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Chemically Modified Sago Waste for Oil Absorption

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ABSTRACT

Oil pollution remains a serious concern especially in Malaysia. Many strategies have been employed to overcome oil pollution. In this research, sago waste material abundantly found in Sarawak was used and chemically modified into an oil adsorbent . Sago waste cellulosic residues were modified using fatty acid derivatives. The capability of the chemically modified sago waste to absorb oil from aqueous solution was studied and compared with the untreated sago waste. The modified sago waste showed higher hydrophobicity than the untreated sago waste, implying that it is less affinity for water and also an excellent affinity for oil. This chemically modified sago waste would be the most suitable for applications where engine oil (i.e., Shell Helix HX5) is to be removed from an aqueous environment. The modified sago waste selectively absorbs the oil and remains on the surface and is to be removed when the application is complete.

Keywords: Ester linkage, hydrophobic, modified sago waste, stearic acid.

INTRODUCTION

Sago, which is scientifically known as *Metroxylon sagu,* comes from genus metroxylon and family palmae (Singhal *et al.,* 2008). Sago palm is commonly found in tropical lowland forests and freshwater swamps. The areas under sago cultivation in wild and semi-wild conditions are estimated to be at 19,720 hectares, with a total planted area of 28,000 hectares. Sarawak is currently one of the world's largest exporters of sago products with annual exports of approximately 43,000 tons. The mass production of sago produces residues during processing. It was estimated that from 600 logs of sago palm per day, 15.6 tons of woody bark, 237.6 tons of waste water, and 7.1 tons of starch fibrous sago pith residue are generated (Bujang & Ahmad, 1999). Sago pith residue is composed mainly of 41.7 - 65% starch and 14.8% fibre, including a fair amount of mineral (Wina *et*

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al., 1986). The residues are either incinerated or discharged into the river, which eventually contribute to serious environmental problems. Thus, there is a need to find ways to utilize these wastes into useable materials.

Sago waste comprises of cellulose and lignin, with hydroxyl functional groups (Quek *et al*., 1998). Several studies have reported on the utilization of sago wastes as fermentable sugar (Kumoro *et al.*, 2008), heavy metal remover (Quek *et al*., 1998) and some other applications (Singhal *et al*., 2008). However, no studies have reported on sago as an oil absorbent, even though sago waste is known to contain lignocellulosic material, as found in previously studied natural oil sorbents such as cotton, wool, bark, kapok, rice straw, barley straw, vegetable fibres, pith bagasse and raw bagasse (Husseien *et al*., 2008; Annunciado *et al*., 2005; Adebajo & Frost, 2004; Said *et al*., 2009).

Herein, we report on the chemical modification of sago waste with fatty acid derivatives via esterification on the cellulosic residues. The capability of the chemically modified sago wastes to absorb oil from aqueous solution was studied for potential commercial application.

MATERIALS AND METHODS

Sago waste (SW) was obtained from Mukah, Sarawak. The engine oil used in all sorption experiments was Shell Helix HX5, Premium Multi-Grade Motor Oil. Dichloromethane was dried under calcium hydride. All chemicals were used as received and all reactions were performed under nitrogen atmosphere. The IR spectra were obtained on a Perkin Elmer Instruments Spectrum Gx1v5.0 using NaCl disc. SEM analysis was conducted to examine the surface morphology of the samples.

Sample Preparation of SW and Chemical Modification

Stearic acid (0.01 mole, 3.0 g) was added to dichloromethane (60 mL). Oxalyl chloride (0.01 mole, 1.30 mL) was added drop wise in 30 minutes. Dimethylformamide (5-6 drops) was also added to initiate the reaction. The solution was stirred continuously at room temperature for 3 hours. SW (3.0 g), which had been ground and dried in an oven at 80±5 ˚C for 24 hours, was added into the prepared solution. Triethylamine (0.01 mole, 1.01 mL) was added drop wise into the solution and stirred continuously for 24 hours at room temperature. The modified sago waste (MSW) was then filtered, washed successively with cold dichloromethane followed by ethylacetate, and dried at room temperature (Cammidge *et al*., 2003).

