

# Acetylation of oil palm empty fruit bunch fiber as an adsorbent for removal of crude oil

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**Abstract** Removal of oil spillage from the environment is a global concern. Various methods, including the use of fibers as sorbents, have been developed for oil spill control. Oil palm empty fruit bunch (OPEFB) fiber is a plant biomass that may be acetylated by acetic anhydride using N-bromosuccinimide (NBS) as a catalyst; here, the extent of acetylation may be calculated in terms of weight percent gain (*WPG*). The modified fiber was used to remove Tapis and Arabian crude oils. The optimum time, temperature, and catalyst concentration were 4 h, 120 °C, and 3 %, respectively, and these parameters could achieve an 11.49 % increase in *WPG*. The optimized parameters improved the adsorption capacity of OPEFB fibers for crude oil removal. The acetylated OPEFB fibers were characterized by using Fourier transform infrared spectroscopy and field emission scanning electron microscopy to observe the functional groups available and morphology. Kinetic and isotherm studies were conducted using different contact times and oil/water ratios. The rate of oil sorption onto the OPEFB fibers can be adequately described by the pseudo-second-order equation. Adsorption studies revealed that

adsorption of crude oil on treated OPEFB fiber could be best described by the Langmuir isotherm model.

**Keywords** Oil spill · Sorption capacity · Oil palm empty fruit bunch fiber · Acetylation · Kinetic and isotherm studies

## Introduction

Fossil fuels are important raw materials and energy sources used worldwide. However, improper handling of these fuels (e.g., during loading, transportation, and unloading) and human commercial activities can bring about hazardous impacts to marine life and the environment (Boopathy 2000). Oil leakage produces unpleasant odors and green algae blooms, which can cause drastic changes to the sea color and landscape (Annunciado et al. 2005). These problems have encouraged academicians, researchers, and industrial personnel to develop methods for oil removal. A robust and effective methodology must be developed to recover leaked oil and eradicate possible hazards caused by oil pollution. The existing management approach for oil spills includes the use of oil booms, skimmers, oil dispersants, oil gelling agents, in situ burning, bioremediation, and oil sorbents (Adebajo et al. 2003; Angelova et al. 2011; Asadpour et al. 2013; Zahed et al. 2010).

Sorbent materials have the potential to eradicate oil spill issues by cleaning and collecting the leaked oil. These materials can be categorized into three types, namely, inorganic materials, synthetic organic polymers, and organic natural materials. Synthetic sorbents, such as polypropylene and polyurethane, are utilized to retrieve oil in commercial applications (Adebajo et al. 2003). These sorbents generally have high oil sorption capacity, good buoyancy, and application simplicity but are non-biodegradable and can persist in the environment for long periods of time. Inorganic materials, such as

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utilized to investigate the reaction and morphology of the sorbent. The pseudo-first-order and pseudo-second-order models were used for kinetic studies, and the Langmuir and Freundlich isotherm models were tested to fit the experimental data.

## Methods

### Materials

OPEFB fibers were used in this study. The fiber was treated and tested to adsorb both Arabian and Tapis crude oils. Other chemicals used in this study included acetic anhydride, NBS, acetone, and ethyl alcohol.

### Mechanical treatment of oil palm empty fruit bunch fiber

OPEFB fibers were mechanically treated by manual hammering. One- to two-centimeter-long fibers were packed in a plastic bag as single sheets and hammered for about 10 min. After hammering, the fibers were subjected to wash by immersion into a 500-mL beaker containing 0.1 N NaOH. The mixture was stirred for 2 h. The treated fibers were washed with distilled water several times to remove the alkaline solution and then dried in an oven at 80 °C for 8 h. Mechanical treatment was used to eliminate SiO<sub>2</sub>, which can increase fiber pore sizes and surface roughness, on the fiber surface.

### Preparation of acetylated OPEFB fiber

Acetate groups feature higher molecular weights than hydroxyl groups and are thus bulkier than the latter. Thus, the acetylated sample is predicted to show larger weight increases, which are reported in terms of weight percent gain (WPG), compared with the raw sample (Teli and Valia 2013a). The acetic acid produced after reaction of the cellulosic material and acetic anhydride must be washed and removed from the sorbent material before the fiber is used. A calculated amount of OPEFB fiber was placed in a 500-mL two-necked round-bottom flask containing acetic anhydride (solid to liquid ratio, 1 g/30 mL) and NBS (1–3 %) as the reaction catalyst under atmospheric pressure. A reflux condenser, a thermometer, and a mechanical stirrer were attached to the flask. The flask then placed in an oil bath set to 90 or 120 °C for 2–6 h. The flask was removed from the oil bath after the required time, the mixture inside the flask was decanted, and the fibers were thoroughly washed with ethyl alcohol and acetone to remove unreacted acetic anhydride and acetic acid by-products. The modified fibers were placed in an oven at 80 °C overnight and weighed to evaluate the WPG. Each treatment was conducted three times under

similar conditions, and average values of WPG, which was calculated according to Eq. (2), are reported.

$$\text{WPG} = \frac{\text{Weight gain}}{\text{Original weight}} \times 100 \quad (2)$$

To show increase in the hydrophobicity of sorbent, the method proposed by Sidik et al. (Sidik et al. 2012) was applied. Base on the method, 1 g of sorbent was mixed with 30 mL of distilled water and was stirred for 20 min. After that, 30 mL of hexane was added and further agitated for 3 min. After termination time, the beaker was put in the static condition for 5 min to separate two immiscible phases. The upper layer of the mixture which placed in the hexane was separated by decanting. The residual was filtered and dried an oven at 110 °C to reach constant weight and weighed. The hydrophobicity degree of hydrophobicity of the sorbent which shows the presence of adsorbent transferred into the organic phase was determined as the ratio of the mass of OPEFB fiber transferred to hexane (g) and the initial OPEFB fiber mass (g), by Eq. (3).

$$\begin{aligned} \text{Degree of hydrophobicity (\%)} \\ = \frac{\text{Weight of OPEFB fiber in hexane}}{\text{Initial weight of OPEFB fiber}} \end{aligned} \quad (3)$$

To investigate how many sorbents are floated on the aquatic system, buoyancy test was carried out. Both types of sorbents modified and unmodified were tested to compare their floating characteristics. The test was carried out in a 500-mL glass beaker, it was filled with 300 mL water and was slowly added 30 mL crude oil, and then, 1 g of sorbents was placed in the middle of the oil slick. The mixture was put on the automatic shaker and set its frequency to 100 rpm and shake for 15 min. At the end of the test, the floated sorbent and oil were gathered by filter and suction, respectively. The settled materials which remain in the beaker were collected of the water, dried, and weighed. The percentage of buoyancy was calculated with the following equation (Eq. (4)):

$$\text{Buoyancy} = \frac{w_s}{w_0} \times 100 \quad (4)$$

where  $w_s$  and  $w_0$  are the mass of settled part and initial of sorbent, respectively.

