Enhancing the hydrophobicity of mangrove bark by esterification for oil adsorption
Robabeh Asadpour, Nasiman Bin Sapari, Mohamed Hasnain Isa and Kalu Uka Orji

ABSTRACT

Oil spills generally cause worldwide concern due to their detrimental effects on the environment and the economy. An assortment of commercial systems has been developed to control these spills, including the use of agricultural wastes as sorbents. This work deals with raw and modified mangrove barks (*Rhizophora apiculata*), an industrial lignocellulosic waste, as a low cost adsorbent for oil-product-spill cleanup in the aquatic environment. Mangrove bark was modified using fatty acids (oleic acid and palmitic acid) to improve its adsorption capacity. The oil sorption capacity of the modified bark was studied and compared with that of the raw bark. Kinetic tests were conducted with a series of contact times. The influence of particle size, oil dosage, pH and temperature on oil sorption capacity was investigated. The results showed that oleic acid treated bark has a higher sorption capacity (2,860.00 ± 2.00 mg/g) than untreated bark for Tapis crude oil. A correlation between surface functional groups, morphology and surface area of the adsorbent was studied by Fourier transform infrared spectrum, field emission scanning electron microscopy images and Brunauer–Emmett–Teller analysis. Isotherm study was conducted using the Langmuir and Freundlich isotherm models. The result showed that adsorption of crude oil on treated mangrove bark could be best described by the Langmuir model.

Key words | fatty acids, mangrove bark, oil spill, sorption capacity

INTRODUCTION

The risk of water pollution by petroleum products has progressively increased due to ongoing exploration, transportation, and storage. Every year, the total inflow of petroleum into water is about 10 million metric tons (Hussein et al. 2009). Among the worst oil spill disasters are Exxon Valdez in Prince William Sound, Alaska, (1989), the Persian Gulf War spill (1991), and the Deepwater Horizon oil spill in the Gulf of Mexico (2010), where millions of gallons of petroleum products and derivatives were spilled into the marine environment (Angelova et al. 2011; Wang et al. 2012). Weathering processes such as evaporation, dissolution, dispersion, photo-oxidation and microbial degradation take place after spills and alter the chemical, physical and biological properties of hydrocarbons. (Hussein et al. 2009; Asadpour et al. 2013). It takes a very long time to restore the environment to its original state. Thus, it is essential to find a rapid, efficient and effective method to eliminate any potential oil pollution hazard and recover the spilled oil concurrently. Several methods are currently employed for the removal of spilled oil from surface water such as booms, skimmers, in-situ burning, bioremediation, chemical agents such as dispersants and oil sorbent (Adebajo et al. 2003; Abdullah et al. 2010; Zahed et al. 2010; Angelova et al. 2011; Zeng et al. 2014). Sorbents are preferable in small-scale applications due to their ability to transfer oil from the liquid phase to the semi-solid or solid phase (Adebajo et al. 2003; Abdullah et al. 2010). Sorbents can be divided into three classes: natural organic sorbent, inorganic sorbent and synthetic sorbent. Effective oil sorbents have properties such as high oil uptake rate, oleophilicity-hydrophobicity, reusability, and biodegradability. Some natural organic fibers such as cotton, milkweed, kenaf, and wool have been reported to have higher oil sorption capacities than most commercial synthetic fibers. Some manmade polymer fibers such as polyvinyl chloride/polystyrene (Zhu et al. 2011) and

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polyurethane sponges treated with SiO₂ sol and gasoline (Wu et al. 2014) have very high oil sorption capacity, but they are not an environmentally acceptable sorbent. Thus, natural materials such as agricultural products are the sorbents of choice due to their low cost, easy availability, environmental friendliness and biodegradability (Sun et al. 2002; Lim & Huang 2007; Paulauskiene et al. 2014).

