Removal of Trace Oil From Palm Oil Mill Effluent Using Polypropylene Nanofibers as Adsorbent

Mohd Hardyianto Vai Bahrun[1], Ernee De Vanesa Halun[1], Zykamilia Kamin[2#], Awang Bono[3]

1 Chemical Engineering Programme, Faculty of Engineering, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, MALAYSIA.
2 Oil and Gas Engineering Programme, Faculty of Engineering, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, MALAYSIA.
3 GRISM Innovative Solutions, Kota Kinabalu, Sabah, MALAYSIA.
Corresponding author. E-Mail: zykamilia@ums.edu.my; Tel: +6088-320000 ext. 3150; Fax: +6088-320348.

ABSTRACT This paper aimed to investigate the removal of trace amount of oil from palm oil mill effluent (POME) by using polypropylene nanofibers (PPNF) as solid adsorbent. The potential on removing trace oil was carried out using synthetic POME in batch adsorption experiment. The investigation on surface morphology of PPNF revealed the lower density of fibrous and porous structure between fibers. The adsorption data of PPNF for removing trace oil were depicted by fitting it using Langmuir and Freundlich isotherms. The adsorption isotherm plot revealed a linear behavior of oil onto PPNF at very low concentration. The Freundlich isotherm shows better fitting on the experimental data with R^2 of 0.8983 and SSE of 0.0249, which suggest heterogeneity of adsorption process on PPNF. This suggest potential employability of PPNF to be used in removing trace amount of oil.

KEYWORDS: Adsorption; Linear isotherm; Low concentration; POME; PPNF
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INTRODUCTION

Palm oil mill effluent (POME) is a major water pollution contributor in Malaysia. Malaysia is a country among the largest POME producers, because it is one of the major palm oil producers in the world. In 2015, Malaysia is reported to generate 60.88 million tonnes of POME (Choong *et al.*, 2018), and the values is expected to increase every year as demand for oleo-based products keep growing exponentially (Bahrun *et al.*, 2020). For every ton of crude palm oil produced, approximately 2.5 – 3.5 tons of POME is generated (Ahmad *et al.*, 2005; Shavandi *et al.*, 2012). POME discharged from palm oil mill contains oil in the form of emulsified which cause difficulty in treatment since it is highly stable (Shariff *et al.*, 2009). The discharge of this huge volume of residual oil polluted effluent into the waterways and ecosystems leads to a serious public health hazard. The presence of oil in the water can interfere with the marine and freshwater life by blocking the gas exchanges necessary for life such as oxygen gas, resulting the surrounding to be anaerobic. Even in very low oil concentration of about 0.1 ppm in water could upset the biological cycle in water bodies (Bassim *et al.*, 2003). Thereupon, a proper effluent treatment method is crucial for a sustainable industry.

There are three classification for oily wastewater, depending on the oil droplet size, d_P (1) free-floating oil (d_P > 150 μm), dispersed oil (20 μm < d_P < 150 μm) and emulsions (d_P < 20 μm) (Waisi *et al.*, 2020). Generally, oils contaminate water in two forms as either free-floating oil or emulsified oil. Most industrial wastes contain oil emulsion, and one of it is POME. Numerous conventional methods can be applied with ease to remove free-floating and dispersed oil, for example, gravity separation, skimming, air floatation, centrifugation, as well as coagulation and flocculation (Han *et al.*, 2019). However, these methods facing difficulty to effectively remove the stable emulsions of oil in water (Wang *et al.*, 2016). In fact, only few methods are practically available to remove emulsified oil content, including chemical de-emulsification or ultrafiltration (Mueller *et al.*, 2003).

Moreover, the existing treatment technologies are mostly expensive, less efficient and needed some complementary treatment to satisfy the standards (Tembhurkar & Deshpande, 2012), as well as generating secondary pollution. This urges a search for more practical methods for oil removal. Adsorption is indicated as one of the suitable methods for removing emulsified and soluble oil (Ahmad *et al*., 2004; Moazed & Viraraghavan, 2005). In regard to that, a variety of sorbent materials have been developed, for instance, lemon peels (Tembhurkar & Deshpande, 2012), barley straw (Shariff *et al*., 2009) etc. A more recent research has explored the use of nanofibrous materials as adsorbent for emulsified oil-water separation, such as PMMA/PCL nanofiber (Barroso-Solares *et al*., 2018) and activated carbon nanofiber (Waisi *et al*., 2020). The shifting in nanofibrous materials as adsorbent for oil-water separation attributed by their excellent wetting properties, simultaneous hydrophobicity/oleophilicity of polymeric nano materials (Wang *et al*., 2016), as well as highly porous structure and high surface to volume ratio of nanofiber materials (Sarbatly *et al*., 2016).

