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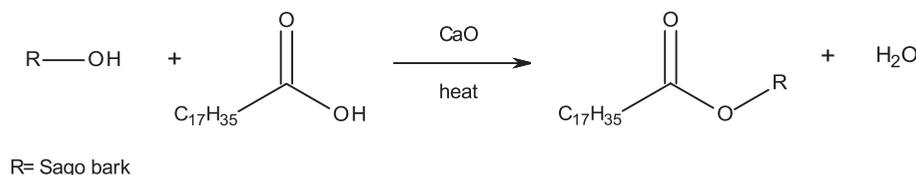
Esterified sago waste for engine oil removal in aqueous environment

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Agro-waste from the bark of *Metroxylon sagu* (sago) was studied as a low cost and effective oil sorbent in dry and aqueous environments. Sorption study was conducted using untreated sago bark (SB) and esterified sago bark (ESB) in used engine oil. Characterization study showed that esterification has successfully improved the hydrophobicity, buoyancy, surface roughness and oil sorption capacity of ESB. Sorption study revealed that water uptake of SB is higher (30 min static: 2.46 g/g, dynamic: 2.67 g/g) compared with ESB (30 min static: 0.18 g/g, dynamic: 0.14 g/g). ESB, however, showed higher oil sorption capacity in aqueous environment (30 min static: 2.30 g/g, dynamic: 2.14) compared with SB (30 min static: 0 g/g, dynamic: 0 g/g). ESB has shown great potential as effective oil sorbent in aqueous environment due to its high oil sorption capacity, low water uptake and high buoyancy.



Sago bark (SB), an agricultural waste, is an effective oil sorbent in aqueous environment due to its high oil sorption capacity, low water uptake and high buoyancy.

Keywords: sago bark; agro-waste; esterification; stearic acid; oil sorption; used engine oil

Introduction

Oil spill has become a major concern in many countries due to its negative impacts on the economy and environment.[1] In marine environment, oil spill causes the formation of a monolayer film which leads to the exchange of moisture, heat and gases between the water reservoir and the atmosphere.[2] Oil spill has ruined the marine ecosystem and destroyed the wildlife habitat and breeding grounds.[3] The formation of oil-in-water emulsion or floating film caused by oil spill could be toxic to microorganisms for biodegradation process.[4]

There are many available techniques for the recovery of oil spill in marine environment.[5,6] However, there are some drawbacks such as cost and limited usage in fast-running rivers and large wind-swept lakes.[5] Many studies on oil sorbent materials has now focused on the effectiveness, feasibility, simplicity and easy handling.[7] A good sorbent usually possess high oleophilic and hydrophobic properties,[8] high oil uptake capacity, buoyancy and retention over time, durability in aqueous media,

reusability, biodegradability,[4] low-cost and environmental friendly.[9]

Natural fibrous sorbents such as straw, corn-cob, sawdust, kapok, bagasse, kenaf and hay have been utilized for oil removal [4,10,11] and available in large quantities.[12] However, natural sorbents tend to submerge in water after saturation due to its ability to remove both oil and water.[12] Several studies have been carried out to increase the performance of natural sorbent in removing oil from aqueous environment via chemical modification. Acetylation, for instance, has improved natural sorbent's properties to become more hydrophobic and decreased hydrophilic property.[13,14]

The bark of *Metroxylon sagu* (sago) is generated significantly in Malaysia as an agricultural by-product during sago flour processing. The sago bark (SB) accounts for 17% of the logs processed, with the estimated production of 5–15 tons per day.[15] Lignin is the main component of the SB and is strongly connected with the hemicelluloses in the cell walls of sago pith.[16] SB is commonly either incinerated or

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discharged into the river which eventually could contribute to serious environmental problems. Thus, there is a need to find ways to utilize these wastes such as converting it into useable material.