Chemical modification of agricultural by-products has been attempted by a number of researchers to improve the adsorption capacity of some materials. These include barley straw modified by surfactant, sawdust grafted with fatty acid, banana trunk fibers modified by fatty acid, wheat straw modified by acid hydrolysis and jute fiber, sugarcane bagasse and rice straw modified by acetylation (Sun et al. 2002; Sun et al. 2004; Banerjee et al. 2006; Ibrahim et al. 2009; Sathasivam & Haris 2010; Sidiras & Konstantinou 2012; Teli & Valia 2013).

The literature contains reports on the use of biosorbents such as raw or modified bark peel for the removal of heavy metals and dyes from aquatic solutions (Tan et al. 2010; Seey & Kassim 2012). Mangrove bark peel is an abundant by-product of the charcoal industry, which produces cooking fuel, particularly for recreational activities. It is readily available from the charcoal industry as a waste material. Currently, the total extent of mangroves in Perak is approximately 43,292 ha. A tree yields an average of 200 kg of bark (Baba et al. 2013). Mangrove bark peel consists of cellulose, hemicelluloses and lignin. The first two constituents are hydrophilic, and the lignin is hydrophobic. This means that cellulose and hemicelluloses are principally responsible for moisture uptake. These properties can be changed by chemical modification or surface modification of the components. The aim of this work was to examine the potential of modified mangrove bark peel to recover spilled oil. Surface modification was applied to improve its hydrophobic properties. Since mangrove bark tends also to absorb water, its oil sorption capacity may be intensely reduced; therefore, esterification using fatty acids was introduced to increase the hydrophobicity of the bark peel. Different factors highlight the various parameters influencing the oil sorption capacity of untreated and treated mangrove bark. The kinetic study in our previous published work showed that the adsorption of crude oil onto mangrove bark exhibits the best fit using the pseudo-second-order kinetics model (Asadpour et al. 2014). In the current study, isotherm studies were used. The experimental data were described by the Langmuir and Freundlich isotherm models to find suitable isotherm models.

### METHODS

#### Materials

Mangrove barks were obtained as waste products from a local charcoal factory. The barks were taken from a mechanical debarker. The collected peels were washed several times with distilled water to remove dust and mechanical impurities, and then dried in an oven at 105°C overnight. A mechanical grinder was used to grind the bark into fine grounds. The ground bark peel was sieved to a constant size using the standard testing sieve No. 300 and 450 microns (ASTM, USA). Crude oil samples used in this study were Tapis Malaysian crude oil obtained from a local refinery in Malaysia. The density measurement of crude oil was carried out using density meter (Anton Paar, Austria). The viscosity of crude oil was measured using an EV1000 Viscometer (Anton Paar, Austria). The physical properties of Tapis crude oil are shown in Table 1.

#### Characterization of sorbent

The bark morphology was analyzed by field emission scanning electron microscopy (FESEM). The chemical structure of mangrove bark and its functional groups were analyzed using the Fourier transform infrared (FTIR) spectrum. This method was carried out by mixing bark (about 5–10% by weight), and KBr (IR-transparent material) followed by compression of the mixture using a mechanical compressor at pressures of 15,000 psi for about 20 seconds to form a pellet. It was scanned over the range of 400 to 4,000 cm⁻¹ wavelength. The physical attributes of the bark adsorbent, including surface area, pore diameter and pore volume were measured via N₂ (g) adsorption in an ASAP 2020 analyzer (Micromeritics, USA) in liquid N₂ using the Brunauer-Emmett-Teller (BET) method.

#### Preparation of mangrove bark

Two grams of untreated bark (450μm and 300μm) was mixed with 0.8 g of oleic acid or 1.2 g of palmitic acid in 200 ml of n-hexane, which contained one to three drops of

### Table 1 | The physical properties of the experimental oil

<table>
<thead>
<tr>
<th>Tapis crude oil 25–30 °C</th>
<th>Density (g/cm³)</th>
<th>0.79</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (cP)</td>
<td>3.32</td>
<td></td>
</tr>
</tbody>
</table>
sulfuric acid (99%) as catalyst. The mixture was refluxed at 60 ± 5 °C for 6 hours. The esterified fatty acid treated bark was then extensively washed with n-hexane and dried in an oven at 105 °C for 24 h and stored in a desiccator for further use (Banerjee et al. 2006). The raw and treated barks were denoted as UTB (untreated bark), oleic acid treated bark (OTB) and PTB (palmitic acid treated bark).

