water adsorption process. In general, adsorption in oil-water mixture involved three steps; adhesion and diffusion of oil into the sorbent surface, adsorb the oil through

capillary action, and lastly coalescence of oil droplets through intermolecular forces on the sorbent structures [16]. Several sorbents have been reported such as rubber powders [17]; kapok fibrous [18]; chitosan , bentonite, activated carbon [19]; and fly-ash boiler [20]. These sorbents are stated to be represent as an effective oil recovery because of high oil adsorption capacity and environmental friendly. However, these techniques have not been commercialized most likely due to the uneconomical and lack of practicality reasons such as reusability and separation after adsorption [21], [22].

In marine and petroleum industry, adsorption using fibrous sorbent materials, both natural and synthetic based have been well established. Several researches such as, adsorption capacity, reusability, adsorption using several type of oil and separation after adsorption were reported [23]–[26]. Despite the fact that PP based fibrous sorbent have been investigated as an ideal materials for oil removal in marine oil-spill due to its low density, low water uptake and excellent physical and chemical resistance [27], the availability of material and feasible fabrication using melting process is one of its advantages. Recently, the number of plastic wastes that composed from polymers increased since it were first introduced [28]. Amongst other, PP is the second highest percentage of waste produced after low density polyethylene (LDPE) [28]. Therefore, the availability of the material is easily to obtain, at the same time helps to reduce the number of plastic waste produced.

In this paper, a novel work on using polypropylene micro/nanofiber (PP-MNF) to recover residual oil from POME is reported. The oil recovery from PP-MNF that consists of adsorption

and extraction processes, reusability and regeneration of used PP-MNF, quality of the oil extracted and the physiochemical study of the PP-MNF are well presented.

2. Methods

2.1. Preparation of polypropylene micro/nanofiber

In this work, PP-MNF was used as the oil adsorbent to recover residual oil from POME. The PP-MNF was produced using melt blowing equipment (Zetta Co. Ltd., Japan) in the Faculty of Engineering, Universiti Malaysia Sabah and assembled like bundle of loose cotton. The melt blowing equipment consisted of four major components such as extruder, die assembly, web formation and winding. The PP granular powder (PP, Sun-Allomer) was gravity fed from the hopper to the extruder and heated at 300°C, to melt the PP. Then, the rotating screws carried the melted PP, to the die assembly at 10 Hz and sprayed through spinneret (0.8 mm of diameter) to a collector or web formation, at a distance of 2.4 m. Hot air, also called as winding was supplied at a maximum flow rate (approximately 25 m^3/min).

2.2. Sample of POME

The POME sample was collected from a local palm oil mill located in Kota Marudu, Sabah, Malaysia. The collection was in the combined POME pit, which is the location before the wastewater flows into the cooling pond. The POME sample collected was kept in 18 gallons containers and stored at room temperature for further experiment.

2.3. Determination of oil adsorption capacity

The determination of oil sorption capacity of PP-MNF was conducted using refined palm oil (Vesawit Cooking Oil). A 400 mL of oil was prepared into a 1000 mL beaker and 1 g of raw PP-MNF was weighed (W_0). Then, the PP-MNF was immersed in the oil for 10 min to allow for

complete adsorption and soaking process. The PP-MNF was removed and suspended for 1 min to remove the loosely attached oil on the fiber. Next, the PP-MNF with oil adsorbed was weighed (W_1). The determination of oil adsorption capacity is expressed by gravimetric basis as in Eq. (1).

$$Oil\ adsorption\ capacity\ \ (g\ of\ oil/g\ of\ MNF) = \ (W_1 - \ W_0)/W_0 \qquad \text{Eq. (1)}$$

Then, the extraction of oil from the PP-MNF was done manually using pressing technique by both hands with wearing glove. The oil was collected and weighed ($W_{oil,\ pressed}$). Afterward, the pressed PP-MNF was weighed (W_2).

The extraction yield by the pressing technique is expressed by the weight of oil extracted from pressing divided by the weight of oil adsorbed on PP-MNF as quoted in Eq. (2). Whilst, the specific oil pressing capacity is expressed as the weight of oil extracted from pressing divided by the weight of raw fiber which quoted in Eq. (3).

$$Pressing\ extraction\ \ yield\ (\%) = ((W_{oil,pressed}\ )/(W_1 - \ W_0)) \times \ 100\% \qquad \text{Eq. (2)}$$

$$Specific\ Oil\ pressing\ capacity\ (g\ of\ Oil/g\ of\ MNF) = \ (W_{oil,pressed}\ )/W_0 \qquad \text{Eq. (3)}$$

Despite the repeated pressing, there was oil retained in the PP-MNF assembly. The amount of oil retained in the PP-MNF after repeated pressing was called as the oil retention capacity of the fiber. The oil retention capacity of the PP-MNF is expressed as the weight of oil retained in PP-MNF divided by the weight of raw PP-MNF as quoted in Eq. (4).

$$Oil\ retention\ capacity\ (g\ of\ oil/g\ of\ MNF) = \ (W_2 - W_0)/W_0 \qquad \text{Eq. (4)}$$

2.4. Recovery of residual oil from POME using PP-MNF

In order to evaluate the industrial applicability of the PP-MNF, it was used to recover residual palm oil from the actual POME sample. In this works, the studies on oil recovery from POME which consisted of adsorption and extraction process were performed using an experimental setup shown in Figure 1. Figure 1 shows the schematic diagram of the experimental setup for oil adsorption process from POME. The tank consisted of three compartments. The PP-MNF was placed in the middle of the tank to ensure the maximum contact between POME and PP-MNF. The tank was filled with 18 L of POME sample that was collected from a local palm oil mill and was used as received without any pretreatment. A pump was used to recirculate the POME to create flow in the tank as well as distributing the heat as desired. Heating was required in order to achieve the desired temperature of the POME to imitate the actual temperature of POME in the mill.

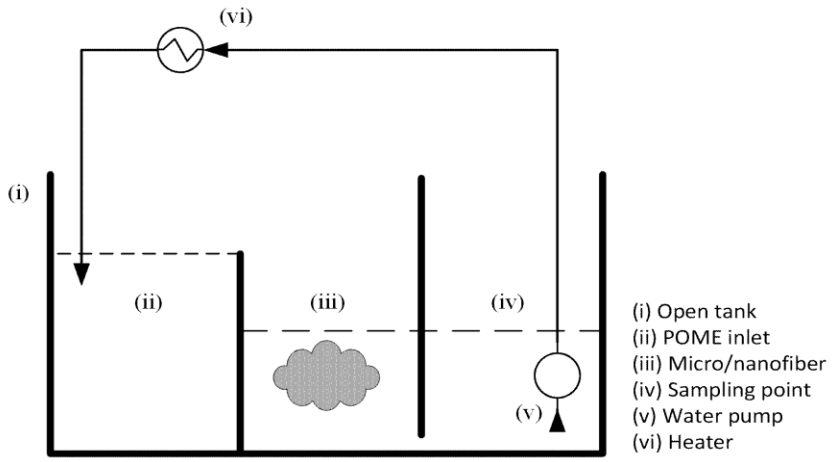


Figure 1. The schematic diagram of the experimental set up for oil adsorption process using PP-MNF. The open tank (i) was divided into three compartments; POME inlet (ii), adsorption process using PP-MNF (iii) and sampling point (iv). This system was supported by 600 L/h of water pump (v) to recirculate the POME and heater (vi) that was set at 60°C.

133 *2.4.1. Adsorption of residual oil from POME*

134 To begin with, 1 g of raw PP-MNF (A_0) was placed in the middle of the tank and let it immersed
135 gravitationally in the POME and was run for 12 h [29]. Then, the PP-MNF was removed and
136 suspended for 1 min to drain out water and the loosely attached oil on the PP-MNF. The PP-MNF
137 with adsorbate was weighed (A_1). Three replication have been performed, to determine the
138 optimum adsorption capacity and oil recovery from POME using one g of PP-MNF. The total oil
139 content in the system ($A_{oil,\ system}$) was implied by determining the oil concentration in the POME
140 sample, where 250 mL sample was collected from sampling point for initial and final oil
141 concentration using the Standard Method of Oil and Grease Determination [30].

142 *2.4.2. Extraction of oil from the PP-MNF*

143 Subsequently, the extraction of oil from the PP-MNF was performed by hand pressing. The
144 pressing was done until no more droplets detached from the PP-MNF. The completely pressed PP-
145 MNF was weighed and labelled as A_2. The extracted adsorbate was weighed ($A_{adsorbate,\ pressed}$),
146 subsequently dewatered in oven at 104-106 °C overnight. Then, the dewatered adsorbate was
147 mixed with 100 mL of n-hexane and filtered using vacuum filter to remove the solid particles. The
148 filtrate was then heated in a distillation unit to evaporate and to recover the solvent. The extracted
149 oil was weighed and labelled as $A_{oil,\ pressed}$.