In the present study, the physicochemical, water uptake and oil sorption characteristics of SB and esterified modified sago bark (ESB) were investigated. The effect of esterification process on oil sorption capacity of ESB were studied in several sorption systems, i.e. the dry, wet-static and wet-dynamic system using used engine oil (UEO).

Materials and methods

Materials

SB was obtained from sago processing mill located in Mukah, Sarawak, Malaysia. UEO was obtained from local automobile workshop. Stearic acid and ethyl acetate (Merck, Germany) were used for esterification reaction.

Preparation of ESB

SB was washed to remove debris, sun-dried, grinded into particle size of 0.5 mm and oven-dried for 24 h at $80 \pm 5^\circ\text{C}$. SB (7.0 g) was added to a mixture of stearic acid (1.0 g) (7:1 w/w ratio) and CaO (0.35 g) in ethyl acetate (150 ml). The mixture was heated at reflux for 3 h and cooled to room temperature. The mixture was filtered, washed (3×50 ml ethyl acetate) and oven-dried (90°C) for 1 h and kept in a desiccator.

Characterization of SB and ESB

Infrared spectra of SB and ESB were recorded on an FTIR spectrometer (Perkin Elmer 1605) under ambient condition using KBr pellets. Surface morphologies of SB and ESB were examined using a scanning electron microscope (SEM, JEOL 7500F-1) at 0.5–30 kV. Apparent density measurement of SB, ESB and UEO was conducted by filling and compacting the sample up to 10 ml volume into a pre-weighed measuring cylinder. Mass of SB, ESB and UEO was recorded and density was calculated by dividing the mass of sample (g) to its volume (cm^3).

The hydrophobicity test was carried out by testing the partition of SB or ESB between aqueous and hexane phases.[17] SB or ESB (1.0 g) was placed in a beaker consisting 20 ml of water, agitated for 3 min and added with hexane (9 ml). The mixture was further agitated for 3 min, and left idle for 5 min. Organic phase was collected, dried and weighed (M_o). The degree of hydrophobicity, H , was calculated using the following equation:

degree of hydrophobicity, H

$$= \frac{\text{mass of sample in organic phase, } M_o}{\text{initial mass of sample, } M_i} \times 100\%. \quad (1)$$

The buoyancy test was performed using deionized water (15 ml) in a 30 ml vial. SB or ESB (0.5 g) was poured on the surface of the water in each vial and observed for 7 days.



Figure 1. Different sorptions. (a) Dry system, (b) wet static system and (c) wet dynamic system (on orbital shaker).

Water uptake study

To check the amount of water adsorbed by SB and ESB, water uptake study was carried out by placing the sorbent kit into a 250-ml beaker consisting of deionized water (100 ml) for 10, 20, 30 and 40 min. Water uptake was determined at both static and dynamic (250 rpm) systems. The sorbent kit was removed after sorption test and weighed. The sorption capacity of the sample was determined by the following equation:

$$\text{water uptake, } S_w = \frac{\text{weight of sorbent containing absorbed water, } W_w - \text{initial weight of sorbent, } W_i}{\text{initial weight of sorbent, } W_i} \quad (2)$$

Sorption study

SB or ESB (1.0 g) was packed in polypropylene bags (0.1 cm mesh, 5 × 5 cm) as a sorbent kit. To simulate oil sorption in the absence of water (dry system), UEO (15 ml) was poured into a 250-ml beaker (Figure 1(a)). Oil sorption in aqueous condition was carried out in non-turbulent (wet static system) and turbulent environment (wet dynamic system). In wet static system, UEO (15 ml) was poured into deionized water (80 ml). The sorbent kit was gently placed

on the oil surface and left to stand for 10, 20, 30 and 40 min (Figure 1(b)). The same experimental set-up was performed for the wet dynamic system, with agitation at 250 rpm (Figure 1(c)). The sorbent kit was removed after sorption test and weighed. The sorption capacity of the sample was determined by weighing the samples before and after the sorption experiment (Equation (3)).