Oil sorption capacity

The sorption experiments were conducted in a dynamic simulated system. A known quantity (5 to 50 g) of crude oil was mixed with 250 ml of artificial sea water (3.5% NaCl) in a 500-ml beaker for 5 min by constantly stirring at room temperature (25 °C). After stirring by magnetic stirrer, the oil formed a layer at the surface of the water. Then, 1 g of sorbent (UTB, OTB, and PTB) was added to the beaker, and the mixture agitated for various lengths of time (5 to 50 min) on an orbital shaker (150 rpm/min). The sorbent and liquid were then separated by filter, and the residue was dried in an oven at 70 °C for 20 min to reach a constant weight. The amount of oil sorbed by each sorbent was calculated by subtracting the weight of the sorbent before sorption from that after sorption, as in the following equation:

\[
\text{Oil sorption capacity} = \frac{w_s - w_c}{w_c}
\]

where \(w_s\) is the weight of the sorbent after oil sorption; \(w_c\) is the initial weight of sorbent before sorption. All tests were conducted in triplicate. The temperature and pH were performed within ranges of 15 to 80 °C and 3.00–10.00, respectively, for the oil–water solution. The pH adjustments were accomplished with 0.1 M HCl or 0.1 M NaOH.

RESULTS AND DISCUSSION

Characterization of the adsorbent

FTIR analysis of sorbent

Plots of FTIR spectra for UTB, OTB, PTB, and oil absorbed oleic acid treated bark (OOTB) and oil absorbed palmitic acid treated bark (OPTB) are shown in Figures 1 and 2. The band at 3,403 cm\(^{-1}\) shows the results of hydrogen-bond (O–H) stretching that indicates the stretching of hydroxyl groups present in cellulose, hemicellulose, and lignin. The two peaks between 2,919 and 2,850 cm\(^{-1}\) indicate the presence of C–H asymmetric stretching of CH\(_3\) and CH\(_2\) groups (Satthasivam & Haris 2010; Wang et al. 2013). The band found at 1,604 cm\(^{-1}\) is specific to the benzene ring stretching vibrations of lignin. The bands observed at 1,440 and 1,374 cm\(^{-1}\) may represent C–H bending vibration and OH bending, respectively. By comparing the FTIR spectra of

![Figure 1](https://iwaponline.com/wst/article-pdf/70/7/1220/470703/1220.pdf)
untreated and treated samples, it can be seen that a weak band was created at 1,735 cm$^{-1}$, related to the stretching vibration of the ester linkages between 1,725 and 1,750 cm$^{-1}$ (Lodha & Netravali 2005), which shows that the sorbent had been esterified. The intensity of the bands at 3,403 cm$^{-1}$ has significantly decreased upon esterification with fatty acid. This is attributed to the replacement of hydroxyl groups with an oxalate group (C$_{17}$H$_{33}$COO$^-$) of oleic acid and (C$_{15}$H$_{31}$COO$^-$) palmitic acid. The bands at 2,919, 2,850, 1,440 and 1,374 cm$^{-1}$ had considerably decreased due to the breaking of C–H band. These results show that the treatment by oleic and palmitic acid removes some C–H band and creates some active sites for interaction with C–H groups from crude oil. This phenomenon can be seen from the FTIR spectrum of crude oil attached onto the surface of OTB and PTB, which demonstrates that the peaks at bands of 2,850, 2,919 and 1,440 cm$^{-1}$ became more prominent after the adsorption process. The adsorption of crude oil was further demonstrated by the presence of a peak at 1,440 cm$^{-1}$, which represents the C–H bending of crude oil. C–C stretching of the aromatics of the crude oil was increased significantly after crude oil adsorption at 1,604 cm$^{-1}$.