### Characterization of OPEFB fiber and experimental oils

FTIR was performed from 400 to 4000 cm<sup>-1</sup>, and results were analyzed to compare the functional groups of the raw and acetylated fiber samples. The surface morphology and cross section of the sorbents were observed by FESEM to determine the surface roughness and pore diameter of the sorbent. The physical features of the OPEFB fiber, including Brunauer–

Emmett–Teller (BET) surface area and pore volume, were measured via  $N_2$  (g) adsorption in an ASAP 2020 analyzer (Micromeritics, USA) in liquid  $N_2$  using the BET method. A density meter (Anton Paar, Austria) and EV1000 viscometer (Anton Paar) were used to measure the density and viscosity of the experimental oils, respectively.

### Measurements of oil sorption capacity

In a 500-mL beaker, 40 mL of the crude oil samples (Tapis) was mixed with 400 mL of standard artificial seawater (3.5 % NaCl). About 1 g each of the raw and acetylated sorbents was then added to the oil/water system at room temperature. The system was kept for 10, 20, 30, 40, or 50 min, and the raw and acetylated OPEFB fibers were filtered using a mesh screen for 1 min. The OPEFB fibers were then re-weighed to calculate their oil sorption capacity (g oil/g sorbent) using Eq. (5).

$$\text{Oil sorption capacity} = \frac{(w_s - w_w - w_c)}{w_c} \quad (5)$$

where  $w_s$  is the weight of the wetted sorbent,  $w_c$  is the initial weight of the sorbent, and  $w_w$  is the weight of water. The weight of the absorbed water in the sample was measured using the Karl Fischer technique as well described in ASTM D1533. The experiment was repeated using heavy crude oil (Arabian).

To find the effect of oil concentration to water ratio on oil sorption capacity of sorbent, different amounts of oil in water from 12,500 to 125,000 mg/L were tested. One gram of the acetylated sorbent was used in this experiment. The sorption capacity of the sorbent was measured after 35- and 40-min contact time for Tapis and Arabian crude oils, respectively.

## Results and discussion

### Characterization of OPEFB fiber as a sorbent

#### *Morphology identification of sorbent*

The main sorption mechanisms include adsorption and absorption. The oil sorption capacity of sorbents is closely associated with the molecular arrangement, chemical properties, and physical properties of the sorbent; these properties include surface roughness, hollow lumens, porosity, twists, and crimps. Oleophilicity and surface energy are significant characteristics associated with the molecular arrangement and chemical properties of the sorbents, while the adsorption mechanism and capillary action are related to their physical configuration (Choi and Moreau 1993).

The physical configuration of the sorbent can be examined using FESEM images. The surface of OPEFB fibers contains

numerous cylindrical holes of about 10  $\mu\text{m}$  in diameter, some of which are filled with  $\text{SiO}_2$  (Fig. 1a, b). If the  $\text{SiO}_2$  is detached from the fiber surface, the resulting voids can improve the surface roughness and pore volume of the fibers, which, in turn, allows the oil to adhere to the surface of the fibers and diffuse into their porous interior through capillary action. Most of the  $\text{SiO}_2$  can be removed by hammering (Ghazali et al. 2009) and washing by 0.1 N NaOH. The treatment results showed reduced attachment of  $\text{SiO}_2$  molecules and increased surface roughness of the OPEFB fibers (Fig. 1c). The EDEX result shows that the silica content (atomic) reduced from 11.29 to 0.28 (as shown in Table 1). However, hammering treatment also destroyed the hollow tubular structure of the fibers and made them flat (Fig. 1d). Therefore, because flat structures and less porosity adsorb less oil, we can conclude that hammering exerts no effect on the oil sorption capacity of OPEFB fibers.

The FESEM cross section of the OPEFB fibers is shown in Fig. 1e, f. OPEFB fibers have a hollow tubular structure with diameters of 10–14  $\mu\text{m}$  and a highly porous interior. During adsorption, the oil penetrates into the porous interior and hollow structure of the fiber. We can conclude that the sorption mechanism in this study involves adsorption of crude oil by filling the porous interior of the sorbent through capillary action.