150 In this technique, the pressing yield was calculated by dividing the weight of adsorbate that
151 pressed from the PP-MNF and the weight of adsorbate that adsorbed on the PP-MNF, which
152 quoted as Eq. (5).

153 $$POME\ pressing\ extraction\ \ yield\ (\%) = ((A_{adsorbate,pressed}\ )/(A_1 - A_0)) \times 100\% \qquad \text{Eq. (5)}$$

Whilst, the specific oil pressing capacity from POME was calculated by using Eq. (6).

$$Specific\ Oil\ pressing\ capacity\ (g\ of\ Oil/g\ of\ MNF) = (A_{oil,pressed})/A_0 \quad \text{Eq. (6)}$$

Then, the oil recovery efficiency was calculated as the weight of oil extracted divided by the total oil content in the system, as expressed in Eq. (7)

$$POME\ oil\ recovery\ efficiency\ (\%) = ((A_{oil,pressed})/(A_{oil,system})) \times 100\% \quad \text{Eq. (7)}$$

The retention capacity was determined by calculating the weight of adsorbate that retained in the PP-MNF ($A_2 - A_0$) divided by the weight of raw PP-MNF (A_0), which similar to Eq. (8).

$$Oil\ retention\ capacity\ (g\ of\ oil/g\ of\ MNF) = (A_2 - A_0)/A_0 \quad \text{Eq. (8)}$$

2.5. Reusability of PP-MNF

The reusability of the PP-MNF was evaluated by recycling the pressed PP-MNF. The procedures in Section 2.4.1 and Section 2.4.2 were repeated by using another 1 g of PP-MNF, which then recycled for 19 times in 18 L of fresh POME.

2.6. Extraction of oil from Pressed PP-MNF using chemical extraction

2.6.1. Solvent extraction

The solvent extraction was performed on the pressed PP-MNF (A_2) from Section 2.4.2. In the solvent extraction technique, the PP-MNF was soaked in 100 ml n-hexane (99% purity) and gently stirred for about 10 min to ensure complete contact between the solvent and the oil in the PP-MNF. The washed PP-MNF was then suspended for 1 min to drain out excess n-hexane and removed

from the beaker, subsequently dried in an oven at 70 °C for 30 min. Then, the PP-MNF was weighed (A_3). The solvent solution was filtered using vacuum pump to remove solid particles and drained using separator funnel through 10 g of anhydrous sodium sulphate, to eliminate water droplets. Then, it was distilled using evaporator to extract the oil and to recover the solvent. The extracted oil was weighed ($A_{oil,\ solvent}$) and stored for oil analysis.

The extraction yield was determined by calculating the weight of oil extracted divided by the initial weight of PP-MNF; as expressed in Eq. (9)

$$Solvent\ extraction\ yield\ (\%) = ((A_2 - A_3)/A_2) \times 100\% \quad \text{Eq. (9)}$$

Eventually, the specific oil extraction capacity using solvent was calculated by dividing the weight of extracted oil using solvent extraction with the weight of raw PP-MNF as shown in Eq. (10).

$$Solvent\ specific\ oil\ extraction\ capacity\ (g\ of\ oil/g\ of\ MNF) = (A_{oil,solvent})/A_0 \quad \text{Eq. (10)}$$

2.6.2. Carbon dioxide supercritical extraction technique

The supercritical CO_2 extraction also performed on the pressed PP-MNF from Section 2.4.2 and carried out at the University of Hull laboratory facility. A 0.5 g of sample from pressed PP-MNF (S_2) was extracted by using supercritical CO_2. Supercritical CO_2 technique was performed in a Pyrex container placed inside a water-jacketed stainless steel cell (Parr®) rated to operate at maximum of 300 bar (30 MPa). CO_2 (99.95%) was supplied to the high pressure cell from a cylinder equipped with a dip tube. The pressures were adjusted (± 0.5 bar) by employing a JASCO BP-2080-81 back pressure regulator and the flow rate was maintained at 2 mL/ min using JASCO CO_2 delivery pump. The temperature was maintained at the desired values using a thermostatic

water circulator (± 0.01 °C). The extraction experiments were conducted in a batch manner. After the required extraction time, the high pressure cell was slowly depressurized and the extract was dissolved in heptane (99%) for analysis. The extract fiber was weighed (S_3) and the extracted oil ($S_{oil,\ supercritical}$) was calculated by subtracting the initial and final extracted fiber ($S_2 - S_3$).

The extraction yield and its capacity were determined using equations as in Eq. (9) and Eq. (10), respectively.

2.7. Characterization of PP-MNF and oil extracted

2.7.1. Physiochemical properties of PP-MNF

The physical and chemical changes of the PP-MNF were analyzed over six samples (before, during and after use); such as raw PP-MNF, saturated PP-MNF, pressed PP-MNF, washed PP-MNF, S-CO_2 PP-MNF and reused PP-MNF. The morphology of the PP-MNF were observed by using a scanning electron microscopy (SEM). All but saturated PP-MNF samples were coated with a layer of gold sputtering coater for 100 s to minimize the charging effect, whilst saturated PP-MNF was undergone in cold stage imaging, where the sample was frozen to stabilize water. The average of diameter on the PP-MNF was also measured using image processing software on the SEM images.

The chemical composition of polypropylene based PP-MNF were analyzed using energy dispersive X-ray (EDX) spectrometer connected to the SEM. The changes of bonding configuration by determining the functional group were characterized by using Fourier transform infrared (FTIR, Cary 360).

2.7.2. Components distribution of oil extracted

The oil recovered from the PP-MNF was analyzed on a gas chromatograph (HP6890) connected to a mass spectrometer (HP5973), to determine the components distribution in the extracted oil. The column used for the analysis was Stabilwax® (30 m x 0.32 mm ID x 0.25 µm). The injection temperature was maintained at 250 °C. The oven temperature was maintained 210 °C for 5 min then raised to 230 °C at a gradient of 20 °C/min.

3. Results and discussion

3.1. Oil adsorption capacity of the PP-MNF

The study of oil recovery from POME using PP-MNF was initiated by determining the actual oil adsorption capacity using clean and refined oil. The determination of PP-MNF sorption capacity using refined palm oil is shown in Table 1. The results showed the adsorption capacity of the PP-MNF was ranged from 26.96 to 30.17 g of oil/g of PP-MNF. As in average, the PP-MNF could adsorbed about 28.65 g of oil/g of PP-MNF. This result was higher compared to Rengasamy [31] and Ying [26], where the adsorption capacity of polypropylene fibers using high density oil were 18.8 g of oil/g of fiber and 10 g of oil/g of fiber, respectively. These results can be justified by the active surface area and its diameter [16]. The oil sorption capacity is increase, when the active surface area also increase. The surface area is depends on the sorbent diameter. The diameter of the PP-MNF in this work, was determined in between of micro and nano scale (0.1 - 1 µm), which smaller than other polypropylene fibers; such as19 µm [31] and 10 -15 µm [26]. Hence, the PP-MNF has more active surface.

Furthermore, the adsorption process was observed to occur very fast and completely saturated after 8 to 10 s. This phenomenon was likely associated with oleophilic properties of the PP-MNF. The oleophilic properties, also known as oil-lover present because of non-polar surface area

between PP-MNF and oil. Theoretically, polypropylene has a long chain of hydrocarbon group, consist of CH and CH_2 group with a CH_3 pendant group, which makes the PP-MNF a very non-polar solid molecule [32]. Whilst, the refined palm oil is also a non-polar molecule, as it consists of a long chain of hydrocarbon group which is triglycerides [33]. According to Wade [32], when non-polar molecules are mixed with non-polar molecules, a weak intermolecular force is present between them and this intermolecular force is called London dispersion force. The London dispersion force is one of the van der Waals forces often present in a non-polar solute dissolves in non-polar solvent [34]. It is correlated to the attraction between two non-polar molecules and two temporary dipole are induced together. Hence, it is called induced dipole-induced dipole interactions [34]. Therefore, the adsorption of oil on the PP-MNF occurred due to the non-polar molecules attracted to each other by these weak intermolecular forces [32].