Hence, this present study is aimed to investigate the removal of a very low concentration of oil in trace amount from synthetic POME by adsorption using polymeric polypropylene nanofibers (PPNF). The PPNF were characterized using field emission scanning electron microscope (FESEM) to visualize the surface morphology of fibrous structure. The measurement on the adsorption equilibrium in batch experiment were conducted and are fitted using the Langmuir and Freundlich isotherms.

METHODOLOGY

Polymeric Polypropylene Nanofiber (PPNF) Adsorbent

The polypropylene nanofibers (PPNF) was used as the solid adsorbent for oil sorption from synthetic palm oil mill effluent (POME). The preparation of PPNF follows the technique described by Kamin *et al*. (2020a). The PPNF is developed using a melt-down blowing system (Japan Zetta Co., Ltd.) in the Nanofiber Research Laboratory, Faculty of Engineering, Universiti Malaysia Sabah. The raw materials for it is polypropylene (PP, Sun Allomer). The PP was melted using the melt-blown machine at 30 Hz by gradual heating from 200°C to 300°C. This is to avoid thermal degradation. Whereas, the air temperature was fixed at 450°C. Upon completion of the melting process, both polymer melt and pressurized air were coextruded by following parameters as indicated in the experimental design. The solidified fibers called PPNF were then collected on the surface of aluminum foil and kept at 25°C prior to characterization. The surface morphology of the PPNF were observed using field emission scanning electron microscope (FESEM) model JEOL JSM-7900F. The mean diameter of the PPNF was measured using image-processing software, ImageJ software (National Institutes of Health, USA).

Preparation of Synthetic Palm Oil Mill Effluent (POME)

Triolein (commercial cooking oil) was used to prepare the synthetic palm oil mill effluent (POME). Triolein was added to a 1000 g of distilled water, and later adding 0.5 g of linear alkylbenzene sulfonate (LABS) surfactant to emulsify the oil in water. The mixture was then further emulsified using a homogenizer at 12,000 rpm for 15 minutes at room temperature. The resulted solution is milky white, which exhibits the characteristic of chemically stabilized emulsions (Alther, 2001; Shariff *et al*., 2009).

Batch Adsorption Studies

The batch adsorption experiments were carried out by adding 2.0 g of polypropylene nanofibers adsorbent, W_s to a 250 mL of synthetic POME, V with initial oil concentration, C_i in a 250 mL

Erlenmeyer flask. The solution-adsorbent mixtures were agitated for 3 hours at room temperature using magnetic stirrer. The mixture is then allowed to equilibrate and the concentration, C_e is measured at equilibrium. The oil concentrations before and after adsorption were analyzed using Ultraviolet-Visible Spectrophotometer (UV-Vis) model JASCOV-650 at a wavelength of 293 nm. Then, the amount of equilibrium adsorption of oil in solid phase, Q_e were calculated using Equation (1).

$$Q_e = \frac{(C_i - C_e)V}{W_s} \quad (1)$$

For adsorption isotherm determination, five low oil concentration varying from 0.09w% to 0.17w%, which corresponding to oil concentration in ppm of 900 to 1,700 ppm were used. This range of oil concentration used is this study are much lower compared to the reported value of oil in POME as reported by Bassim *et al.* (2003), indicating very low concentration adsorption study.