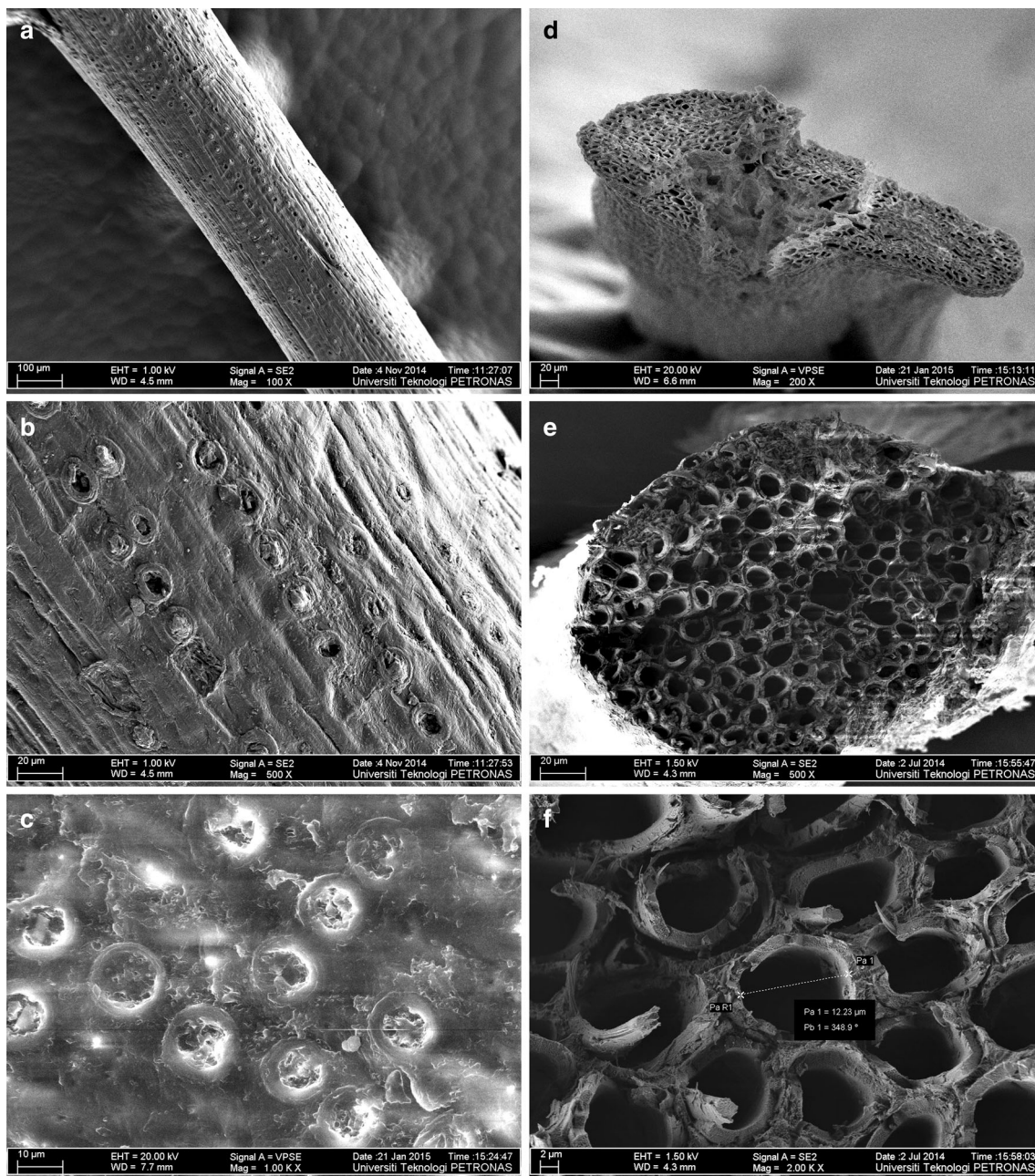
#### *FTIR analysis of sorbent*

Figure 2 shows the FTIR spectra of raw and acetylated OPEFB fibers at different reflux time.

The important bands recognized in the spectra are

- |                       |  |
|-----------------------|--|
| 3404 $\text{cm}^{-1}$ | Stretching vibrations of hydroxyl groups (O–H) present in cellulose, hemicellulose, and lignin of OPEFB fiber. |
| 2930 $\text{cm}^{-1}$ | C–H asymmetric stretching of $\text{CH}_2$ groups.   |
| 1740 $\text{cm}^{-1}$ | Stretching vibration of the carbonyl group $\text{C}=\text{O}$ in ester.                                       |
| 1640 $\text{cm}^{-1}$ | Bending mode of the absorbed water.  |
| 1375 $\text{cm}^{-1}$ | C–H bending vibration in $-\text{O}-(\text{C}=\text{O})-\text{CH}_3$ .   |
| 1240 $\text{cm}^{-1}$ | C–O stretching vibration in ester.   |

Comparison of the raw and acetylated fiber spectra indicates four major differences. Very weak adsorption at 1740  $\text{cm}^{-1}$  in raw fiber FTIR spectrum was dramatically increased in the acetylated fiber which shows an increase in carbonyl group  $\text{C}=\text{O}$  in the ester. Although the intensity of two ester bands around 1375 and 1240  $\text{cm}^{-1}$  were increased, the reduction of the hydroxyl groups at 3404 and 1640  $\text{cm}^{-1}$  demonstrated the substitution of the hydroxyl groups with the acetyl group. The effect of reaction time on the FTIR spectrum was also investigated by the peak intensity of acetylated OPEFB fibers. As shown in Fig. 2, an increase in reflux time from 2 to 6 h resulted in an increase in the intensity of the three



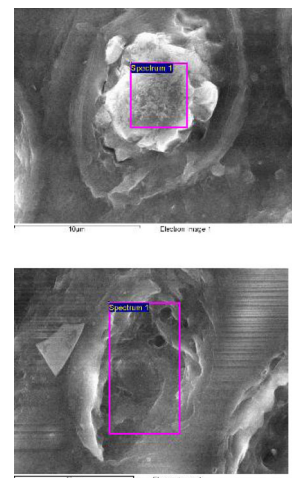
**Fig. 1** FESEM images of the **a–c** surface and **d–f** cross section of OPEFB fiber

ester bands at 1240, 1375, and 1740  $\text{cm}^{-1}$  but a decrease in hydroxyl groups (O–H), demonstrating a raise of acetylation, which agreed to the data of WPG as will be discussed in “Effect of different parameters on WPG” section. Although by comparing the FTIR spectra of the 4 and 6 h, there is no obvious change in the intensity of spectrum with increase in the reaction time, increase in carbonyl group in acetylated fiber create a non-polar layer on the surface of the fiber, which leads to a dramatic increase in degree of hydrophobicity (%DH) as approved by the experimental result before and after acetylation from 21 to 57%. Thus, all evidence confirms that the OPEFB fiber was successfully modified.

Although, increasing the reaction time from 2 to 6 h increases the intensity of the peak at the relative bands. This shows the effect of reaction time on the acetylation degree; nevertheless, there are only minor differences between the bands at 4 and 6 h. The bands that appeared at 3600 and 3800  $\text{cm}^{-1}$  are due to the O–H stretch of  $\text{H}_2\text{O}$  which appeared at 6-h reflux time. Varying degree of hydrogen bonding interactions among hydroxyl groups in the cellulose, hemicellulose, and lignin will result in wider peak in the OH stretching vibration region (3000–3800  $\text{cm}^{-1}$ ) (Barnette et al. 2012).