Table 1. Characteristic of refined palm oil sorption on the PP-MNFPP-PP-MNF

Replication	Adsorption capacity (g of oil/ g of PP-MNF)	Extraction yield by pressing (%)	Specific Oil pressing capacity (g of oil/ g of PP-MNF)	Oil retention capacity (g of oil/ g of PP-MNF)
1	26.96	95.23	25.67	2.59
2	28.81	79.89	23.02	2.26
3	30.17	81.44	24.57	2.32
Average	28.65	85.52	24.42	2.39
SD	1.61	8.44	1.33	0.18

Despite the recovery of oil from the PP-MNF, the pressing technique showed that up to 95.23% of oil could be desorbed from the PP-MNF (Table 1). However, variation in the oil desorption yield occurred and showed average of 85.52% yield by pressing technique. The standard deviation was relatively high implying low reproducibility of the pressing technique. This could be due to the random error associated with low weight of PP-MNF used. Oil could stick on fingers during pressing and this oil loss could contribute significantly on the standard deviation because of the

little amount of PP-MNF used. Mechanized pressing that could deliver constant force and larger amount of PP-MNF are expected to produce more reproducible data. The specific oil pressing capacity showed average of 24.42 g of oil/g of PP-MNF, which indicated that approximately up to 20% of oil still remained in the PP-MNF (Table 1). Wade [32] further explained that the London dispersion force requires only small energy to break the forces. This is because the temporary dipoles are not always perfectly symmetrical, hence the induction to another non-polar will be occasionally attracted. However, the attraction could be fairly strong when the size of molecules increase [34]. This is because there are more opportunities for the induced dipole distortion. Hence, there was oil retained in the PP-MNF after pressing.

The oil retention capacity of the PP-MNF after repeated pressing showed an average of 2.39 g of oil/g of PP-MNF (Table 1). This result defined the minimum amount of oil retained in the PP-MNF, hence the optimum pressing performed in desorption process. However, the oil retention capacity is expected to be lower if the pressing was done at higher temperature as it was opposed to the ambient temperature because high temperature could decrease the viscosity of the oil and lower the molecules attractions [35] . According to Davarcioglu [34], the London dispersion force could be affected by the fluid viscosity. High viscosity causes them to resist flow more strongly because the attraction between molecules are strong. In fact, the viscosity is expected to be temperature dependent. Hence, the extraction was intended for ambient condition. Moreover, the oil retention capacity is a critical factor to be determined as excessive force could damage the fiber.

3.2. Recovery of oil from POME using PP-MNF

The actual application of the PP-MNF in industry is critical to be determined. For instance, testing the capability of the PP-MNF to recover residual oil from POME is important because POME contains not just oil but other materials such as water, organics, metals, and also suspended

278 solids [6]. In this study, the recovery of oil from POME consisted of oil adsorption and extraction
279 studies. The adsorption process was done using the experimental setup as shown in Figure 1, whilst
280 extraction was performed physically, by hand pressing. The initial oil content in the setup was
281 determined by measuring the oil concentration of POME and obtained 34.42 to 44.45 g oil in 18
282 L of POME (approximately 1900 - 2500 mg/L of initial concentration).

283 **Table 2.** Residual oil recovery from POME using pressing technique

Replication	Weight of oil in the system (g), $W_{oil, system}$	Adsorption capacity (g of adsorbate [a]/ g of PP-MNF)	Extraction yield by pressing (%)	Specific Oil pressing capacity (g of oil/ g of PP-MNF)	Oil recovery efficiency of pressing (%)	Adsorbate retention capacity (g of adsorbate [a]/ g of PP-MNF)
1	43.21	51.10	97.93	15.90	37.54	5.83
2	44.45	45.25	86.03	10.70	28.42	5.39
3	34.42	43.52	84.92	6.17	20.98	5.85
Average	40.69	46.62	89.62	10.93	28.98	5.69
SD	5.47	3.97	7.21	4.87	8.30	0.26

[a] Adsorbate is a mixture of oil, suspended solid and water

284 *3.2.1. Adsorption of oil from POME*

285 During the adsorption process, the raw PP-MNF was initially observed floated on the POME
286 surface. The floatation of the PP-MNF was due to the present of hydrocarbon chain from
287 polypropylene, hence make it non-polar and hydrophobic (repel water) [16]. However, the raw
288 PP-MNF was slowly sunk in the POME because of the oil adsorbed into the PP-MNF assembly.
289 After 12 h, the PP-MNF was fully soaked and the color was changed into blackish yellow from
290 white fiber. According to Alrawi [36], natural sediments mainly consist of solid particles and
291 debris fibers from mesocarps that completely covered by the residual oil which believed due to the
292 van der Waals interaction forces between them. This is why the PP-MNF became black due to the
293 oily sediments adsorbed in the PP-MNF surface assembly, subsequently increased the capacity of

PP-MNF in POME than using refined palm oil. The result showed an average of 46.62 g of oil/g of PP-MNF, for the adsorption capacity using POME (Table 2).

3.2.2. Extraction of oil from POME by physical separation

The oil adsorbed on the PP-MNF was extracted physically by hands pressing technique. The pressing process obtained an oil that contained suspended solid (solid particles) and water. Therefore, dewatering and oil filtration were carried out to remove water and filter the solid particles in the oil by drying overnight in oven and diluting it with solvent and filtered using vacuum filter, respectively.

Table 2 shows the pressing extraction yield and specific oil pressing capacity from the PP-MNF. The results showed the yield by pressing extraction were ranging between 84.92 to 97.93%. This result indicates that the pressing technique could be the potential desorption technique, as it can desorbed more than 80% from its adsorption capacity. However, the specific oil pressing capacity shows only 10.93 g of oil/g of PP-MNF was desorbed from the PP-MNF, while the rest was solid particles, water and the oil that retained in the PP-MNF (Figure 2). Compared to the refined palm oil adsorption capacity, this result showed a lot lower. This was suggested to the difference between POME and refined palm oil behaviors. Rajakovic and co-workers [37] reported that sorption in real oily wastewater have a very complex interactions between oil, surfactants and wool fibers. Like POME, this oily wastewater from palm oil industry also have a complex mixture due to the presence of water, residual oil and natural sediments [36]. Hence, that is why the adsorption in POME contained of water and solid particles (Figure 2), subsequently lower the oil adsorption capacity.

The low oil adsorption capacity could be explained by the effect of initial oil concentration [16]. Low oil concentration need times to form an attraction between oil and the fiber surface.

Whilst, high oil concentration helps the PP-MNF occupies with oil and reach its saturation capacity faster. The initial oil concentration in this work was ranged between 1900 – 2500 mg/L, which provides an average of 40.69 g of oil in the whole system (Table 2). The PP-MNF should be able to adsorb the oil, however due to emulsified oil dispersed in POME which mainly water, hence reduced the probability of oil contact on the PP-MNF. This could be correlated to the attraction or repulsion interactions between polar and non-polar molecules exist around the PP-MNF [34], thus lower the oil adsorption capacity in 12 h contact time. Wahi and co-workers [16] explained that increasing the contact time could increase the oil adsorption capacity, as well as oil removal from the POME. Therefore, the oil adsorption capacity is expected to be increase as the contact time is increased.

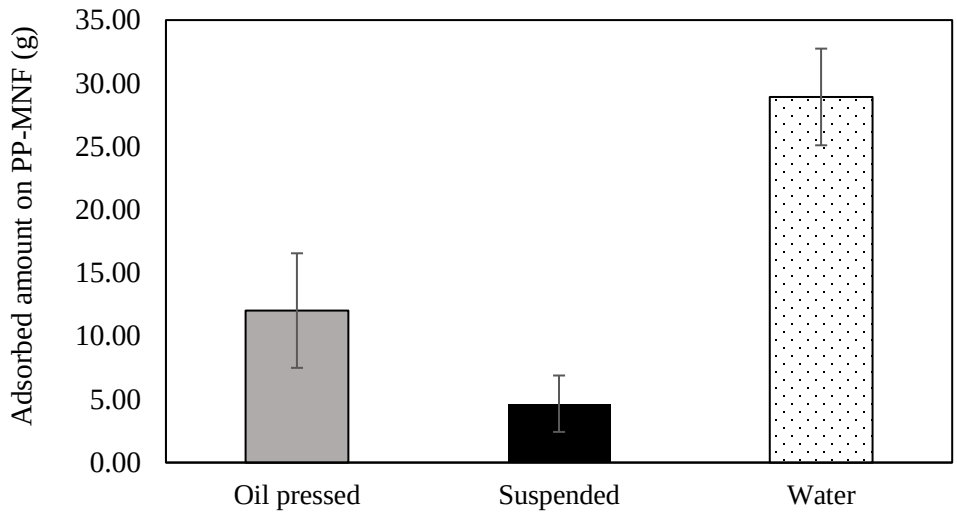
In addition, Table 2 shows the results of adsorbate retention capacity. In this work, adsorbate defined as a mixture of residual oil, water and natural sediments that adsorbed on the PP-MNF during the adsorption process. Thus, the adsorbate retention capacity is defined as the amount of adsorbate retained in the PP-MNF. This also could defined as the maximum compression of the PP-MNF with present of adsorbate, which important to be study because the fiber could be damaged if excessive pressure was applied. The results showed average of 5.69 g of adsorbate/g of PP-MNF that remained on the PP-MNF. This value higher than preliminary result, due to the mixture of oil, water and suspended solid. However, the oil retained on the fiber could be desorbed via chemical extraction due to its polarity effect [32].