Characterization of SW, MSW and Used Engine Oil (UEO)

Density

A measuring cylinder was pre-weighed and SW was packed up to 1 mL measurement. The weight of SW was recorded. Three replicates were done and the density of SW was calculated using the mathematical formula shown below:

$$\text{Density (kg/m}^3\text{)} = \text{mass / volume}$$

The same steps were repeated to determine the density of MSW. A measuring cylinder was pre-weighed and UEO (10 mL) poured into it. Then, the weight of UEO was recorded. Three replicates were done and the density of UEO was calculated using the same mathematical formula.

Water Sorption Test

De-ionised water (70 mL) was poured into a 100 mL beaker. SW (0.1 g) was spread evenly on the surface of de-ionised water for different absorption times at 10, 20, 30 and 40 min. SW was then collected, air dried on filter paper for 10 minutes, weighed, and recorded. The same steps were applied to determine the water sorption capacity for MSW (Said *et al*., 2009). Water uptake was calculated using the formula below:

$$\text{Water uptake (\%)} = (\text{Sorption}_{\text{wet,static}} - \text{Sorption}_{\text{dry}})/\text{Sorption}_{\text{dry}} \times 100\%$$

Hydrophobicity Test for SW and MSW

De-ionised water (15 mL) was poured into a 30 mL vial, while SW (0.07 g) was poured onto the surface of the de-ionised water. The precipitations for these two mixtures were observed for 7 days. The same method was applied for MSW.

UEO Sorption Tests

Three systems applied to determine the sorption capacity of SW and MSW to UEO were the dry system, wet system (static) and wet system (dynamic). The study was performed at room temperature. The sorption capacity was calculated using the following mathematical formula (Husseien *et al*., 2008):

$$\text{Sorption (g/g)} = (S_t - S_o) / S_o$$

S_t = Total mass of absorbed sample

S_o = Initial weight of sample

Dry System

UEO (4 mL) was poured into a beaker. SW (0.1 g) was spread evenly on top of UEO. The sorption capacity test of SW was performed at 10, 20, 30 and 40 minutes. SW was collected, filtered and air dried on filter paper to remove excess oil. SW was weighed and recorded. Three replicates were carried out for each respective time. The same procedure was also performed on MSW (Husseien *et al*., 2008).

Wet System (static)

De-ionised water (70 mL) was poured into 100 mL beaker followed by UEO (4 mL). SW (0.1 g) was spread evenly on top of UEO. The sorption capacity of SW was performed at 10, 20, 30 and 40 minutes. SW was collected, filtered and air dried on a piece of filter paper to remove the excess oil, before it was weighed and recorded. Three replicates were performed each respective time. The same procedure was performed on MSW.

Wet System (dynamic)

De-ionised water (70 mL) was poured into a 100 mL beaker, followed by UEO (4 mL). SW (0.1 g) was spread evenly on top of UEO. The mixture was stirred for sorption capacity at 10, 20, 30 and 40 minutes. SW was collected, filtered and air dried on a piece of filter paper to remove the excess oil, before it was weighed and recorded. Three replicates were performed each respective time. The same procedure was performed on MSW.

RESULTS AND DISCUSSION

The lignocellulosic material of SW was modified *via* esterification of the hydroxyl groups with stearic acids. The conversion of stearic acids to acyl chlorides efficiently formed ester bonds onto SW network via hydroxyl groups, which contributed to hydrophobicity in the MSW.

IR spectra (Fig.1) showed the introduction of long alkyl (CH_2) groups onto the SW network at 2918 cm^{-1} and 2849 cm^{-1}. The presence of peaks at 3416 cm^{-1} and 3442 cm^{-1} (Fig.1c) indicated that the hydroxyl groups were not fully substituted with stearic acid. This is due to the properties of sago waste which comprises mainly of starch, cellulose and lignin (Kumoro *et al*., 2008; Quek *et al*., 1998). In addition, it also consists of a higher number of hydroxyl groups. The peak attributed to the formation of ester is shown at 1723 cm^{-1} (see Fig.1c). The peaks for carbonyl groups in MSW were fairly notable due to the massive network of MSW which overshadowed the carbonyl groups of ester linkage.