**Table 1** The EDEX result of SiO<sub>2</sub> body before and after mechanical treatment

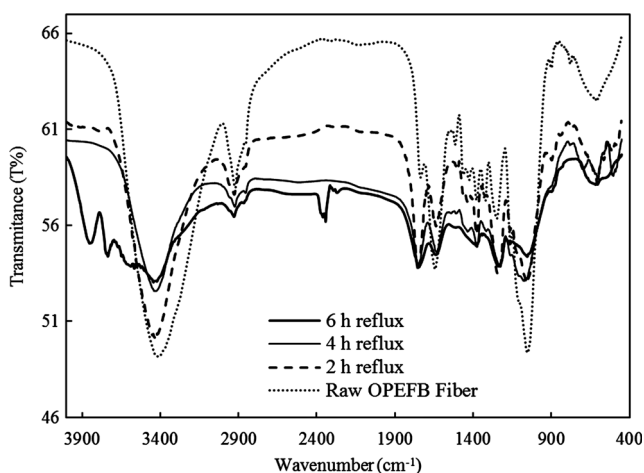
Before mechanical treatment			After mechanical treatment		
Element	Weight%	Atomic%	Element	Weight%	Atomic%
C K	31.34	41.21	C K	60.01	66.92
O K	47.56	46.94	O K	38.67	32.37
Na K	0.55	0.38	Na K	0.72	0.42
Si K	20.09	11.29	Si K	0.59	0.28
K K	0.45	0.18			
Totals	100.00		Totals	100.00	



*Surface area measurement*

The physical properties of raw and treated OPEFB fiber were analyzed. Table 2 shows surface area and average pore diameter of sorbent. According to the criterion established by the International Union of Pure and Applied Chemistry (IUPAC), pore sizes are classified into the following three groups: micropores (diameter (*d*) < 20 Å), mesopores (20 Å < *d* < 500 Å), and macropores (*d* > 500 Å) (Rouquerol et al. 1994). Based on the BET analyzes, raw and acetylated OPEFB fibers have a surface area of 0.4077 and 0.3463 m<sup>2</sup>/g, respectively. The BET surface areas of all samples were analyzed in triplicate. Based on the morphology of fibers discussed in “Morphology identification of sorbent” section and shown in Fig. 1d–f, OPEFB fiber has a porous interior and hollow structure, the main factors which contribute to enhance oil sorption. This low value of surface area does not explain the apparent high oil sorption capacity of fibers compared to mangrove bark, published in our previous work (Asadpour et al. 2014a). It is

reported elsewhere (Eric et al. 1998) (RAHMAH 2009) that some intermolecular structures of agricultural biomass collapsed during N<sub>2</sub> gas adsorption in the BET test. This happened during dehydration process to dry water molecules by vacuum drying (conditions of sample preparation before the N<sub>2</sub> adsorption). During this process, the intramolecular water molecules were removed during vacuum drying, which was followed by the collapsing cellulose chains. Simultaneously, all the pores in the intermolecular structure are clogged. This linkage is so strong to repair by N<sub>2</sub> molecules. Therefore, only the external surface of fibers was measured (Eric et al. 1998). The similar result was archived for cotton and kapok fiber which have high sorption capacity, but BET method showed the low surface area that only measured the external surface area which does not represent the true values (Eric et al. 1998; RAHMAH 2009). It is suggested that the same phenomenon resulted in measurement of low BET surface area in this study as well. The average pore diameter of the sorbent was slightly increased after acetylation.



**Fig. 2** FTIR spectra of raw and acetylated OPEFB fibers

**Effect of hammering on sorption capacity**

No significant change in sorption capacity was observed in the raw and pre-treated samples. As mentioned in “Morphology identification of sorbent” section, some of the SiO<sub>2</sub> are removed from the fiber surface during hammering treatment, and improvements in surface roughness and pore size may be expected. Although oil adheres to the surface and diffuses into the porous interior of the fibers, the flat interior structure of the sorbent cannot adsorb as much oil as the raw fibers. Thus, oil remained on the fiber surface and filled up its pores. This theory confirms the results achieved in this study. Figure 3 illustrates the sorption capacity of raw, hammered treated fibers. Pre-treatment (hammering) exerted no significant effect on oil sorption capacity in this study.

**Table 2** BET surface area and average pore diameter of raw and acetylated OPEFB fiber

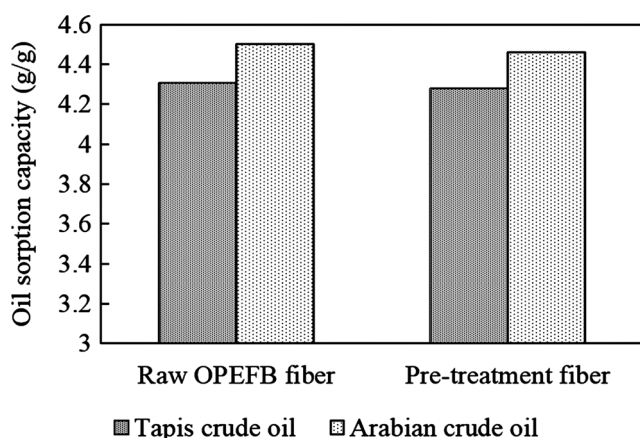
Adsorbent	BET surface area (m <sup>2</sup> /g)	Adsorption average pore diameter (Å)
Raw OPEFB fiber	0.4077 m <sup>2</sup> /g	54.7377 Å
Acetylated OPEFB fiber	0.3463 m <sup>2</sup> /g	63.6576 Å

### Effect of different parameters on WPG

Optimization of the experimental data was carried out by changing various parameters affecting WPG and oil sorption capacity, including reaction time, temperature, and catalyst percentage. Changes in these parameters were correlated with the acetylation conditions. The acetylated fibers showed more hydrophobicity and adsorbed more oil. The maximum oil sorption capacity was also associated with the maximum WPG. Table 3 describes the various parameters employed in each experiment. The experimental data showed that the maximum WPG (11.49 %) may be observed at 4 h of reaction time, refluxing at 120 °C, and 3 % NBS as the catalyst. Under these conditions, sorption of Tapis and Arabian crude oils reached 6.80 and 7 g/g, respectively.