3.2.3. Characterization of Adsorbate Adsorbed on PP-MNF

Adsorbate defined as a mixture of water, suspended solid and oil. Figure 2 shows the amount of adsorbate that get adsorbed on the PP-MNF during the adsorption process. The histogram shows that water adsorbed was higher than oil, followed by suspended solid. The results obtained is

suggest affected by the web assembly of the PP-MNF, which packed in loosely form (cotton-like) fiber. The loose fiber assembly or fibers packing structure was noted has pore space between the fibers, which measured around 10 – 50 μm (Figure 3a), thus attributes the large content of air gap. The air gap in the fibers assembly provides a superhydropobic surface [38], hence increase the permeability of oil to the fibers wall through capillary when exposed with bulk of oil (refined palm oil) [34]. However, when exposed with water bulk, the water would interact with air inside the fibers (liquid-air interface), leading to water uptake [38]. Lim and Huang [34] suggested that the interaction of water and air interface might begin when the external pressure (hydraulic pressure) overcame the capillary entry pressure. The capillary entry pressure or also known as breakthrough pressure is corresponds to the gravity, degree of saturation, pore size, pore shape and interfacial forces [39]. Therefore, the PP-MNF assembly in this work might have overcame the capillary entry pressure through the interfacial force (liquid-air interface), pore size and shape (cotton-like assembly and air gap between the PP-MNF) and the adsorption under gravity process, which

353 results the penetrating of water in passing through the PP-MNF assembly (Figure 3a and Figure
354 3b).



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356 **Figure 2.** Amount of adsorbate adsorbed on the PP-MNF during adsorption process; oil pressed (grey bar),
357 solid particles (black bar) and water (dotted bar)

358 Despite the interaction of water and air gap between PP-MNF occurred during the adsorption
359 process, the interaction of PP-MNF and residual oil (adsorption process) also occurred based on
360 polarity effect and London dispersion force [34]. Hence, the phenomenon of water uptake during
361 the adsorption could explained by the water trapped between oil phases that adsorbed on the PP-
362 MNF assembly (Figure 3c). The water molecules would became unstable when interact with air in
363 the PP-MNF. This was likely due to repulsion forces present between water-oil and water-PP-
364 MNF (electronegativity effect) [40], [41] and break into droplets, then leads into water-oil
365 emulsion [9]. Figure 3c illustrates the water droplets in bulky oil phenomenon. The water droplets

dispersed in oil phase and trapped in the air gap between the PP-MNF, during the adsorption process (Figure 3b).

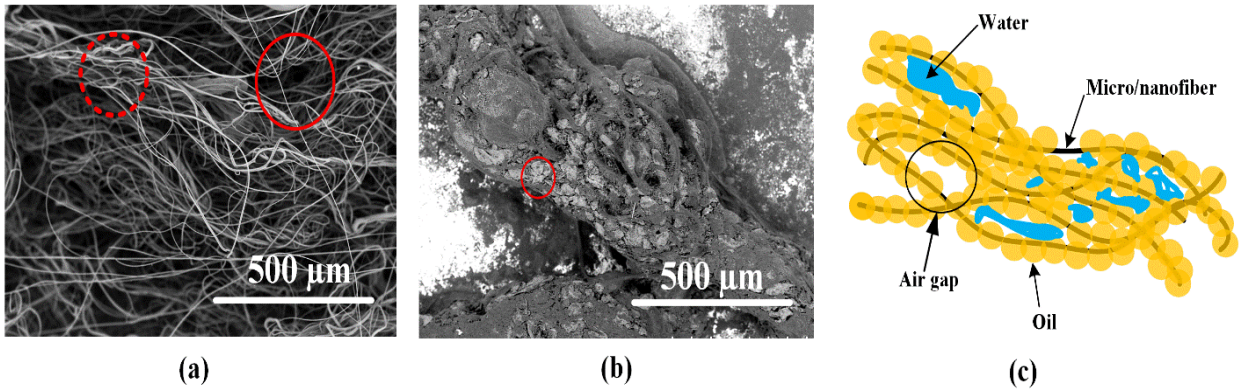


Figure 3. SEM images of (a) Air gap in the PP-MNF assembly small (dotted red circle) and large (red circle); (b) Dispersed water trapped between oil adsorbed on the PP-MNF (red circle); (c) Graphical illustration of PP-MNF assembly during adsorption process.

Beside than water uptake, suspended solid also contributes in the adsorbate adsorption. The suspended solid is mainly content of solid particles and silts (oily debris fiber) which also known as natural sediments [36]. These natural sediments were investigated ranging from 38 to 1000 µm and even less than 38 µm size of particles which found under the light microscopy [36]. These solid particles were generated due the harsh pressing, stripping and digestion of fruit bunches and the mesocarps [42], then mixed with the wastewater. Thus, the residual oil was attached or adsorbed to the surface of the fibrous solid residues which believed due to non-polar surface and capillary adsorption effect. Hence, these natural sediments were found on the PP-MNF during the adsorption process because of the adhesion between oily sediments and the oleophilic surface on the PP-MNF, as well as the pore space between the PP-MNFs (Figure 7k and Figure 7g).

3.3. Reusability of used PP-MNF

The reusability of polypropylene PP-MNF had been studied over 20 batch of recycles. A 1 g of clean and white PP-MNF was used at the first cycle and was further reused for 19 cycles of oil

adsorption and pressing technique for oil recovery, using fresh POME for every new cycle. The oil concentration of fresh POME was ranged between 3000 to 6000 mg/L (approximately 50.74 – 112.94 g of oil in 18 L of POME volume).

Figure 4 shows the oil recovery efficiency and adsorption capacity of used PP-MNF over 20 batch of recycling. The histogram results show a pattern of the oil recovery efficiency. An increased of oil recovery efficiency gradually from the first to the fourth reuse but suddenly dropped on the fifth reuse. This observation was consistent throughout the 20 cycles. This trend could be explained by the oil adsorption property of the PP-MNF. The interaction between the oil and PP-MNF occurs because of the hydrophobic property of the oil [43]. A sudden drop of the oil recovery efficiency after reaching the maximum capacity is most likely associated with the inability of the oil layer on the PP-MNF surface to attract oil from the bulk.

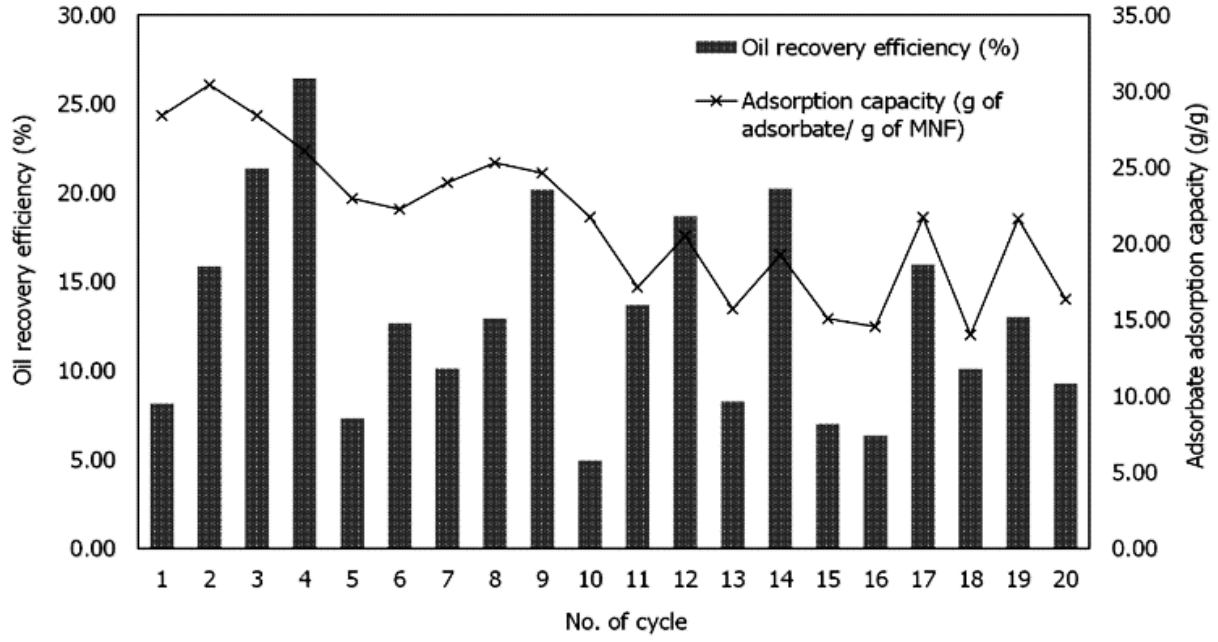


Figure 4. Efficiency of oil recovery and adsorption capacity from 1 g reused PP-MNF over 20 batch recycles using pressing technique

