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ADSORPTION OF OIL IN WATER ONTO MODIFIED OIL PALM MESOCARP FIBERS

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Abstract: The ability of modified oil palm mesocarp fiber (OPMF) in adsorbing oil from synthetic oily wastewater was investigated. OPMF is one of the lignocellulosic materials which have hydrophilic characteristics. In order to improve the adsorbance efficiency, OPMF was modified using alkali and acetylation treatments. Both treated and untreated OPMFs were analyzed using Scanning Electron Microscope (SEM), Fourier transform infrared spectrophotometer (FTIR), and Accelerated Surface Area and Porosity Analyzer (ASAP). Batch adsorptions study was carried out by varying the sorbent dosages from 0.02–4.0 g and contact times from 0–900 minutes. Acetylated-OPMF showed the highest adsorption capacity with 95% oil adsorbance compared to 63% and 58% by alkali-treated and untreated OPMFs respectively. Meanwhile, the kinetic data obtained for all OPMFs was fitted well with the pseudo-second-order kinetic model.

Keywords: Oil palm mesocarp fiber; fiber alkali treatment; fiber acetylation treatment; oil adsorption.

Introduction

Palm oil is one of the common vegetable oils used worldwide especially in food industries such as cooking oil products, used in the making of margarine and shortening, as an ingredient in fat blends and other vast arrays of food products (Imoisi *et al*., 2015). Hence, the accumulation of cooking oil waste generated from used cooking oil also increases. Cooking oil waste is disposed by small and medium food stalls, food industries and domestic household were usually poured down into the sink, end up in pipe lines and flows into drainage system or landfills without any prior treatments. These disposed activities can give adverse effect to the environment. The oily wastewater treatment is known to be difficult, costly and almost impossible to thoroughly remove all oil waste in the water body. Thus an efficient method and material are necessary in order to eliminate or at least to minimise the amount of oil waste in water.

Nowadays, natural organic sorbents were used in oil adsorption processes because of their adsorption capacities, higher biodegradability and cost effectiveness (da Silva Jr. *et al*., 2003; Wang *et al*., 2010). Various types of natural organic sorbents were used as an oil adsorbent including banana pseudostem fiber (Husin *et al*., 2011), cotton fiber (Deschamps *et al*., 2003), barley straw (Ibrahim *et al*., 2010) and kapok fiber (Dong *et al*., 2015). However, to the best of authors' knowledge, there is no report found on the adsorption of oil by oil palm mesocarp fiber (OPMF). OPMF is an abundance left-over produced from oil extraction process in agricultural productivities of local palm oil mill plantations. Usually OPMF was burnt as a boiler fuel to generate steam and electricity for the palm oil mill Then *et al*., 2014. It was also being used as a reinforcing material in polymer composites (Eng *et al*., 2014) and can be converted into a valuable feedstock for the production of biosugar, biocompost, biochemicals and bioethanol (Yunos *et al*., 2012).

In this study, OPMF was chosen as an organic sorbent for oil waste adsorption in synthetic oily wastewater. It is believed that OPMF has the affinity towards oil waste due to the fact that oil itself is originated from the palm oil mesocarp. However, natural fiber has hydrophilic properties (Sreekala & Thomas, 2003) therefore it needs to be modified in order to enhance its oil absorption ability. This study reported on two types of mesocarp fiber modifications; alkali treatment and acetylation treatment. Alkali treatment was done in order to disrupt the hydrogen bonding in mesocarp network structure thus can change the fiber surface topography (Li *et al*., 2007). While acetylation treatment has been reported as a treatment that can reduce the hydrophilicity of the fibers hence increase the oil sorption capacity (Wang *et al*., 2013).

Materials and Method

Materials

All chemicals were used as received without any purification and were purchased from different suppliers as follows: sodium hydroxide, acetic anhydride, acetic acid and sulfuric acid (Merck); n-hexane (R&M Chemicals); and refined cooking oil (Lam Soon). Oil palm mesocarp fiber was obtained from local oil palm mill. OPMF was washed with distilled water, dried in an oven at 80^{o}C until constant weight was obtained and then it was cut, ground and sieved to size ≤ 250 µm.