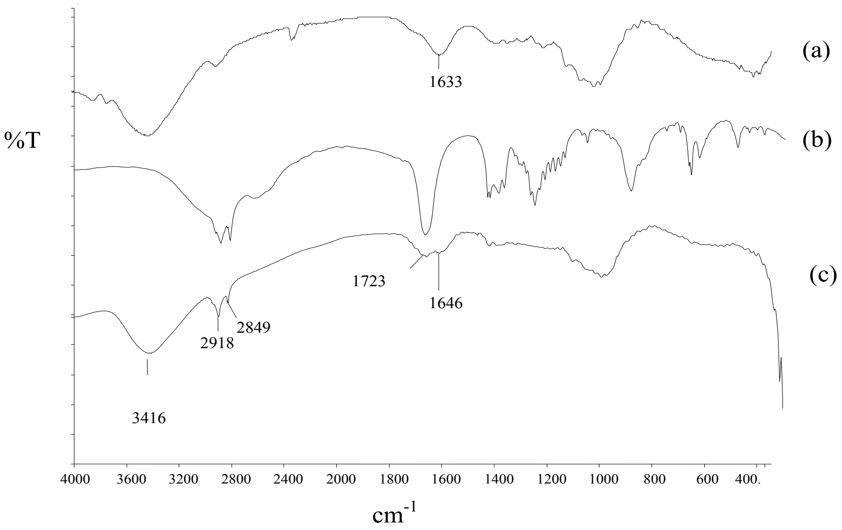

Fig.1: FT-IR spectra of (a) SW, (b) stearic acid, and (c) MSW

Scanning electron microscope (SEM) of SW and MSW is shown in Fig.2. There were no significant changes in the physical structure of SW before and after modification. This occurrence suggested that it was a chemical modification instead of physical modification (Erra *et al*., 2002).

Table 1 shows the density obtained for SW, MSW and UEO. The density of UEO was higher compared to SW and MSW. The difference in density for SW and MSW influenced their performances in the dry system, where only UEO was present. The density of water (1000 kg/m^3) affected the performance of SW and MSW in the wet system (static) in terms of the buoyancy (Husseien *et al*., 2008). The densities of SW and MSW were lower than water and thus, they remained on top of the water.

The water sorption capacity tests for SW and MSW were used as a control study to determine their ability to absorb oil. The sorption capacity was calculated in g/g unit and shown in Table 2. SW gave higher water sorption capacity compared to MSW.

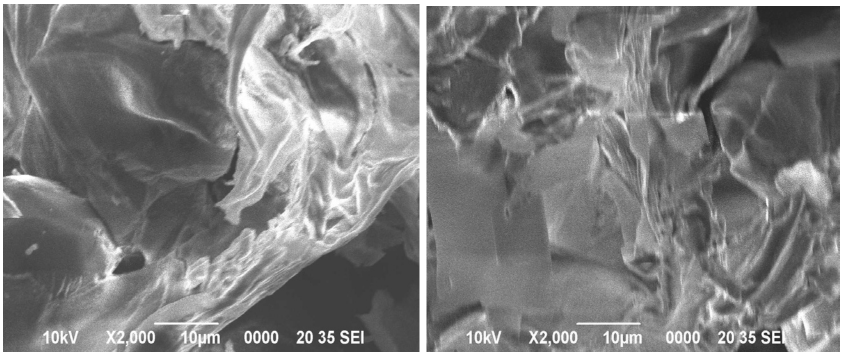

Fig.2: Scanning electron microscope of SW (left) and MSW (right)

TABLE 1
Density of SW, MSW and UEO

Sample	Density (kg/m^3)
SW	297.5±2.30
MSW	226.9±2.01
UEO	829.7±9.06

TABLE 2
Water sorption capacity (g/g) for SW and MSW

Time (min)	SW	MSW
10	2.2130±0.227	0.8330±0.288
20	2.7250±0.292	1.4593±0.243
30	3.1817±0.531	1.6524±0.194
40	3.3150±0.501	1.8379±0.199

SW and MSW were also subjected to hydrophobic tests to compare the level of hydrophobicity in both the samples. Both SW and MSW floated on the surface of water. SW was slowly submerged and completely accumulated at the bottom of the vial after 7 days (Fig.3a). However, MSW remained on the surface of water level. This observation suggests the formation of bonding between lignocellulosic hydroxyl groups with stearic acid *via* esterification.