One of the main factors affecting acetylation is reaction time. WPG increased with increasing reaction time up to 4 h and slightly decreased afterward. Diffusion of the acetylation agent into the OPEFB fiber molecules increased with increasing time. However, prolonged reaction times negatively affected WPG because the acetic acid released as a by-product reduced the acetic anhydride concentration and, consequently, the reaction rate. The optimum reaction time was found to be 4 h, after reflux.

Refluxing temperatures of 90 and 120 °C were tested. Table 1 shows that a higher WPG could be achieved at the higher temperature. During acetylation, hydrogen bond networks with hydroxyl groups are broken to allow the acylating agent to modify the intermolecular structure of the fibers.



**Fig. 3** Maximum oil sorption capacity of raw and pre-treatment fiber for Arabian and Tapis crude oils

High temperature assists the breaking of hydrogen bond networks and swelling of the OPEFB fibers to create reactive chemical sites that are favorable for accepting the acylating agent; thus, the acetylation process is enhanced. Therefore, a refluxing temperature of 120 °C is more effective than 90 °C. Temperatures higher than 120 °C were also tested, and the results show no significant WPG change. Therefore, to obtain an energy-efficient and cost-effective procedure, 120 °C was selected as the optimum temperature.

Catalyst concentration is another factor that plays an important role in acetylation. Increases in NBS concentration considerably accelerated the acetylation process. With 3 % NBS and refluxing at 120 °C for 4 h, WPG reached a maximum value of 11.49 %. NBS (C<sub>4</sub>H<sub>4</sub>BrNO<sub>2</sub>) contains Br, which can activate the carbonyl group of acetic anhydride and yield-reactive acylating agents (Teli and Valia 2013b). However, since the WPG at 5 % NBS was similar to that at 3 % NBS, the optimum NBS concentration was considered to be 3 %. In summary, the highest WPG (11.49 %) and oil sorption capacity (6.80 g/g for Tapis and 7 g/g for Arabian crude oils) were obtained by refluxing at 120 °C for 4 h with 3 % NBS.

Figure 4 shows the relationship between the oil sorption capacities of OPEFB fibers and their WPG. The oil sorption capacity of OPEFB fibers was directly correlated with their WPG; oil sorption capacity increased with increasing WPG.

### Effect of contact time on sorption capacity

Low- and high-viscosity crude oils were immediately adsorbed by the sorbent within the first 15 min of contact (Fig. 5). The sorption process continued slowly until equilibrium was achieved at around 35 and 30 min for the Arabian and Tapis crude oils, respectively. Sorption indicated three stages, namely, the rapid, slow, and steady stages. In the rapid stage, crude oil was taken up at a high rate, likely because of the bare surface and interiors of the sorbent fibers. In the slow stage, adsorption increased gradually as small oil droplets were created by breakage of the crude oil that diffused into the interior of the fibers (Stang et al. 1994). Finally, the steady stage occurred after 35 and 30 min of sorption for the Arabian and Tapis crude oils, respectively. In this stage, adsorption remained constant and reached equilibrium because the OPEFB fibers were saturated by the crude oil particles. The adsorption time differed between the two oils because of

**Table 3** Effect of reaction time, temperature, and catalyst concentration on acetylation and oil sorption capacity of OPEFB fiber

No.	Reaction time	Temperature (°C)	Catalyst (%) <sup>a</sup>	WPG (%) <sup>b</sup>	Oil absorbcency	
					Arabian	Tapis
1	2	90	1	4.62	4.76	4.4
2	2	120	1	6.1	4.8	4.51
3	2	90	3	6.89	5.3	4.9
4	2	120	3	7.86	5.62	5.25
5	2	90	5	6.8	5.2	4.85
6	2	120	5	7.7	5.58	5.15
7	4	90	1	7.68	5.56	5.23
8	4	120	1	9.3	6.3	5.9
9	4	90	3	9.75	6.58	6.3
10	4	120	3	11.49	7	6.8
11	4	90	5	9.72	6.47	6.2
12	4	120	5	11.05	6.82	6.48
13	6	90	1	7.5	5.45	5.1
14	6	120	1	8.8	6	5.67
15	6	90	3	9.58	6.23	5.82
16	6	120	3	10.26	6.75	6.3
17	6	90	5	9.32	6.34	6.08
18	6	120	5	10.14	6.49	6.15

<sup>a</sup> Catalyst (%) represents 1, 3, and 5 g NBS in 100 mL acetic anhydride

<sup>b</sup> WPG represents the weight percent gain of OPEFB fiber due to acetylation, and it was measured according to  $WPG (\%) = [\text{weight gain}/\text{original weight}] \times 100$

differences in their viscosity. Tapis oil is a low-viscosity oil that flows and penetrates faster than Arabian oil, which is a high-viscosity oil. Arabian crude oil reached the porous interior of the sorbent within 35 min.

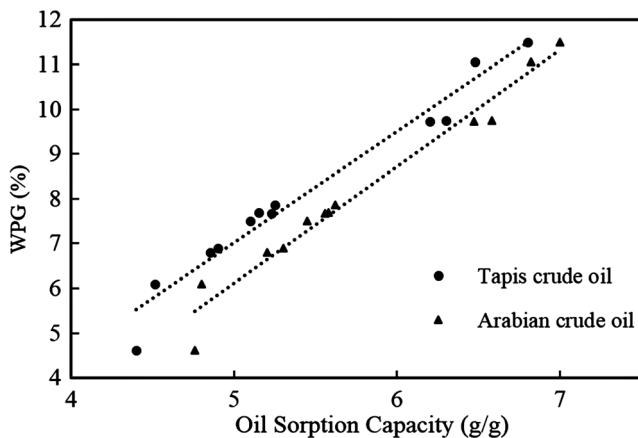
**Buoyancy test**

The result of the test shows that buoyancy of OPEFB fiber was varied from 95.3 to 93.7 after 5- and 15-min buoyancy time, although the raw sample shows the lowest value of 91.2

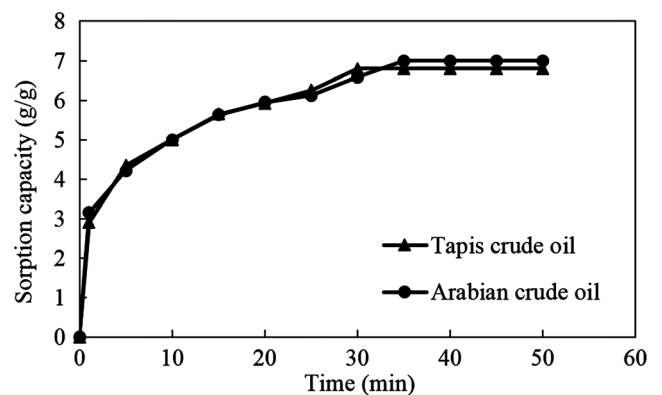
which is acceptable by ASTM. The good buoyancy of acetylated OPEFB fiber goes them into an effective adsorbent in real conditions for the removal of crude oil spills.