Modification of OPMF

Alkali-treated OPMF was prepared by immersing 30 g of washed OPMF in 5% sodium hydroxide for 48 hours. Then OPMF was washed several times with distilled water containing 1% acetic acid and dried in an oven at 80°C. Alkali-treated OPMF sample was kept in a sample bottle for further use.

Acetylated OPMF was prepared by pre-treating 30 g of the washed OPMF with 2% of NaOH for 30 minutes. Then, OPMF was placed in 500 ml round bottom flask containing 125 mL acetic anhydride and 30 mL acetic acid with addition of one drop concentrated sulfuric acid as a catalyst. The flask was then placed in water bath with reflux condenser set at 60°C for 2 hours. Finally, the treated acetylated OPMF was washed with acetone and dried at 80°C in an oven before kept in a sample bottle.

OPMF Characterizations

The morphological identification of all samples was carried out using Scanning Electron Microscope (SEM) (JEOL JSM-6360LA) operating at 10kV. The presence of functional groups in OPMFs was examined by Fourier transform infrared spectrophotometer (FTIR) model Spectrum 100-Perkin Elmer using KBr pellets technique from 400 to 4000 cm^{-1}. The surface area and average pore diameter of OPMFs were examined using accelerated surface area and porosity analyzer (ASAP) of Micromeritics ASAP 2020.

Adsorption studies

For adsorption studies, the method for preparing synthetic oily wastewater was adopted from previous work carried out by Husin *et al.* (2011) in which 11.5 g palm oil was mixed with 1000 mL water. The solution was then stabilized using high speed blender for 15 minutes until solution became milky white. Two parameters were investigated; different OPMFs dosages (0.02–4.0 g) and preset contact times (0–900 minutes). The studies were performed by adding OPMFs into Erlenmeyer flask containing 100 ml synthetic oily wastewater solution. The mixtures were stirred under constant agitation speed of 170 rpm. The oil concentration was determined by standard partition gravimetric method (5520B) liquid-liquid extraction recommended by APHA (2005) Standard Method of Examination of Water and Wastewater, with n-hexane as the oil extraction solvent. The amount of adsorbed oil at time t, q_t (mg/g), was calculated by equation 1

$$q_t = \frac{C_o - C_t}{W} V \quad \text{Equation 1}$$

where C_O and C_t is the concentrations of oil at initial and at any time respectively (mg/L). V (L) is the volume of the solution and W (g) is the mass of OPMF used.

Results and Discussion

OPMF Characterizations

Scanning Electron Micrographs (SEM) images of an untreated OPMF (Figures 1(a) & (b)) clearly show high surface roughness of lignocelluloses due to residual of lignin on their surfaces. The surface was covered with a layer of substances including pectin, lignin and other impurities as suggested by Rokbi *et al*.(2011). After alkali (Figures 1(c) & (d)) and acetylation (Figures 1(e) & (f)) treatments, there were significant changes in the fiber surface morphologies compared to the untreated OPMF. It is apparent, the surface of the treated OPMFs become cleaner and smoother indicating that almost all lignin residual and impurities had been removed from the fiber surfaces. Surface of the alkali treated OPMF (Figure 1(d)) became degraded (Sreekala *et al*., 1997) and the fibrillation appeared after interaction with sodium (Na). In acetylation treatment (Figure 1(f)), wax and cuticle in the surface were eliminated when interacted with acetyl (Bledzki *et al*., 2008). It was noticed that some of the silica bodies and pit-like opening were appeared on the entire fiber surfaces.