oil sorption capacity, S

$$= \frac{\text{weight of sorbent containing absorbed oil, } W_f - \text{initial weight of sorbent, } W_i}{\text{initial weight of sorbent, } W_i} \quad (3)$$

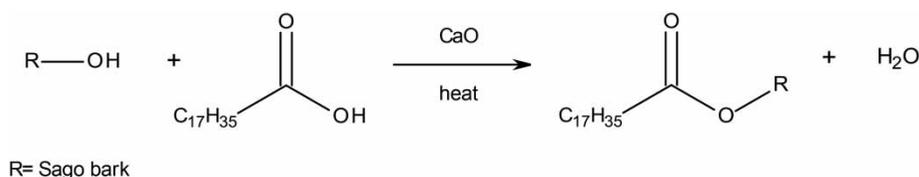
Results and discussion

Preparation of ESB

Esterification of SB was carried out by reaction of stearic acid with readily available hydroxyl (–OH) groups in SB. The introduction of stearic acid onto SB network has reduced the hydrophilic properties of SB.[14] The proposed reaction is shown in Scheme 1.

Characterization of SB and ESB

The infrared spectrum of SB (Figure 2(a)) showed strong absorption bands at 3448 cm⁻¹ which attributed to



Scheme 1. Esterification of SB with stearic acid.

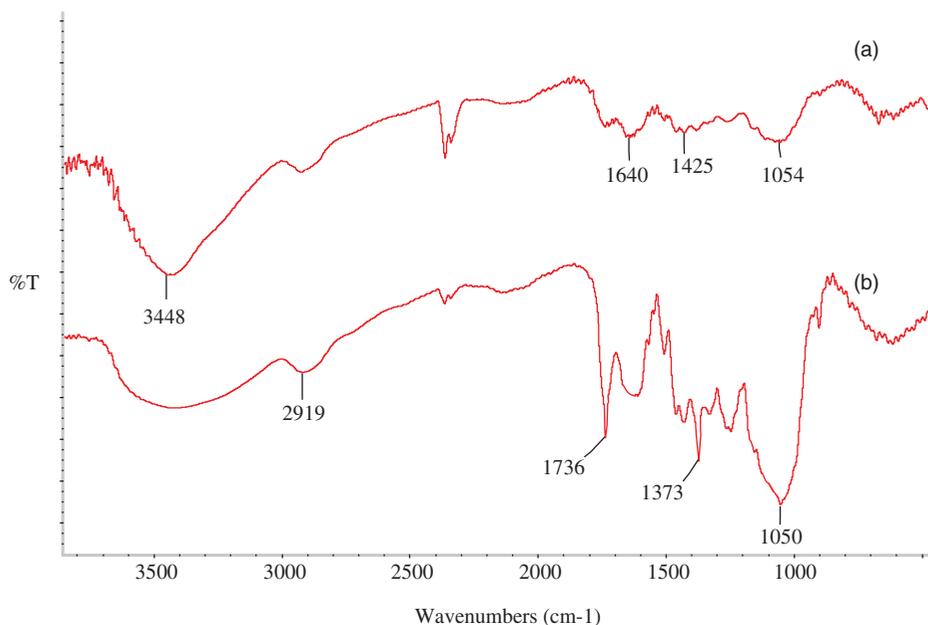


Figure 2. FTIR spectrum of (a) untreated SB and (b) ESB.

high content of $\nu(\text{OH})$ in cellulose, hemicelluloses and lignin.[18] Successful esterification was indicated by the appearance of ester bands in ESB at 1736 cm^{-1} which corresponded to the presence of carbonyl group ($\text{C}=\text{O}$ ester) (Figure 2(b)). The absorption band at 3448 cm^{-1} decreased in ESB, which indicated that the hydroxyl groups in SB were reduced by esterification.[13]