RESULT AND DISCUSSION

Surface Characterization of the Polypropylene Nanofiber (PPNF)

The surface morphology of the PPNF was characterized by FESEM at varying magnifications and scales. Figure 1 shows the morphology of PPNF produced using melt-blown technique with a structure of lower density with larger spaces between the fibrous. The mean diameter of the PPNF was ranging from 1.3 to 3.0×10^3 nm, which indicates the nano-sized fiber. The mean diameter observed here is comparable with the results of previous study (Kamin *et al.*, 2020b), as the fibers formed had diameters larger than 1.0×10^3 nm. The loose fiber assembly was observed to have larger spaces between the fibers, which measured between 7 and 15 µm. The larger spaces mean larger air gap because it traps a large amount of air (Liu *et al.*, 2019). The larger content of air filled between the fibrous structure makes the PPNF to be more hydrophobic/oleophilic (Lee *et al.*, 2013) by reducing the surface free energy of the fibrous strands (Liu *et al.*, 2019). The hydrophobic/oleophilic properties of PPNF also contributed by the rough surface of the fiber strand (Yao *et al.*, 2011), as shown in Figure 1c and d. This property could facilitate the adhesion of oil onto the surfaces of fiber strands, hence improving adsorption (Zhu *et al.*, 2011; Sarbatly *et al.*, 2016).

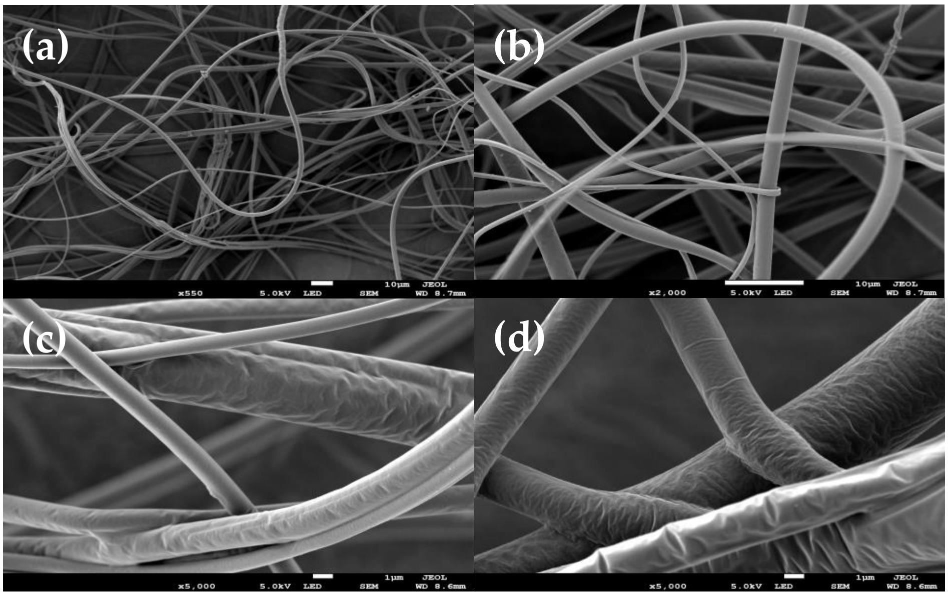

Figure 1. FESEM images of PPNF at different magnifications and scales (a) ×550 magnification (b) ×2,000 magnification (c) and (d) ×5,000 magnification.

Equilibrium Adsorption Isotherms

The equilibrium adsorption isotherm of oil towards PPNF were investigated by conducted experiments using different initial oil concentrations ranging from 900 to 1,700 mg/L. Plotting the amount of metal adsorbed by PPNF, Q_e against equilibrium concentration of oil oil-water mixture, C_e showed that the adsorption capacity increased with the increase of oil concentration, as shown in Figure 2. It is worth noting that the plot Q_e versus C_e resembles a linear relationship. Under the condition of very low initial concentration of oil (0.09% to 0.17%) where the oil is visually soluble in water, the uptake of oil by PPNF shows linear isotherm behaviour (Khayyun & Mseer, 2019).