**Kinetic study**

To understand the sorption process, a kinetic adsorption study was conducted. Two well-known models, namely, the pseudo-first-order and pseudo-second-order models, were used to understand the kinetics of

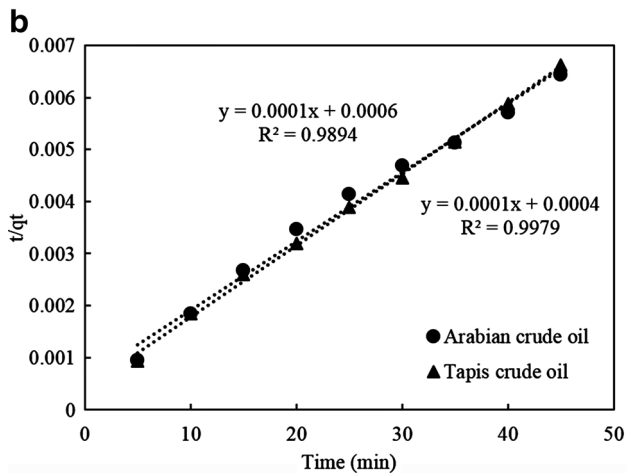
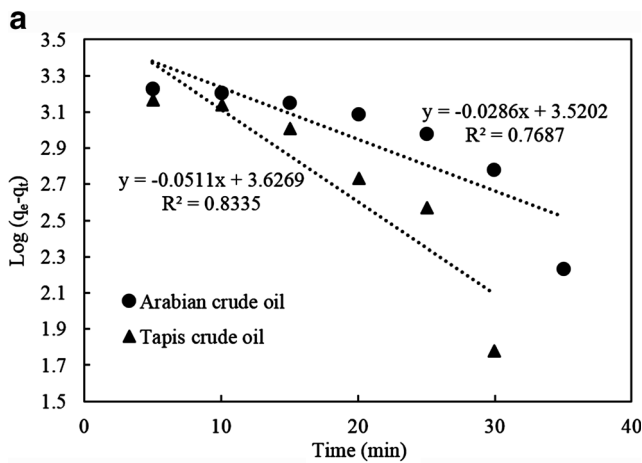


**Fig. 4** Relations between oil sorption capacity and WPG



**Fig. 5** Effect of sorption time on oil sorption capacity of acetylated OPEFB fiber





**Fig. 6** a Pseudo-first- and b pseudo-second-order rate equation models for acetylated OPEFB fiber

adsorption of crude oil onto the OPEFB fiber. The linear forms (Eqs. (6) and (7)) of these two models are as follows:

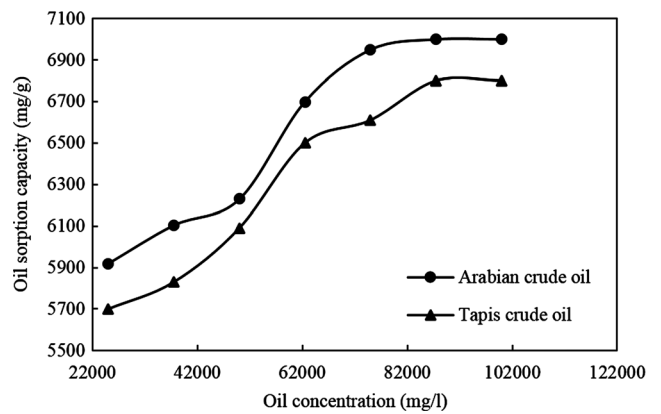
$$\text{Log}(q_e - q_t) = \text{Log} q_e - \frac{K_1}{2.303}t \tag{6}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

where  $q_e$  and  $q_t$  (mg/g) are the amounts of oil adsorbed onto the sorbent at equilibrium and time  $t$ , respectively, and

**Table 4** Pseudo-first- and pseudo-second-order adsorption rate constants, correlation coefficients ( $R^2$ ), and calculated and experimental  $q_e$  values for Tapis and Arabian crude oils

Type of oil	$q_e$ (mg/g) (experimental)	First-order kinetic model			Second-order kinetic model		
		$q_e$ (mg)	$R^2$	$K_1$	$q_e$	$R^2$	$K_2$
Tapis	6,800	4,235.45	0.8335	0.117	10,000	0.9979	$2.5 \times 10^{-5}$
Arabian	7,000	3,312.8	0.768	0.065	10,000	0.9894	$1.6 \times 10^{-5}$



**Fig. 7** Effect of oil concentration on oil sorption capacity

$K_1$  and  $K_2$  (1/min) are the rate constants of first-order and second-order models, respectively. Figure 6a, b shows the linear plots of the two models.  $K_1$  and  $q_e$  were determined from the plot of  $\text{log}(q_e - q_t)$  against  $t$  for the first-order model, and  $K_2$  and  $q_e$  were calculated from the plot of  $t/q_t$  versus  $t$  for the second-order model. The calculated parameters, namely,  $R^2$ ,  $K_1$ ,  $K_2$ , and theoretical  $q_e$ , for both models, are listed in Table 4. The pseudo-second-order model showed a better fit with the experimental data because this model yielded a higher  $R^2$  value than the first-order model as well as fairly matching experimental and theoretical  $q_e$  values.

**Effect of oil concentration to water ratio and isotherm study**

Figure 7 shows the effect of oil concentration on sorption capacity. The highest adsorption rate was achieved at 87,500 mg/L oil concentration. At equilibrium, no further adsorption was observed. This equilibrium can be attributed to the saturation of active sites on the OPEFB fiber at high oil concentrations.