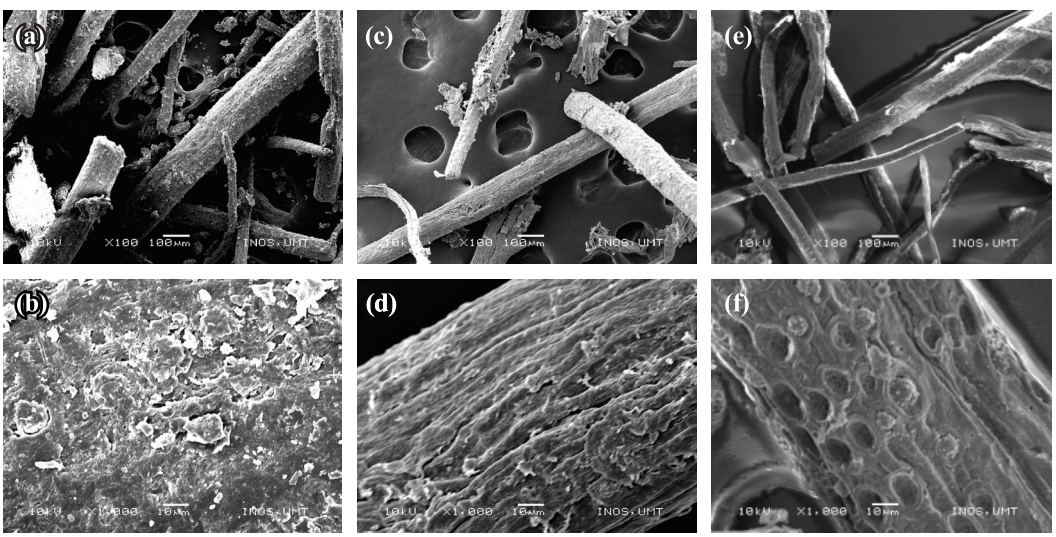


Figure 1: Scanning electron micrographs of untreated OPMF at magnifications of 100X (a) and 1000X (b); alkali-treated OPMF at magnifications of 100X (c) and1000X (d); acetylated OPMF at magnifications of 100X (e) and 1000X (f)

Confirmation of the functional groups of OPMFs before and after treatment was conducted using Fourier transform infrared (FTIR) spectrophotometer. Result shows that FTIR spectra for all samples are almost identical due to their similar functional groups (Figure 2). However the intensity and peaks location shifted a bit due to the treatment process. A broad absorption bands at 3433 cm^{-1}, 3414 cm^{-1} and 3413 cm^{-1} are assigned to O–H stretching vibrations of untreated, alkali-treated and acetylated OPMF respectively. The absorption bands at 2925, 2922 and 2923 cm^{-1} of untreated, alkali-treated and acetylated OPMF

are corresponded to the stretching of the C-H aliphatic group. Decreased in intensity of this peak in treated OPMFs was due to the removal of hemicelluloses (Sreekala & Thomas, 2003). The presence of peak at 1740 cm^{-1} in untreated OPMF is corresponded to C=O stretching of acetate group originated from acetyl in hemicellulose (Marín *et al*., 2010). However, this band disappeared in alkali-treated OPMF, suggesting on the elimination of non-cellulosic components (pectin, lignin & hemicellulose) from the fiber. Peak at 1719 cm^{-1} in acetylated OPMF is attributed to the stretching vibration of C=O ester groups after the acetylation process. The vibration of C=C aromatic stretching can be observed at 1651 cm^{-1}, 1642 cm^{-1} and 1655 cm^{-1} for untreated, alkali-treated and acetylated OPMF respectively.

An adsorption-desorption of nitrogen gas was carried out for further investigation on the characteristics of OPMFs. Surface area and the average pore diameter were analyzed using BET and BJH methods (Table 1). Significant increase in BET surface area was observed after OPMF was treated with sodium