The percentages of water uptake for SW in the wet system (static) and the wet system (dynamic) are shown in Table 3. In the wet system (static), the negative percentage values indicated that there was no water absorption. In the wet system (dynamic), the absorption of water occurred when SW was exposed to the system for 30 and 40 minutes. On the other hand, positive percentage values indicated that water absorption had occurred. The higher percentage of water uptake for SW was due to the higher number of hydroxyl groups in its lignocellulosic network (Kumoro *et al*., 2008) which easily formed hydrogen bonding with water molecules.

The percentage of water uptake for MSW is shown in Table 4. Similarly, the negative percentage values for water uptake in both the wet system (static) and wet system (dynamic) indicated that there was no absorption of water. This was due to the presence of long hydrophobic chains of stearic acid in the MSW network. The increasing hydrophobic property of MSW was explained by the negative percentage of water uptake in both wet system (static) and wet system (dynamic).

The sorption capacity of UEO onto SW and MSW is shown in Fig.4 to Fig.6. SW showed a higher sorption capacity compared to MSW in the dry system (see Fig.4) (Annunciado *et al*., 2005; Kumoro *et al*., 2008). MSW, however, showed lower sorption capacity. This was due to the lower density and higher buoyancy of MSW compared to SW (Fig.3) and UEO and thus, remained on the surface of UEO. The effectiveness of MSW to penetrate into UEO and absorb oil was lower due to the minimal contact between MSW and UEO.

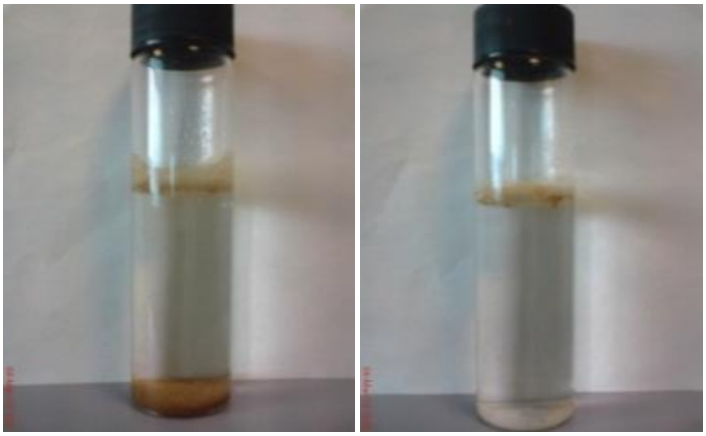

Fig.3: (a) Accumulation of SW at the bottom of vial; (b) MSW remained on the surface of water after 7 days