**Morphology identification**

The FESEM images of mangrove bark before and after esterification and after oil sorption are shown in Figure 3 for comparison. UTB has a smoothed surface, which cannot hold oil in its exterior part; however, after treatment by the fatty acids, the surface of the bark became rougher than UTB and revealed many perforations on the surface. The activity of the acidic chemicals (fatty acids) is possibly responsible for the perforations. Perforations on the surface would increase the surface area of treated bark, which is discussed in the section on surface area measurement. The surface morphology of mangrove bark treated by oleic acid and palmitic acid showed the same result after oil sorption. Hence, only one FESEM image is shown in Figure 3(d). The result indicated that the adhesion of crude oil is clearly improved and the surface of the treated sample was agreeable to the adhesion of crude oil.

**Surface area measurement**

Table 2 shows the physical properties of UTB, OTB and PTB based on surface area and pore size. According to the criterion established by the International Union of Pure and Applied Chemistry, pore sizes are classified into three groups: micropores (diameter (d) < 20 Å), mesopores (20 Å < d < 500 Å), and macropores (d > 500 Å). The pore diameter measured for UTB, OTB and PTB in this study was attributed to the mesopores group. The BET surface area of fatty acid treated bark is three times bigger than untreated bark. However, the average pore diameter size was in the same range for all untreated and treated barks. Thus, the higher sorption capacity of treated bark is due to the increase in surface area.
Effect of modification of mangrove bark on sorption capacity

Tests were conducted using UTB, OTB and PTB as sorbents to remove crude oil from artificial sea water. UTB showed low efficiency for crude oil removal with an oil uptake of 1,120 ± 2.00 mg/g. This low sorption capacity is probably because of the existence of hydroxyl groups on its surface. These groups are mainly hydrophilic; they force back the crude oil molecules and thus lower the oil sorption uptake. Treated mangrove bark (OTB and PTB) showed higher affinity to oil. The sorption of oil by OTB and PTB were up to 2,860.00 ± 2.00 and 2,640.00 ± 2.00 mg/g, respectively. This indicates that fatty acid treatment is effective in increasing the oleophilicity of UTB. These results reveal that removal of hydroxyl groups from cellulose, hemicelluloses and lignin using the esterification process could improve the sorption capacity of the bark by more than twice. The reaction scheme for the modification of bark with oleic acid and palmitic acid are shown in Figure 4.

Effect of contact time on sorption capacity

The effect of contact time on the uptake of oil by UTB, OTB and PTB is shown in Figure 5. The highest sorption capacity of crude oil was observed at 30 min contact time. The results also show no significant sorption after 30 min, indicating that the sorbents were almost saturated with oil.

Table 2 | Physical characteristics of untreated bark, oleic acid treated bark, and palmitic acid treated bark

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>BET surface area (m²/g)</th>
<th>Average pore diameter (Å)</th>
<th>Total pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated bark</td>
<td>444.947</td>
<td>44.125</td>
<td>0.361</td>
</tr>
<tr>
<td>Oleic acid treated bark</td>
<td>1,205.158</td>
<td>44.087</td>
<td>0.956</td>
</tr>
<tr>
<td>Palmitic acid treated bark</td>
<td>1,198.166</td>
<td>44.056</td>
<td>0.955</td>
</tr>
</tbody>
</table>


Figure 4 | The reaction scheme for the surface modification of mangrove bark with oleic acid (a) and Palmitic acid (b).
Effect of particle size on sorption capacity

Two different particle sizes (450 and 300 μm) of sorbent were investigated. Figure 6 compares the oil sorption capacity of untreated and treated bark with respect to their particle sizes. The result indicates that the smaller particle size (300 μm) sorbed more oil from the oil–water mixture because of its larger specific surface area. It can be seen from the figure that the sorption capacity of OTB is slightly higher than that of PTB. Table 2 shows OTB has a slightly larger surface area than PTB, which could contribute to its higher sorption capacity.