The capacity of PP-MNF in adsorption process can be seen decreases in Figure 4. At the beginning of adsorption, the PP-MNF can adsorb more than 20 g of adsorbate/ g of PP-MNF. As the PP-MNF was reused up to 20 cycles, the adsorbed capacity dropped gradually to 10 g of adsorbate/ g of PP-MNF. This is likely due to the fouling effect on the PP-MNF [15], which was caused by the natural sediments uptake [36] and non-extractable adsorbate using hand pressing method. Nevertheless, the PP-MNF was still able to recover approximately 10 % of oil and expected to recover another 10 % of oil, if re-used for more 5 to 10 cycles. In summary, these results showed that polypropylene PP-MNF had a good reusability.

3.4. Oil extraction by solvent extraction and supercritical-CO_2 techniques from pressed PP-MNF

In this section, the non-extractable adsorbate on the pressed PP-MNF from Section 2.4.2 was further extract using chemical extraction. Two techniques were performed to determine the quantity of oil that retained on the PP-MNF; such as solvent washing [44] and supercritical-CO_2 [45]. Generally, these techniques called as solid-liquid extraction, where solvent is needed to diffuse and desorb oil from the sorbent or samples [46]. In chemistry point of view, the non-polar molecules of solvent will attract the non-polar molecules of residual oil through van der Waals interaction and will repel the polar molecules like water [32]. Hence, two layer of solution were

observed. In addition, these works indirectly studied the regeneration of the PP-MNF [47]. Figure 5 shows the extraction yield from solvent washing and supercritical-CO_2.

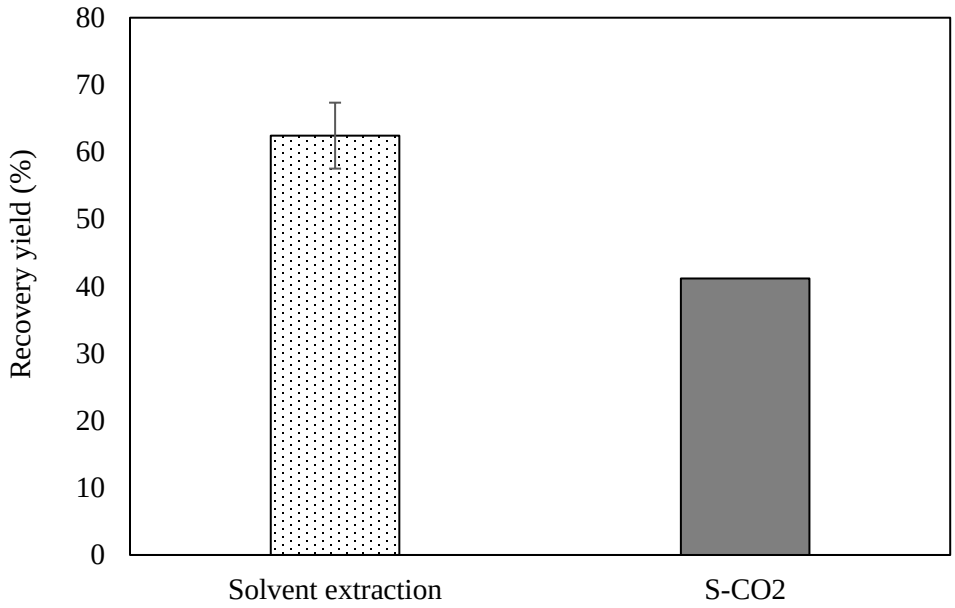


Figure 5. Extracted oil from solvent extraction (dotted bar) and supercritical-CO_2 (grey) from pressed PP-MNF

3.4.1. Extraction oil from PP-MNF using solvent washing

In solvent washing, n-hexane (99% purity) was used to wash the pressed PP-MNF. The pressed PP-MNF consist adsorbate, such as oil and suspended solid. Water does present in the solvent solution after washed, however the amount was negligible. Hence, anhydrous sodium sulphate was used to adsorb the emulsion water in the solvent solution [11].

Most of researches reported that extraction using n-hexane gives highest oil yield [46], [48], [49]. This solvent was used due to its non-polar molecules, where it consist of hydrocarbon group that able to attract the same molecules in the residual oil. Like the general rule stated by Wade

[32], “like dissolves like” where non-polar substances will dissolves in non-polar solvents. Thus, a single batch of solvent washing using n-hexane was done from the pressed PP-MNF.

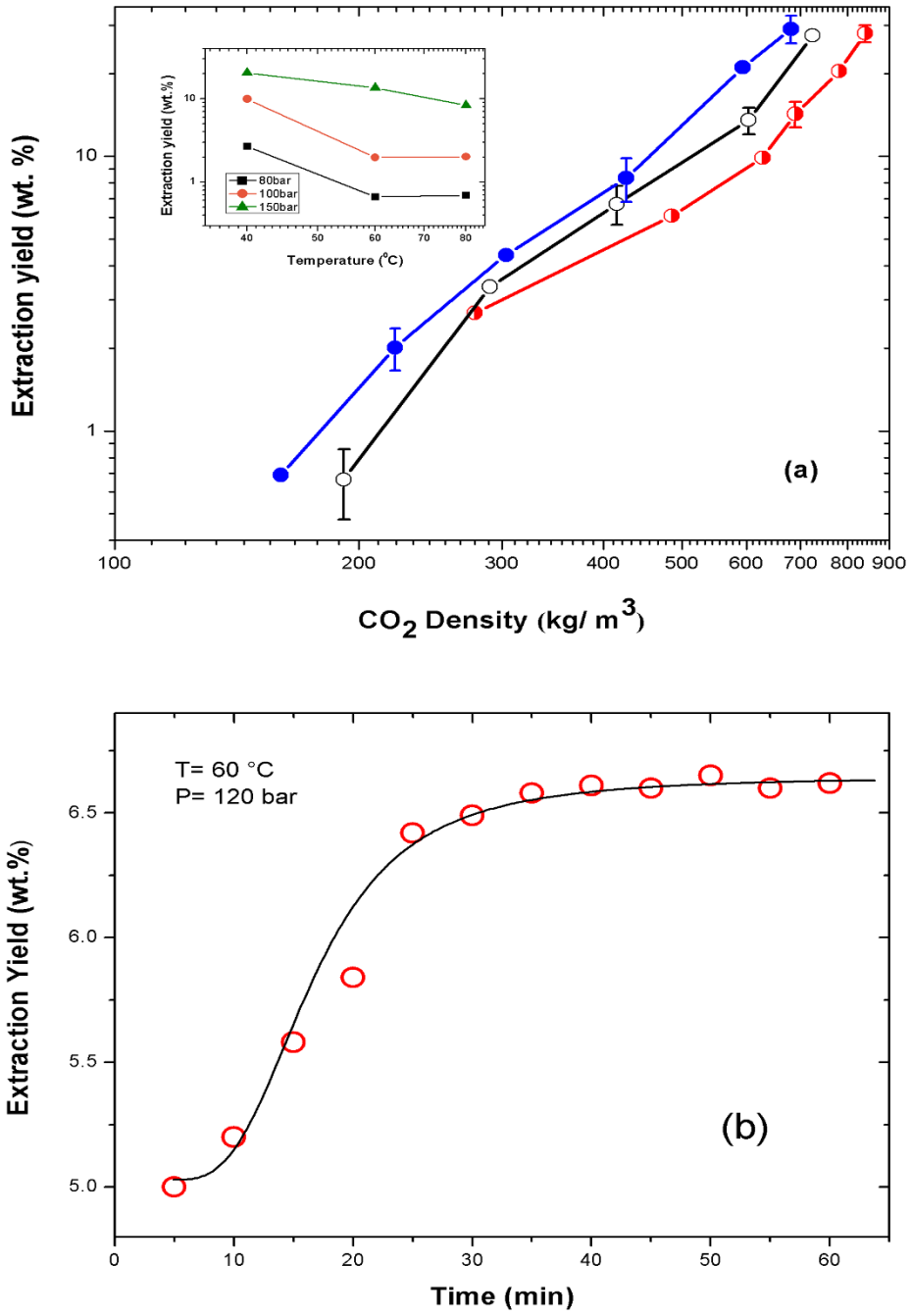
Figure 5 shows that 62.44% of extraction yield obtained from the solvent extraction technique.. This could be due to the intermolecular forces between solvent, residual oil and the PP-MNF. These three components were non-polar molecules [6], [16], [36], thus the potential of induced dipole-induced dipole attraction was high and strong [34]. But, the interactions would depends on its physical properties [50]. Solid molecules have strong intermolecular forces to keep neighbor molecules locked besides them because the kinetic energy of solid molecules are lower than liquids. The PP-MNF was a mass of solid non-polar molecules, hence it has stronger forces than solvent and residual oil. The solvent and the residual oil were present in liquid form, thus the kinetic energy of non-polar molecules were free to move past or slide over one another to form an intermolecular forces [50]. Therefore, the oil retained in the PP-MNF was able to extract out due to polarity effect.