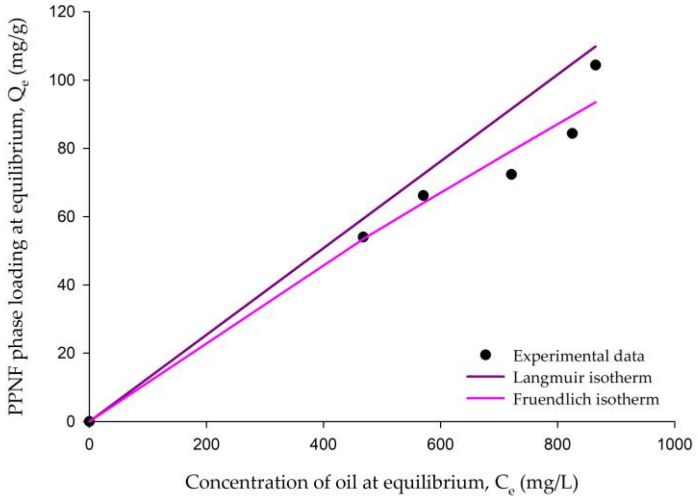

Figure 2. Adsorption isotherm of low oil concentration on the PPNF, fitted using Langmuir and Freundlich.

To interpret the adsorption data, it is necessary to correlate the equilibrium adsorption data to different isotherm equations such as Freundlich and Langmuir isotherm equations. The Langmuir isotherm describes the sorption of oil molecules occuring uniformly via monolayer adsorption on a surface which is homogenous with no transmigration between the adsorbed molecules (Tan *et al.*, 2020). The linearized form of Langmuir isotherm can be expressed as in Equation (2).

$$\frac{1}{Q_e} = \frac{1}{Q_{max} b} \cdot \frac{1}{C_e} + \frac{1}{Q_{max}} \tag{2}$$

where C_e is the concentration of oil at equilibrium (mg/L), Q_e is the PPNF phase loading at equilibrium (mg/g). Q_{max} and b are the Langmuir constants; Q_{max} is the maximum adsorption capacity (mg/g) and b is the Langmuir adsorption affinity (L/mg).

The Freundlich adsorption isotherm is used to describe the multilayer heterogenous adsorption process due to the interaction between the adsorbed molecules. The linearized form of Freundlich isotherm is given by Equation (3).

$$\log Q_e = n \log C_e + \log K_F \tag{3}$$

where K_F represents the Freundlich adsorption capacity ([mg/g]/[mg/L]^n) and n is the dimensionless adsorption affinity.

The collected experimental data were fitted to the Langmuir and Freundlich isotherms. The coefficient determination, R^2 and sum of squared error, SSE were used to measure fit quality. The results obtained from linear regression by Langmuir and Freundlich isotherms are presented in Table 1. From Table 1, it is seen that the Langmuir isotherm fitted well the experimental data if the comparison is made based on R^2 only. However, Freundlich isotherm shows better fitting if comparison is made based on SSE. Graphical representation between these two isotherms in Figure

2, however, agree with the SSE decision. Freundlich isotherm generally shows better fitting on the experimental data, with R^2 of 0.8983 and SSE of 0.0249. Therefore, the uptake of oil onto PPNF preferably follows multilayer heterogenous adsorption process. Another noteworthy finding is that, the Freundlich constant n is approaching 1, indicating the linearity of the adsorption at very low oil concentration. When the Freundlich constant n equals to 1, the Freundlich isotherm equation reduces to a linear equation. Further experimental works is required for determining the adsorption of pure component system of synthetic POME, preferably containing single component of triglyceride and fatty acid, to validate and compare with this current finding.

Table 1. Estimated adsorption isotherm constants of oil onto PPNF for Langmuir and Freundlich isotherms by linear regression using Equation (2) and Equation (3), respectively.

	Langmuir				Freundlich			
	Q_{max}	$b\times10^4$	R^2	SSE	K_F	n	R^2	SSE
PPNF	588.24	2.1593	0.9240	0.1517	0.1987	0.91	0.8983	0.0249

CONCLUSION

The present study investigates the removal of trace oil from synthetic POME using polypropylene nanofiber (PPNF). It has been proven experimentally that the adsorption of very low concentration of oil in trace amount (0.09w% to 0.17w%) behaves linearly. The Freundlich isotherm showed the best fitting towards the experimental data, with R^2 of 0.8983 and SSE of 0.0249. This suggest the heterogeneity in the structure of PPNF. The capability of PPNF to adsorb oil can be contributed to a multi-porous structure between the fibers and the roughness of fiber strand that enhance the simultaneous hydrophobicity/oleophilicity of PPNF. Further investigations are required for confirming the adsorption behavior of PPNF towards oil-in-water emulsion.

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