Effect of pH on sorption capacity

One of the important parameters for control of the oil sorption process is the pH of the mixture, because it has a strong influence on the surface properties and surface binding sites (–NH2, –CO–NH2, –CO–NH–) of the adsorbent, especially on organic sorbents (Radetic et al. 2005). The effect of the pH value of the oil–water mixture on the sorption process was studied (3, 5, 7, 8, 9, and 11), and the result is shown in Figure 7. The oil sorption capacity of UTB, PTB and OTB at the mixture pH of 3 to 8 increased from 860 to 1,120, 2,375 to 2,640 and 2,520 to 2,860 mg/g, respectively. At a higher pH, the oil sorption capacity was slightly decreased. Oil coalescence occurs in strongly acidic conditions. This occurrence increases the size of crude oil droplets in the adsorption mechanism; larger oil droplets are not stable and can be easily desorbed from the adsorbent (Ibrahim et al. 2009). Therefore, as shown in Figure 7, the optimum pH for adsorption of Tapis crude oil from the oil–water mixture by UTB, PTB and OTB was pH = 8 and the sorption capacity was 1,120, 2,640, and 2,860 mg/g, respectively.

Effect of temperature on sorption capacity

Figure 8 shows the effect of temperature on oil sorption capacity. With an increase in the mixture’s temperature up to 40 °C, the uptake of oil increased. The result showed that the optimum temperature for the highest capacity is 40 °C. Oil viscosity is directly related to the temperature, and it decreases with increased temperature; low viscosity oil can easily be captured onto the rough surface and
penetrate the pores. However, increasing the temperature beyond 40°C decreases oil retention and oil will be released from the pores and surface of the sorbent. High viscosity oil may plug the pores and prevent oil penetration into the interior structure of sorbent at a lower temperature. Thus, for low viscosity oil such as Tapis, a higher temperature causes an increase in oil drainage from the sorbent surface.

**Effect of oil concentration on oil sorption capacity**

Figure 9 shows the plot of oil sorption capacity (mg/g) against oil concentration (g/l). The sorption capacity of crude oil by the sorbent is dependent on the concentration of oil in water. The results were achieved by varying the concentration of oil in the water from 12.5 to 125 g/l at the optimum contact time, temperature and pH. The oil removal increased with increasing crude oil dosage from 12.5 to 87.5 g/l when they reach equilibrium. Maximum sorption capacity was achieved when the oil floating on water was 87.5 g/l. The result showed that the adsorption capacity is considerably influenced by the initial concentration of the oil in water mixture, and adsorption capacity increases from 1,228 to 2,860, 1,045 to 2,640 and 410 to 1,120 mg/g for OTB, PTB and UTB, respectively. The increase in adsorption capacity is due to the concentration gradient that promotes mass transfer. The equilibrium stage showed that the sorbent reaches saturation point.

**Isotherm study**

The adsorption isotherm is important for interpretation of the experimental data and to describe the correlation of theoretical data and practical design. The experimental equilibrium data for the adsorption of oil on OTB, PTB, and UTB with different initial concentrations were fitted with adsorption isotherm models. The two most widely employed isotherm models were used to analyze the sorption data, namely Langmuir and Freundlich. The Langmuir isotherm model is applicable for only one molecular layer of adsorbate coverage on a surface. The linear form of the Langmuir isotherm is expressed as

\[
\frac{C_e}{q_e} = \frac{1}{q_0} \frac{1}{b} + \frac{1}{q_0} C_e
\]

where \( q_e (\text{mg/g}) \) is the amount of oil adsorbed at equilibrium time, \( C_e (\text{mg/L}) \) is the equilibrium concentration of oil, \( q_0 \) and \( b \) are Langmuir constants related to adsorption capacity and rate of adsorption. Figure 10(a) shows the graph plot of \( C_e/q_e \) vs. \( C_e \). The slope and intercept of the straight line obtained were used to calculate the values of \( q_0 \) and \( b \) (Table 3). The result shows a good fit of the Langmuir isotherm to the experimental data with high \( R^2 \).