SEM analysis showed that esterification afforded a new surface morphology of ESB.[19] SB microstructure (Figure 3(a)) showed the presence of starch granules on its surface, which disappeared in the SEM micrograph of ESB (Figure 3(b)). The stearic acid deposited on the external surface of SB together with the volatility of ethyl acetate and refluxing process has generated a rougher surface of ESB compared with SB. A rough surface morphology is a desirable characteristic of an oil sorbent, and is linked to high sorption capacity due to the presence of abundant active sites for oil sorption.[20,21] The disappearance of starch granules also leaves behind hollow, tube-like structures in the sample. This kind of structure is favourable for oil sorption due to the rough surface, which increased the surface area, thus increases the oil sorption capacity.

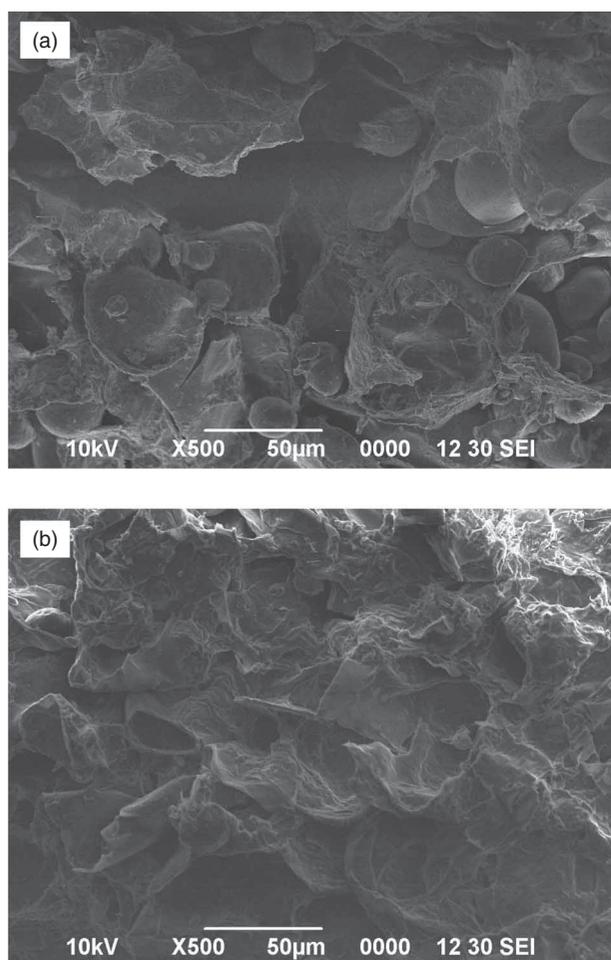


Figure 3. Micrograph of (a) untreated SB and (b) ESB.

Table 1. Density and hydrophobicity for untreated SB and ESB.

Sample	Density (g/cm^3)	Hydrophobicity (%)	Number of floating days (days)
Untreated SB	0.3137	2 ± 0.0089	1
ESB	0.2269	60 ± 0.0707	7

Low density of the sorbent afforded good floating effect. The densities of SB and ESB were determined to evaluate the effect of esterification on the density of SB. The density of ESB is lower than SB, thus produced a better floating effect (Table 1). Table 1 also showed that ESB exhibited considerably higher degree of hydrophobicity compared with SB. The hydrophobic property of ESB was supported by the buoyancy test. The hydrophobicity increased as the buoyancy increased.[10,22,23] The density, hydrophobicity and buoyancy of ESB enabled the conglomerate to stay afloat on the water surface up to 7 d. The presence of long hydrocarbon chains in ESB has increased its hydrophobic properties.[24]

Water uptake study

Water uptake of SB and ESB was studied at different sorption times, both in static and dynamic systems (Figure 4(a) and 4(b)). Between the two systems, SB showed approximately 90% higher water sorption capacity compared to ESB. High water uptake by SB could be attributed to its hydrophilic nature. High cellulose content in SB leads to low ability to repel water as cellulose molecules were more attracted to hydrophilic than hydrophobic materials.[25] Water uptake of SB was higher with the increasing contact time (maximum 2.8 g/g at 40 min for both static and dynamic systems). The high water uptake makes it an unreliable sorbent in oil spill cleanup, as it will increase the volume of water instead of oil. In contrast, ESB showed very low water uptake ($<0.35\text{ g/g}$) between the two systems due to its hydrophobic nature (Table 1).