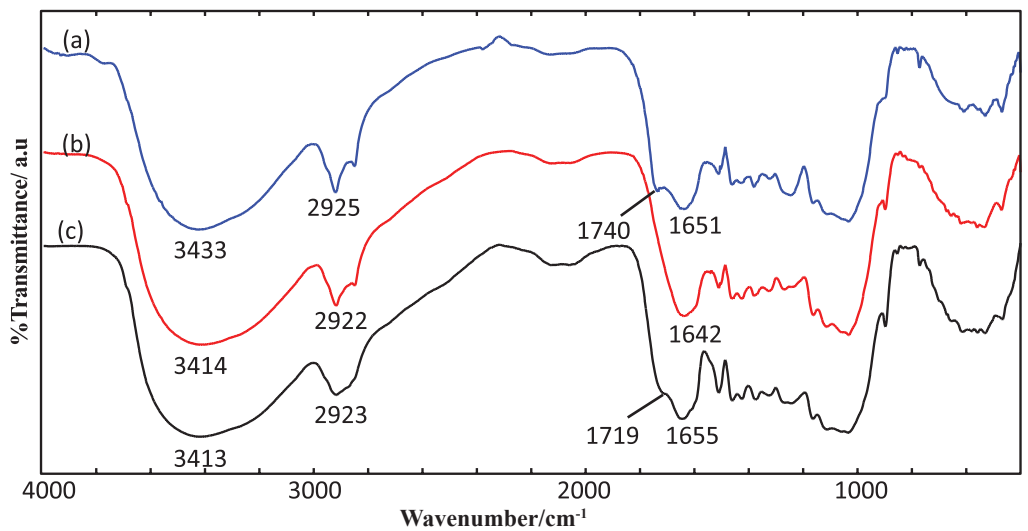


Figure 2: FT-IR spectra for untreated OPMF (a), alkali-treated OPMF (b) and acetylated OPMF(c)

hydroxide and acetic anhydride. It showed that acetylated OPMFs exhibited highest surface area compared to untreated and alkali-treated OPMF. It is suggested that the appearance of pit-like opening after the acetylation process (as previously observed in Figure 1(f)) provides more surfaces of the fiber. The average pore diameter of acetylated OPMFs was lower than untreated OPMFs due to degradation of cellulose (As'ari *et al*., 2015) after the acetylation treatment. However, the average pore diameter for alkali-treated OPMFs was slightly higher than untreated OPMFs due to fibrillation after OPMF interaction with sodium hydroxide.

Oil Adsorption onto Different OPMFs Dosages

All OPMFs show similar trend of oil uptake in which the removal percentage increases as amount of OPMF increased, indicating that removal of oil is dependent to OPMFs dosage (Figure 3). The greater number of vacant sites available as OPMFs dosage increased thus increases the number of binding site and surface area for oil adsorption (As'ari *et al*., 2015). However at some point, the sorption capacity became slower with the increases of OPMFs dosages until the optimum mass was achieved at 0.5 g for both untreated and alkali-treated OPMFs

Table 1: Surface properties of OPMFs

Sample	BET surface area (m^2/g)	BJH desorption average pore diameter (Å)
Untreated OPMF	1.6	186.4
Alkali-treated OPMF	2.0	192.8
Acetylated OPMF	3.4	126.1

while 3.0 g for acetylated OPMF. There was no significant changes in oil removal percentage beyond the optimum OPMFs dosage. This trend may be due to overlapping of binding sites as a result of overcrowded adsorbent particles (Mary *et al*., 2015). Untreated OPMFs was able to adsorb 58% of oil, suggesting that OPMF has ability to adsorb oil without any treatment but their oil uptake is limited. Alkali-treated OPMF did not show much different in terms of oil removal percentage as it was only adsorbs 63% of oil. While acetylated OPMFs shows superior oil adsorption of 95% at optimum mass. This result shows that surface area of OPMF (Table 1) is an important parameter to ensure good adsorption capability.