3.4.2. Extraction oil from PP-MNF using supercritical-CO_2

The effect of the CO_2 density on the extraction yield was studied at various temperatures (40 °C, 60 °C and 80 °C) and pressure range (80 to 200 bar). Temperature is a critical parameter which affects the solubility and extraction capacity of the fluid [51]. Hence, temperature effect was studied and the optimum condition was determined.

Figure 6 shows the yield of extraction using supercritical-CO_2 at various temperatures and pressure range. Figure 6a inset shows the highest extraction yield is at its maximum (20 wt. %) for 40 °C at a particular pressure. The yield then decreases at least 4-folds with higher temperature up to 100 bar (Figure 6a inset). Whereas, above 100 bar, the yield decreases only twice. This can be explained by CO_2 density being highly affected by the temperature near the critical state. An

increase in temperature usually leads to a large decrease in fluid density which reduces oil solubility in CO_2 hence the extraction yield [52]. This is clearly seen for the extractions carried out at 60 °C and 80 °C (Figure 6a). At temperature above 60 °C, the pressure can be increased to at least 120 bar to reach the density necessary for ca. 10 wt. % extraction yield.



458

459 **Figure 6.** Extraction yield dependence on CO_2 density at (a) 40 °C (half closed symbols) 60 °C (open
460 symbols) 80 °C (closed symbols) at 80, 100, 120, 150 and 200 bar. Error bars indicate data scatter over
461 three experiment at a particular CO_2 density. Inset- Extraction yield dependence on temperature at 80, 100
462 and 150 bar. (b) Extraction yield dependence on time at 60 °C and 120 bar.

463 It is well accepted that high temperature increases the vapor pressure of the extractable

464 compounds which enhances the extraction efficiency and accelerates mass transfer hence enhances

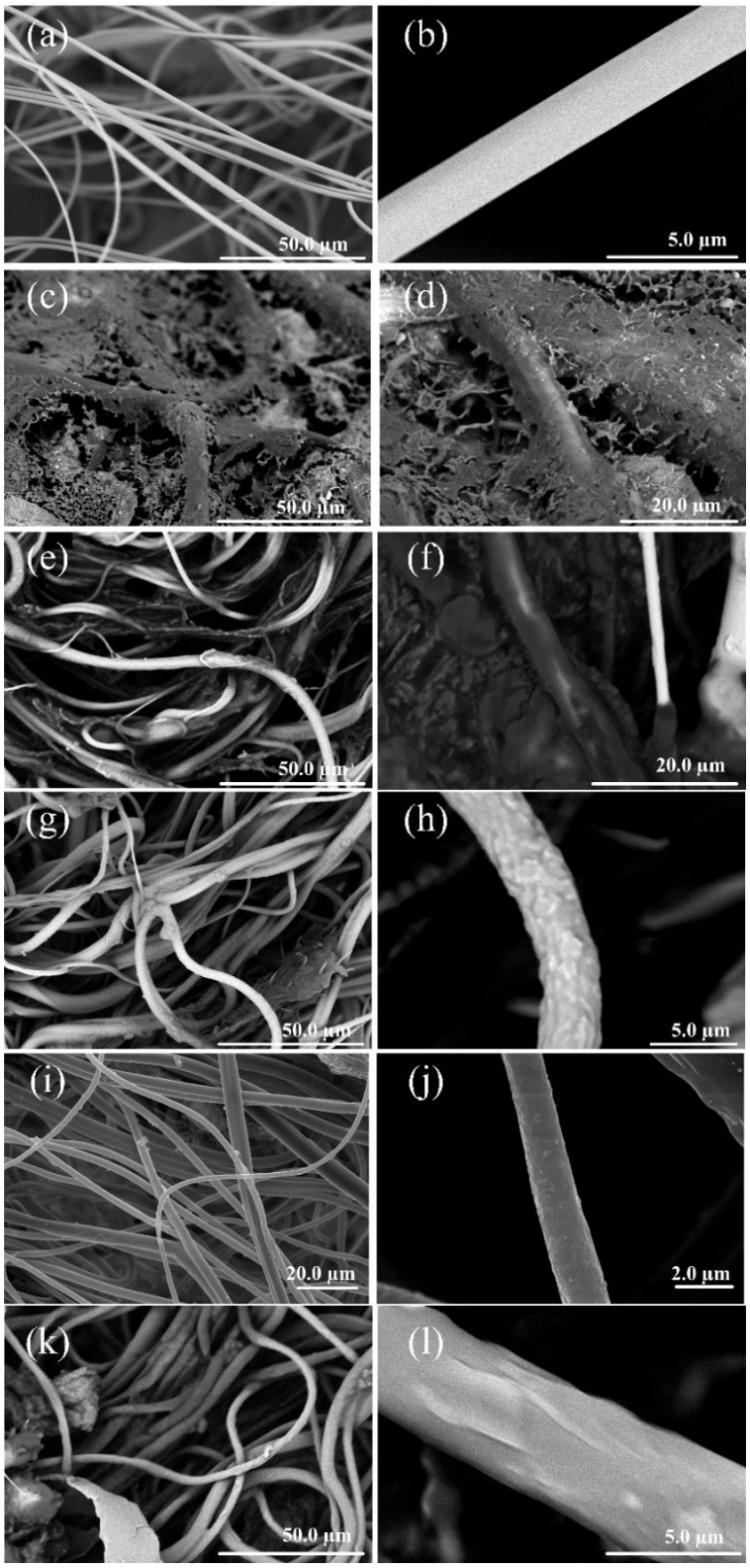
the yield [51]. However, in the current work the temperature was found to affect the yield only when the pressure is increased beyond 100 bar where the CO_2 density is high enough for extraction. This is not surprising since the solubility of oil is below very low (0.01g oil per g of CO_2) at 40 °C and pressure <100 bar [53], [54]. Figure 5b shows the extraction yield dependence on time at 60 °C and 120 bar. The extraction yield increases 1.3 folds over the first 25 min. The optimum extraction time at which experiments were conducted was 35 min.

Based on Figure 5, the histogram shows the extraction yield using supercritical-CO_2 with total of 41.17 wt. % over 8 runs at optimum condition of 80 °C and 200 bar. The first extraction resulted in 22.00 % yield, about half of this amount (9.57 %) was further extracted from the same sample PP-MNFs. The yield continued to drop by around half the previous amount until the 8th extraction, the PP-MNFs weight remained constant indicating no residue oil is extracted at these conditions.

3.5. Characterization of PP-MNF and oil extracted analysis

3.5.1. Physical and chemical properties of PP-MNF

Polypropylene PP-MNF was fabricated using melt blowing system. The average diameter of PP-MNF was ranging between 10^2 to 10^4 nm, which indicates that this fiber consists of micro and nanofiber. Figure 7 shows the SEM images of the PP-MNF, before, during and after oil recovery experiment. The changes of physical structure were scanned with SEM analyzer and countable images captured with vary magnifications (0.1 kX – 9.0 kX) and scales (500 µm – 5.0 µm), depending on the availability and sharpness of the images obtained.