Oil sorption capacity in dry system

ESB was observed to have a slightly higher oil sorption capacity compared with SB in the absence of water, i.e. dry system (Figure 5(a)). The SB and ESB performed at an equal efficiency (2.10 g/g oil sorption capacity) in 10 min. After 20 min, ESB consistently showed better oil sorption capacity than SB. The high oil sorption capacity of ESB was believed to be due to the improvement of its surface topography (Figure 3(b)). The rough surface of ESB enhanced the oil adsorption performance.[26]

Oil sorption capacity in wet system

The ability of a sorbent to remove oil in aqueous state is important as oil spill cases eventually ended up in water environment.[19] Figure 5(b) represented oil in water sorption capacity, S_o of SB and ESB based on the following

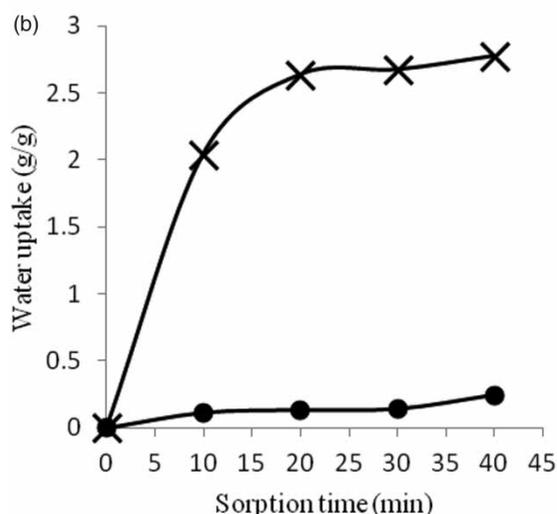
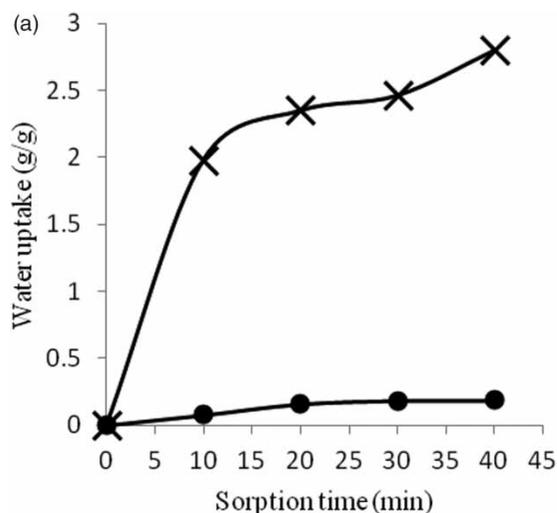


Figure 4. Water uptake of untreated SB and ESB in (a) static system and (b) dynamic system.

equation:

$$\begin{aligned} & \text{oil in water sorption capacity, } S_o \\ & = \text{sorption capacity in wet system, } S \\ & - \text{experimental water uptake, } S_w. \end{aligned} \quad (4)$$