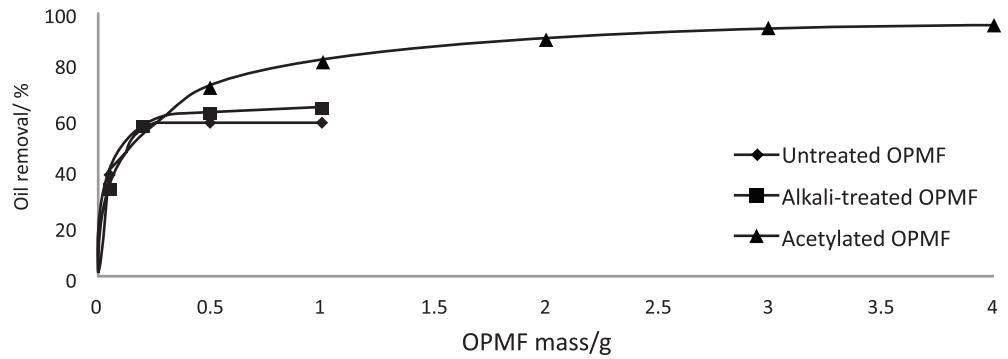


Figure 3: Oil adsorption at different dosages of untreated and treated OPMFs

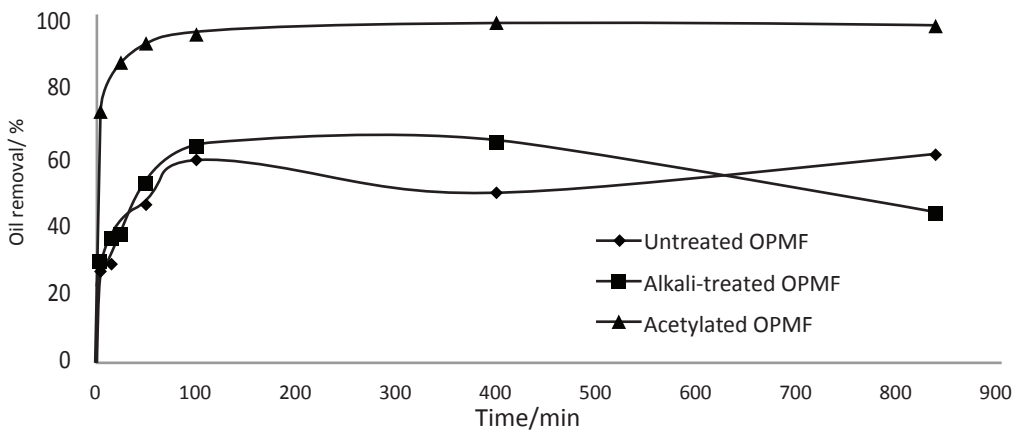


Figure 4: Oil removal percentage at different contact times

Oil Adsorption onto OPMFs at Different Contact Times

Batch adsorption studies were continued at various contact times using optimum OPMF mass obtained. Oil removal percentage for all samples increased rapidly at initial stage (0–50 minutes) which may attribute to the existence of more available vacant sites on the OPMFs surfaces. Contact time plays an important role at the beginning of oil adsorption and gave less contribution while approaching optimum contact time. The adsorption curve (Figure 4) shows that oil removal percentages increased with time and reach the equilibrium approximately at 100 minutes. As contact time was prolonged, there is no significant change in oil removal percentage of acetylated OPMF. However for alkali-treated OPMF, oil removal was started to decrease after 400 minutes suggesting a weak interaction force between the adsorbed oil and OPMF surfaces. The weak forces can only hold oil for some time before it is released back into the water. As for untreated OPMF, the removal percentage was found to be fluctuated.

Kinetic studies

The kinetic models were studied to understand the mechanism of oil adsorption and

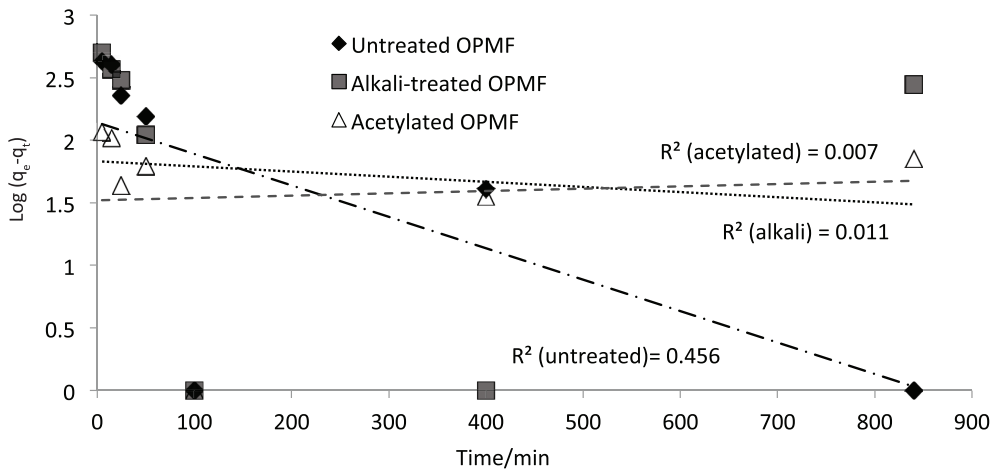


Figure 5: Pseudo-first order sorption kinetics of oil onto OPMFs

performance of OPMFs for oil removal. In this work, two models have been tested, pseudo-first-order and pseudo-second-order kinetic models. The linear form of the pseudo-first-order equation is given as follows:

$$\log q_e - q_t = \log q_e - \frac{k_1}{2.303} t \quad \text{Equation 2}$$

where q_e and q_t are the amount of oil adsorbed (mg/g) on adsorbent at equilibrium and time, t, respectively and k_1 is the rate constant of the first order adsorption (min^{-1}) (Husin *et al.*, 2011). From the result obtained (Figure 5) it shows that the linear regression coefficients (R^2) for pseudo-first-order kinetic model were found to be low indicating that this model is not suitable in describing the adsorption kinetic of oil onto all OPMFs. The experimental data was also tested by pseudo-second-order kinetic model which the linearized equation form is shown below:

$$\frac{t}{q_t} = \frac{1}{(K_2 q_e^2)} + \frac{1}{q_e} t \quad \text{Equation 3}$$

where k_2 is the pseudo-second-order rate constant of adsorption (g mg^{-1} min^{-1}). Straight lines were obtained in plot t/q_t versus t (Figure 6). This shows that the adsorption process of all OPMFs obeys pseudo-second-order kinetic model as regards to R^2 values that is almost

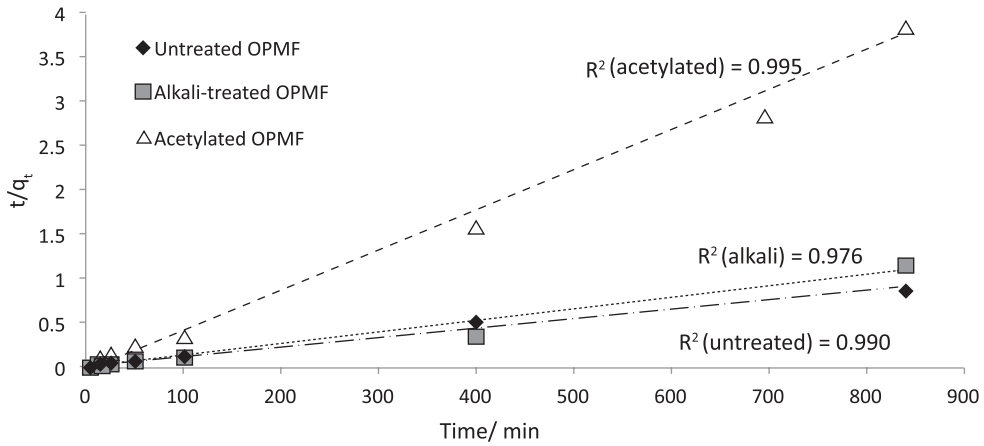


Figure 6: Pseudo-second order sorption kinetics of oil onto OPMFs

equal to 1. The similar results were reported by Husin *et al.,* (2011) for the adsorption of oil onto banana pseudostem fibers. It is recommended that oil sorption onto OPMFs governed by chemisorption process which being the rate controlling step for valency forces through sharing or exchange of electrons between oil and OPMFs (Ho & McKay, 1999).

Conclusion

In this study, oil palm mesocarp fiber (OPMF) was modified via alkali and acetylation treatments in order to enhance their sorption capacity. Untreated OPMF was able to adsorb oil in water with limited capacity while alkali-treated OPMF adsorption decreased started at 400 minutes. Acetylated OPMF exhibited the highest performance in oil removal compared to other OPMFs. The kinetic data for all OPMFs suits well with pseudo-second order as R^2 value is almost equal to 1 for all OPMFs (untreated = 0.99, alkali-treated = 0.976, acetylated = 0.995). The obtained results show that modification of OPMF do increased the performance of oil uptake and it is convinced that the OPMF could be used as an alternative adsorbent for the cleanup of oil waste in water.

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