485

486 **Figure 7.** Morphology of the surface on the PP-MNF; (a, b) raw PP-MNF, (c, d) saturated PP-MNF, (e, f)
487 pressed PP-MNF, (g, h) washed PP-MNF, (i, j) S-CO_2 PP-MNF and (k, l) reused PP-MNF

Figure 7a shows the raw PP-MNF that obtained at the collector was pile up and agglomerated into bundles as a cotton-like. As discussed in section 3.2.1, the PP-MNF assembly has large pore space, which contributes to large content of air gap. This could explained by the strand of PP-MNF, which in disordered form, hence produced large pore and rough assembly surface. However, the disordered PP-MNF could attributes more active sites for oil adsorption through intra pores between fibrous [16], [55]. Thus, high oil adsorption capacity (Table 1) were obtained if exposed to bulk of oil and high water uptake if exposed to water bulk (Figure 2). A strand of raw PP-MNF image showed it has a smooth surface of morphology and clean fiber before adsorption, squeezing, washing and extraction process (Figure 7b). This indicates that the fiber has a large surface area for oil binding site [26].

The saturated PP-MNF that obtained during the adsorption process was expected wet and occupies with oil adsorbed (Figure 7c), hence cold stage analysis were performed. Due to present of oil, water and suspended solid in the POME [36], hence the oil adsorption were confirmed containing water and oily sediments (Figure 2). The adhesion of suspended solid was due to the intermolecular forces between layer of oil on the suspended solid and the PP-MNF [36]. Whilst, water uptake was due to the interaction between water and air, hence leads the dispersed water that trapped between the oil adsorption and the PP-MNF (Figure 3b). Figure 7d shows a strand of fiber that covered with dark grey color, which assumed as frozen oil. Whilst, light grey color and anthill-like assumed as frozen ice (water). Other than that, Zhou and co-workers [56] explained that the adsorption water through hydrogen bonding exist between oil and water.

In physical desorption, manual pressing is a practical option and feasible for synthetic materials [35], where highly strength to withstand the pressing force and durable. The PP-MNF used in this work was synthetic, as it was made up by polypropylene based polymer. Hence, it was expected to endure the pressure given to the PP-MNF for oil recovery. Figure 7e and 7d show the pressed

PP-MNF using hand pressing technique. No damage has been observed on the PP-MNF after one time used and pressing. However, there were oil and oily sediments observed on the PP-MNF (Figure 7e and Figure 7d). The adhesion of oil and sediments were due to London dispersion force presents between solid non-polar molecule (the PP-MNF) and liquid non-polar molecule (the layer of oil).

Figure 7g and Figure 7i show the washed PP-MNF and S-CO_2 PP-MNF, respectively. The PP-MNFs were observed much clear, compared to the saturated and pressed PP-MNFs. These indicating that the PP-MNFs have been regenerated by chemical extraction. However, changes on PP-MNF morphology were observed (Figure 7h and Figure 7j), where the PP-MNF became shrink. This could be suggested that the solvents (n-hexane and CO_2) have reaction with the PP-MNFs surface. However, these changes has not been well understand, whether it is chemically changes or only physically changes (i.e. porosity).

Lastly, the reused PP-MNF for 20 cycles were shown in Figure 7k and Figure 7l. No severe damage have been observed, only several strand of PP-MNF were stretched (Figure 7l). This was likely due to squeezing effect during desorption process. Thus, the mechanical and physical desorption technique should be studied to optimize the oil recovery without damaging the fiber. Somehow, solid particles were observed stuck between the fiber assemblies. This could explain the increase of fouling effect, hence reduce the active sites for oil adsorption and the intermolecular forces [16], [34].

The chemical composition of the polypropylene PP-MNF surfaces were analyzed by EDX connected to the SEM. Figure 8 (a-d) showed the EDX spectra of raw PP-MNF, saturated PP-MNF, pressed PP-MNF and washed PP-MNF samples, respectively. Table 3 shows the weight of elemental composition in each PP-MNF. The signals of carbon (C) and oxygen (O) were observed in every sample, where the weight of element C were increased as the PP-MNF used in oil

recovery. This could be due to present of residual oil on saturated and pressed PP-MNF. The weight kept increasing on the washed PP-MNF was probably due to the presence of solvent molecules which are mainly hydrocarbon group [32]. The EDX result on the washed PP-MNF confirmed that the shrink PP-MNF (Figure 7h) was not chemically changes. Thus, it was suggested by physically changes where the surface morphology was shrink due to cold solvents.

Whilst, the weight of O element showed inversely to C element, but slightly increased compared to washed PP-MNF (Table 3). These results could supported by Fahma and co-workers [57], where there is air exist in the PP-MNF and hydrogen bonding between residual oil-water.

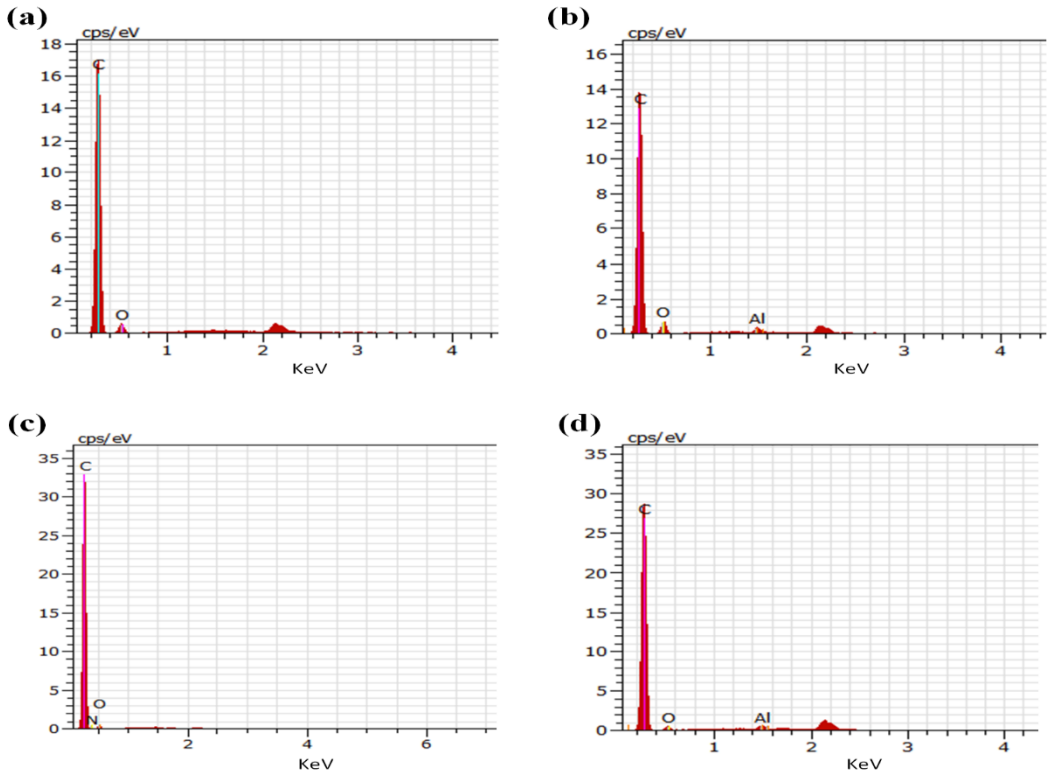


Figure 8. EDX spectra of polypropylene PP-MNF; (a) raw fiber, (b) saturated fiber, (c) pressed fiber and (d) washed fiber

Table 3. Elemental compositions of PP-MNFs

PP-MNF	Weight of Carbon (C), %	Weight of Oxygen (O), %	Weight of Aluminum (Al), %	Weight of Nitrogen (N), %
Fresh	88.77	11.23	-	-
Saturated	88.93	9.10	1.97	-
Pressed	92.11	4.97	-	2.92
Washed	92.34	7.04	0.61	-

Other than that, the EDX spectra revealed the presence of aluminum (Al) and nitrogen (N) on the saturated, pressed and washed PP-MNFs, respectively. This is not surprised because the elements were contained in POME, such as phosphorus (P), potassium (K), magnesium (Mg), calcium (Ca), boron (b), iron (Fe), manganese (Mn), copper (Cu) and zinc (Zn) [6]. Hence, these elements could attributed from the suspended solid that stuck and adhered on the PP-MNF surface (Figure 7g).