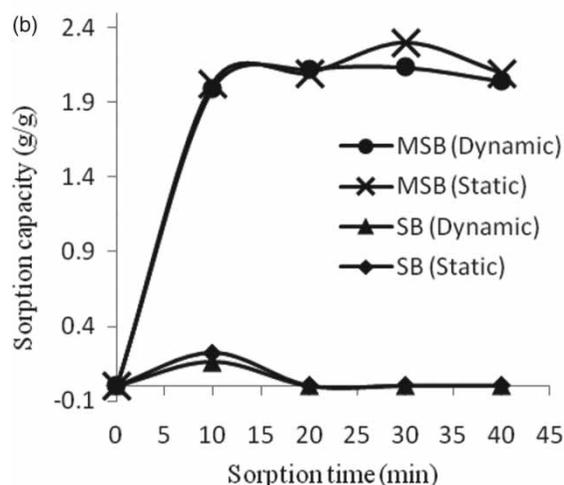
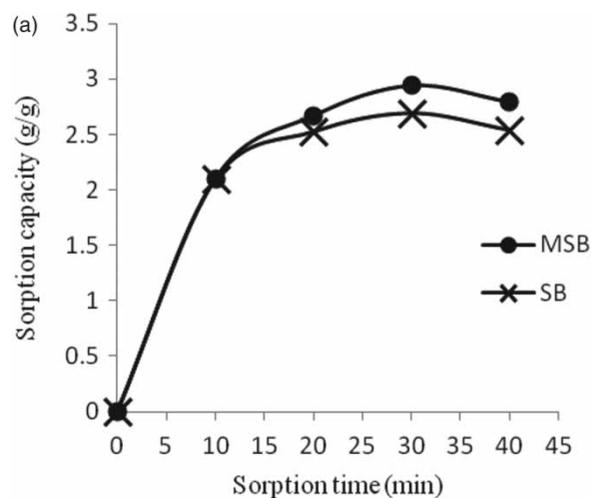


Figure 5. Oil sorption capacity of untreated SB and ESB in (a) dry system (b) wet static and dynamic systems.

Negative value of S_o indicated that no oil has been removed in the SB and ESB. Results showed that S_o of ESB in both static and dynamic conditions increased with increasing contact time and eventually reached sorption saturation at 40 min (2.10 and 2.04 g/g, respectively). In general, ESB showed a greater S_o value in comparison to SB which gave near-zero oil removal. ESB would operate effectively as an oil removing material for oil and water mixtures as it

Table 2. SB (untreated and ESB) and other natural sorbents for the removal of engine oil.

Sorbent	Sorbent treatment	Water uptake (g water/g fibre)	Sorption capacity (g oil/g fibre)
SB (<i>Metroxylan sagu</i>) [present study]	Raw fibre	2.80	0.16–0.22
	Esterification with stearic acid	0.24	2.14–2.30
Coconut husk (<i>Salvinia cucullata</i> Roxb) [27]	Oven-drying, 60°C, 24 h	–	0.058
	Oven-drying, 60°C, 24 h	–	0.944
Sugarcane bagasse [25]	Esterification with stearic acid	0	1.3–3.2
Reed canary grass (<i>Phalaris arundinacea</i>) [28]	Co-milling and screening with Flax (<i>Linum usitatissimum</i> L.) and Hemp fibre (<i>Cannabis sativa</i> L.)	3–11	1
Cattail fibre [27]	Oven-drying, 60°C, 24 h	–	1.107
Wool fibres [29]	Drying	–	0.225

would selectively remove oil and able to remain on the water surface for easy collection after used.

Table 2 summarizes the oil sorption capacity of ESB in comparison with other oil sorbents for motor oil. ESB has higher oil sorption capacity compared with several natural sorbents in removing engine oil such as coconut husk, sugarcane bagasse and wool fibre, indicating its potential as an excellent oil sorbent due to its high oil sorption capacity, low water uptake, high hydrophobicity and good buoyancy.

Conclusions

Esterification of SB with stearic acid afforded ESB with better oil sorbent characteristics. ESB has higher buoyancy and density, and lower water uptake capacity compared with SB. ESB would be most suitable for application where oil is to be removed from an aqueous environment. ESB showed higher oil sorption capacity for removal of engine oil in comparison to many other natural oil sorbents and has potential to be used in the future.

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