In this study, two isotherms models, namely, the Langmuir and Freundlich models, were used to describe the mechanism of oil sorption. Equations (8) and (9), respectively, represent

**Table 5** The constants and coefficients of the Langmuir and Freundlich isotherms for Arabian and Tapis crude oils onto acetylated OPEFB fiber

Type of oil	Langmuir isotherm coefficient			Freundlich isotherm coefficient		
	$q_0$ (mg/g)	$R_l$	$R^2$	$K_f$	$1/n$	$R^2$
Tapis	10,000	0.073	0.9983	2,235.6	0.0983	0.925
Arabian	10,000	0.080	0.9979	2,466.6	0.0925	0.8984

the linear forms of the Langmuir and Freundlich isotherm models.

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{1}{q_0} C_e \tag{8}$$

$$\log q_e = \log k_f + \frac{1}{n} (\log C_e) \tag{9}$$

where  $q_e$  (mg/g) is the amount of oil adsorbed at equilibrium time or monolayer adsorption,  $C_e$  (mg/L) is the equilibrium concentration of oil,  $q_0$  is the theoretical maximum adsorption capacity, and  $b$  is the Langmuir constant related to the rate of adsorption. The critical features of the Langmuir isotherm can be explained by the constant separation factor  $R_l$ , which is dimensionless. Here, the isotherm model is favorable if

$0 < R_l < 1$ , unfavorable if  $R_l > 1$ , linear if  $R_l = 1$ , or irreversible if  $R_l = 0$ .  $R_l$  is calculated using Eq. (10).

$$R_l = \frac{1}{1 + bC_0} \tag{10}$$

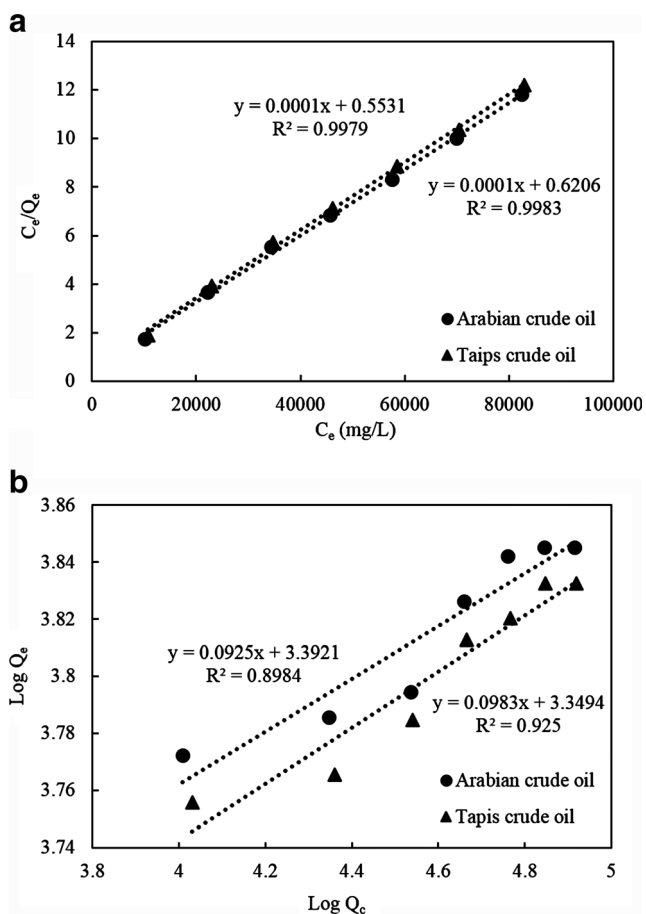
where  $C_0$  is the initial oil concentration.

In the Freundlich equation,  $q_e$  (mg/g) is the maximum adsorption capacity,  $C_e$  is the equilibrium concentration of oil (mg/L),  $K_f$  (mg/g) (L/mg) $^{1/n}$  is the adsorption capacity in multilayer adsorption, and  $n$  is the dimensionless Freundlich constant. When  $1/n$  is between 0 and 1, the adsorption process is favorable. The values of  $n$  and  $K_f$  are obtained from the slope and intercept of the plot of  $\log q_e$  versus  $\log C_e$ . All of the calculated values are shown in Table 5. Figure 8a, b illustrates the Langmuir and Freundlich plots of the sorption data for Arabian and Tapis crude oil sorption onto the acetylated OPEFB fibers. The Freundlich model describes the multilayer adsorption of the crude oil onto a heterogeneous sorbent surface, whereas the Langmuir model assumes that adsorption of oil onto the adsorbent surface is monolayer in nature and homogeneous (Salarirad et al. 2011).

The results show that fitting via the Langmuir isotherm model produced a higher correlation coefficient ( $R^2$ ) than fitting via the Freundlich isotherm model. The  $R_l$  obtained (0.073 and 0.080 for Arabian and Tapis crude oils, respectively) reveals that adsorption favored the Langmuir model. Although the  $1/n$  Freundlich constant is between 0 to 1 (indicating favorable fitting), this model produces an  $R^2$  lower than that obtained from the Langmuir model. These findings indicate that sorption of the crude oils onto OPEFB fibers occurs via a monolayer approach through homogeneous sites with uniform energy-level distributions.

**Conclusion**

Acetylated OPEFB fibers are more hydrophobic than raw fibers. The optimum conditions for acetylation of the fibers included acetic anhydride with 3 % NBS as a catalyst at 120 °C and 4 h of refluxing time. Significant differences in the FTIR spectra of the raw and acetylated fibers were observed with increasing acetyl and ester groups and decreasing hydroxyl groups. The optimum contact time for oil adsorption



**Fig. 8** a Langmuir and b Freundlich isotherms for Arabian and Tapis crude oils onto acetylated OPEFB fiber

was influenced by the oil viscosity. Arabian crude oil (heavy crude) required 35 min to reach equilibrium, whereas Tapis (light crude) required only 30 min. The sorption rate and adsorption mechanism of crude oil onto the acetylated sorbent can be described by the pseudo-second-order model. The oil concentration equilibrium fitted the Langmuir isotherm model. The results of this study reveal the potential use of waste materials such as OPEFB fibers as an environmentally acceptable and economical sorbent for oil spill cleanup.