However, critical features of the Langmuir isotherm can
be expressed in terms of a dimensionless constant separation factor \( R_L \) that is expressed as

\[
R_L = \frac{1}{1 + bC_0}
\]

This equation shows that the isotherm model is favorable \((0 < R_L < 1)\), unfavorable \((R_L > 1)\), linear \((R_L = 1)\), or irreversible \((R_L = 0)\). The values of \( R_L \) were found to be more than 1, despite the high correlation coefficient \( (R^2) \), suggesting the isotherm to be unfavorable at the concentrations studied.

The Freundlich isotherm model is a practical equation that describes multilayer adsorption on heterogeneous surfaces that have unequal available sites with different energies of adsorption. The logarithmic form of this equation is described as

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]

wherein \( C_e \) is the equilibrium concentration of the adsorbate \((mg/l)\), \( q_e \) maximum adsorption capacity \((mg/g)\), \( K_f \) and \( n \) are Freundlich constants. \( K_f \) is the adsorption capacity of the adsorbent and can be represented as the adsorption coefficient; \( n \) shows how favorable the adsorption process is. The value of \( 1/n \) between 0 and 1 reveals that adsorption intensity or surface heterogeneity and adsorption are favorable. When its value gets closer to zero the sorbent is more heterogeneous. The linear graph plotted \( \log q_e \) versus \( \log C_e \) is shown in Figure 10(b). The amount of \( K_f \) and \( n \) were achieved at the slope and intercept of the straight line.

A comparison of correlation coefficient, \( R^2 \), of the studied isotherms for both models is acceptable for describing the adsorption of crude oil; the values of \( R_L \) in the Langmuir model were found to be between 0 and 1, which shows the adsorption is favorable. Although the value of \( 1/n \) in the Freundlich parameter is less than 1 (Table 3), it indicates that the adsorption is also favorable. This result shows that the experimental data of Tapis crude oil onto sorbent studied here were best fitted to both the Langmuir and Freundlich isotherm models, with the former being slightly better, as indicated by higher \( R^2 \) values.

### CONCLUSIONS

The present work shows the oil sorption capacity of raw and treated mangrove bark. The results of this study indicate that the sorption capacity of mangrove bark can be improved by oleic acid or palmitic acid treatment. The treated barks are more hydrophobic than the raw bark and so have less affinity for water. OTB has a slightly better sorption capacity for crude oil than PTB. Contact time, particle size, temperature, pH and oil concentration were other factors that affected the sorption capacity. The optimum contact time was 30 min, and a smaller particle size was found to be more efficient. Maximum sorption capacity was achieved at \( pH = 8 \); temperatures above 40 °C caused a decrease in sorption capacity. Oil removal was enhanced with an increase in crude oil dosage from 12.5 to 87.5 g/l. The applicability of the Langmuir as well as Freundlich adsorption isotherms was evaluated. Both the Langmuir and Freundlich models could describe the adsorption of crude oil on mangrove bark. The former isotherm model yielding slightly better fits regarding its \( R^2 \). Oil sorption was observed using a FESEM. The geometry of the treated barks showed a difference compared with that of the untreated bark. The significant change is related to the surface properties of the sorbents. The untreated bark showed a smooth surface, while the surface roughness of the treated bark increased remarkably, with many perforations on the surface. The roughness of the treated bark surface has an important role in oil sorption. Thus, oil sorption involved diffusion of crude oil to the surface of barks followed by physical entrapment on the surface. The study showed the potential of a waste material, mangrove barks, to be used as sorbent for oil-spill cleanup.

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