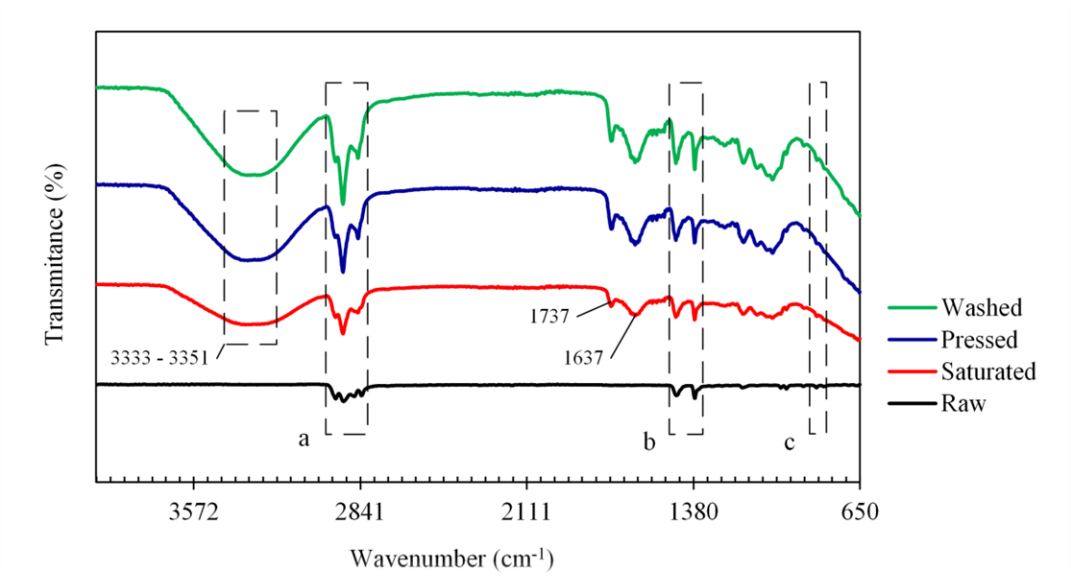


Figure 9. FT-IR spectra of the polypropylene PP-MNF; (black line) raw PP-MNF, (red line) saturated PP-MNF, (blue line) pressed PP-MNF and (green line) washed PP-MNF

In addition to the SEM-EDX, changes on the chemical structure of PP-MNFs and to reveal the presence of oil component that was attached on the PP-MNF before, during and after oil recovery

were determined by FT-IR spectrometer. The FTIR spectra was recorded in the wavenumber range of 600-4000 cm^{-1}. The FT-IR spectra of the raw PP-MNF exhibited peaks between 2950 cm^{-1} and 2860 cm^{-1} (Figure 9a inset). These peaks indicates the presence of symmetric stretching vibration of $–CH_3$ group (2867 cm^{-1}) and asymmetric stretching vibration of $–CH_3$ and $–CH_2$ group (2949 cm^{-1} and 2914 cm^{-1}, respectively) [58] of the polypropylene structure. The structure was further evidenced by the two peaks observed at 1452 cm^{-1} and 1373 cm^{-1} (Figure 9b inset), indicated the presence of asymmetric and symmetric scissoring vibrations of the methyl group, respectively [59]. Moreover, a weak peak at 840 cm^{-1} indicates of $–CH_2$ stretching [59].

Similar peaks were observed to the saturated PP-MNF, pressed PP-MNF and washed PP-MNF. These indicated no chemical changes in polypropylene based PP-MNF. However, a strong band between 3333 cm^{-1} to 3351 cm^{-1} were observed which attributed the presence of a broad intermolecular hydrogen bonded (O-H) stretching [57]. The presence peaks between 1637 cm^{-1} and 1737 cm^{-1} were observed respectively on the saturated, pressed and washed PP-MNF, where the vibration of C=C stretching mode were attributed to the stretching of the carbonyl group [60]. A peak at 654 cm^{-1} were observed after adsorption, followed by desorption and it was represented the presence of bending alkyne group. Therefore, these peaks revealed the presence of oil that adsorbed on the polypropylene PP-MNF.

3.5.2. Components distribution as function of pressure and temperature

Table 4 shows fatty acids concentration in the extract as function of the pressure applied. Major fatty acids detected are methyl decanoate C10:0, methyl stearate C18:0 and oleate C18:1. Saturated fatty acids such as methyl decanoate C10:0 and methyl laurate C12:0 concentration increase with high pressure this is explained by their highly solubility in sc-CO_2. Whereas, unsaturated fatty acid

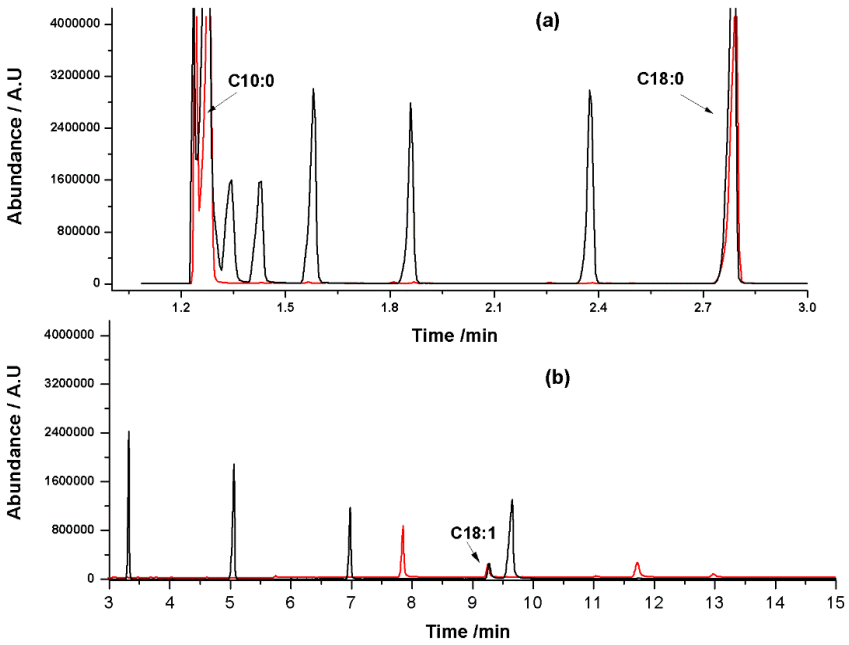
584 mainly methyl stearate C18:0 concentration decrease with high pressure. Methyl oleate C18:1
585 concentration fluctuates with the pressure applied.

586 **Table 4.** Fatty acids concentration (ppm) in the extract by SFE CO_2 as function of the pressure applied

Pressure (bar)	C10:0	C18:0	C18:1	C12:0	C20:0
80	369.67	168.22	23.49	14.90	-
100	33.16	156.34	19.11	-	trace
120	21.58	153.87	30.06	156.10	-
150	35.71	119.21	17.31	156.42	-
200	29.09	158.67	26.12	-	-

587

588 A chromatogram showing the oil extracted using sc-CO_2 (40 °C and 80 bar) and fatty acid
589 methyl esters (FAME) standard mix is illustrated in Figure 10. The extracts at the conditions
590 investigated were analyzed by UV-Vis from 250-600 nm wavelength. Carotene which absorbs
591 light at 450 nm was not present in these extracts.



592

593 **Figure 10**. Chromatograms of: (red) oil extract by SFE CO_2 at 40 °C and 80 bar and (black) FAME
594 standards. (a) Retention time 1 to 3 min. (b) retention time 3 to 15 min.

4. Conclusions

The potential of PP-MNF as oil adsorbent in POME had been investigated. The oil adsorption capacity of PP-MNF using refined palm oil was 28.65 g of oil/ g of PP-MNF in average, whilst the oil recovery from POME was 10.93 g of oil/g of PP-MNF. The yield of physical extraction using hand pressing was 89.62% in average, where the rest still retained in the PP-MNF. The chemical extraction was performed and the yield were comparable between the solvent and supercritical CO_2 extraction techniques which 62.44% and 41.17%, respectively and these techniques contributed to the regeneration of used PP-MNF. No significant physical changes were observed on the PP-MNF using FTIR and EDX, however extraction using solvents showed significant change was detected to the PP-MNF using SEM. No trace of polypropylene was detected using GC-MS in the recovered oil, suggesting that the PP-MNF did not dissolved into the oil during the recovery process. The PP-MNF showed significant reusability after 20 trials indicating high commercial value. The limitation of the study lies in the representation of POME samples. In an actual situation, the concentration of oil in POME varies over time, this is contrary to the POME sample used in this study. Hence, future work can be done by performing the study on mill site to get realistic POME samples. In addition, the pressing of PP-PP-MNF can also be mechanized in order to get consistent and replicable force. All in all, this study shows that PP-MF is commercially viable to recover residual oil from POME.

Acknowledgement

References