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## References

- Adebajo MO, Frost RL, Klopogge JT, Carmody O, Kokot S (2003) Porous materials for oil spill cleanup: a review of synthesis and absorbing properties. *J Porous Mater* 10:159–170
- Angelova D, Uzunov I, Uzunova S, Gigova A, Minchev L (2011) Kinetics of oil and oil products adsorption by carbonized rice husks. *Chem Eng J* 172:306–311
- Annunciado T, Sydenstricker T, Amico S, Annunciado T, Sydenstricker T, Amico S (2005) Experimental investigation of various vegetable fibers as sorbent materials for oil spills. *Mar Pollut Bull* 50:1340–1346
- Asadpour R, Sapari NB, Tuan ZZ, Jusoh H, Riahi A, Orji KU (2013) Application of sorbent materials in oil spill management: a review Caspian. *J Appl Sci Res* 2:46–57
- Asadpour R, Sapari NB, Isa MH, Orji KU (2014a) Enhancing hydrophobicity of mangrove bark by esterification for oil adsorption. *Water Sci Technol* 70:1220–1228. doi:10.2166/wst.2014.355
- Asadpour R, Sapari NB, Isa MH, Orji KU (2014b) Investigation of modified mangrove bark on the sorption of oil in water. *Appl Mech Mater* 567:74–79
- Asadpour R, Sapari NB, Isa MH, Kakooei S, Orji KU (2015) Acetylation of corn silk and its application for oil sorption. *Fibers Polym* 16:1830–1835. doi:10.1007/s12221-015-4745-8
- Asadpour R, Sapari NB, Isa MH, Kakooei S, Orji KU, Daneshfozoun S (2016) Esterification of corn silk fiber to improve oil absorbency. *Adv Mater Res* 1133:552–556
- Barnette AL et al (2012) Quantification of crystalline cellulose in lignocellulosic biomass using sum frequency generation (SFG) vibration spectroscopy and comparison with other analytical methods. *Carbohydr Polym* 89:802–809
- Bastani D, Safekordi A, Alihosseini A, Taghikhani V (2006) Study of oil sorption by expanded perlite at 298.15 K. *Sep Purif Technol* 52:295–300
- Boopathy R (2000) Factors limiting bioremediation technologies. *Bioresour Technol* 74:63–67
- Carmody O, Frost R, Xi Y, Kokot S (2007) Adsorption of hydrocarbons on organo-clays—implications for oil spill remediation. *J Colloid Interface Sci* 305:17–24
- Choi HM, Moreau JP (1993) Oil sorption behavior of various sorbents studied by sorption capacity measurement and environmental scanning electron microscopy. *Microsc Res Tech* 25:447–455
- Eric H, Chongrak K, Noureddine A, Jean P (1998) Application of methylene blue adsorption to cotton fiber specific surface area measurement. *J Cotton Sci* 2:164–173
- Ghazali A, Wan Rosli W, Law K (2009) Pre-treatment of oil palm biomass for alkaline peroxide pulping. *Cellul Chem Technol* 43:331–338
- Hamzah F, Idris A, Shuan TK (2011) Preliminary study on enzymatic hydrolysis of treated oil palm (*Elaeis*) empty fruit bunches fibre (EFB) by using combination of cellulase and  $\beta$  1–4 glucosidase. *Biomass Bioenergy* 35:1055–1059
- Isa MH, Ibrahim N, Aziz HA, Adlan MN, Sabiani NHM, Zinatizadeh AAL, Kutty SRM (2008) Removal of chromium (VI) from aqueous solution using treated oil palm fibre. *J Hazard Mater* 152:662–668
- Karimi B, Seradj H (2001) N-bromosuccinimide (NBS), a novel and highly effective catalyst for acetylation of alcohols under mild reaction conditions. *Synlett* 4:519–520
- RAHMAH AU (2009) Characterization of physicochemical properties and process design for oil removal using *Ceiba pentandra* (L.) Gaertn. as a natural sorbent. Dissertation, Universiti Teknologi Petronas
- Rouquerol J et al (1994) Recommendations for the characterization of porous solids (Technical report). *Pure Appl Chem* 66:1739–1758
- Salarirad MM, Behnamfard A Modeling of equilibrium data for free cyanide adsorption onto activated carbon by linear and non-linear regression methods. In: International Conference on Environment and Industrial Innovation, Singapore, 2011. IACSIT Press.
- Shuit SH, Tan KT, Lee KT, Kamaruddin A (2009) Oil palm biomass as a sustainable energy source: a Malaysian case study. *Energy* 34:1225–1235
- Sidik S, Jalil A, Triwahyono S, Adam S, Satar M, Hameed B (2012) Modified oil palm leaves adsorbent with enhanced hydrophobicity for crude oil removal. *Chem Eng J* 203:9–18
- Stang M, Karbstein H, Schubert H (1994) Adsorption kinetics of emulsifiers at oil–water interfaces and their effect on mechanical emulsification. *Chem Eng Process* 33:307–311
- Sun X-F, Sun R, Sun J-X (2002) Acetylation of rice straw with or without catalysts and its characterization as a natural sorbent in oil spill cleanup. *J Agric Food Chem* 50:6428–6433
- Sun X, Sun R, Sun J (2004) Acetylation of sugarcane bagasse using NBS as a catalyst under mild reaction conditions for the production of oil sorption-active materials. *Bioresour Technol* 95:343–350
- Teli M, Valia SP (2013a) Acetylation of banana fibre to improve oil absorbency. *Carbohydr Polym* 92:328–333
- Teli M, Valia SP (2013b) Acetylation of jute fiber to improve oil absorbency. *Fibers Polym* 14:915–919
- Toyoda M, Inagaki M (2003) Sorption and recovery of heavy oils by using exfoliated graphite. *Spill Sci Technol Bull* 8:467–474
- Tryba B, Morawski AW, Kalenczuk RJ, Inagaki M (2003) Exfoliated graphite as a new sorbent for removal of engine oils from wastewater. *Spill Sci Technol Bull* 8:569–571
- Wang J, Wang A (2013) Acetylated modification of kapok fiber and application for oil absorption. *Fibers Polym* 14:1834–1840
- Zahed MA, Aziz HA, Isa MH, Mohajeri L, Mohajeri S (2010) Optimal conditions for bioremediation of oily seawater. *Bioresour Technol* 101:9455–9460