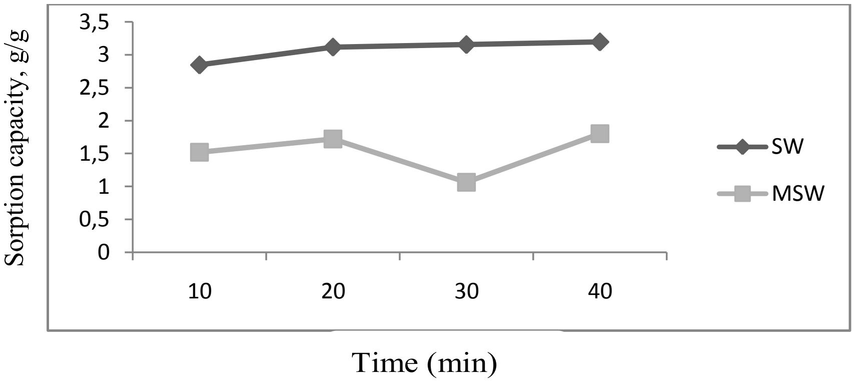

Fig.4: Sorption capacity of SW and MSW in dry system

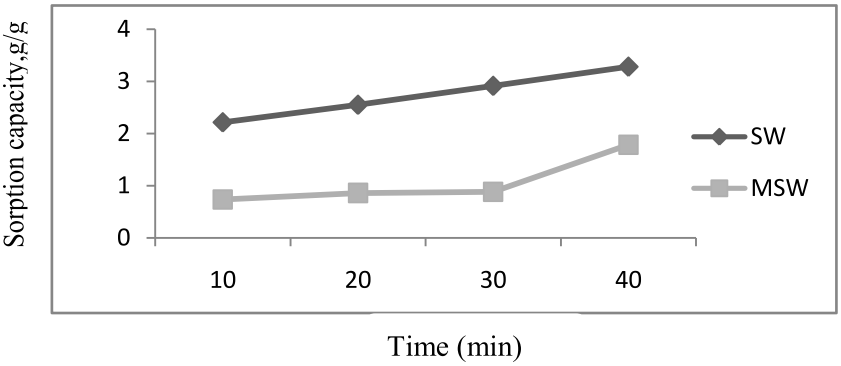

Fig.5: Sorption capacity of SW and MSW in the wet system (static)

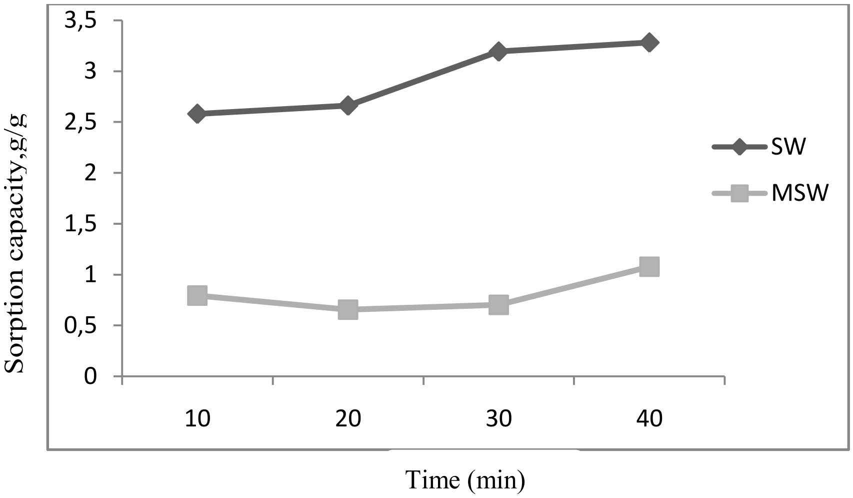

Fig.6: The sorption capacity of SW and MSW in the wet system (dynamic)

SW showed a higher sorption capacity compared to MSW in the wet system (static) (Fig.5). For the static system, the sorption capacity is inversely proportional to the buoyancy of fibres (Annunciado *et al*., 2005). MSW has higher buoyancy compared to SW and remained on the surface of UEO, thus reducing the fibre-oil contact. This might limit oil sorption ability.

Fig.6 shows the sorption capacity of SW and MSW in the wet system (dynamic). The weight gain for SW is not only contributed by the oil sorption. The incorporation of water into the fibres which ranged from 0.0-2.8% (Table 3) contributed to higher values in sorption capacity. The presence of lignocellulosic material in the SW network afforded SW to absorb hydrophobic and hydrophilic materials. Vigorous agitation and frequent water-fibres contact have affected the sorption capacity of SW (Annunciado *et al*., 2005). On the other hand, the sorption capacity of MSW is solely from UEO. This may have happened due to its higher buoyancy compared to SW and also to the presence of higher hydrophobic moieties which therefore selectively absorbed oil compared to water. Therefore, MSW showed a relatively better performance to absorb oil in dynamic aqueous condition compared to SW.

TABLE 3

Calculated percentage of water uptake for SW in wet system (static) and wet system (dynamic)

Time (min)	Dry system (g/g)	Wet system (static) (g/g)	Calculated water uptake (%)*	Wet system (dynamic) (g/g)	Calculated water uptake (%)*
10	2.8452±0.145	2.2144±0.238	-22.1	2.580±0.376	-9.3
20	3.1145±0.133	2.5507±0.241	-18.1	2.6611±0.280	-14.5
30	3.1525±0.199	2.9135±0.108	-7.5	3.1925±0.544	1.3
40	3.1931±0.221	3.0190±0.284	-5.5	3.2815±0.466	2.8

*Note: negative value represents "no water uptake and equiv. to 0%"

TABLE 4

The calculated percentage of water uptake for MSW in the wet system (static) and wet system (dynamic)

Time (min)	Dry system (g/g)	Wet system (static) (g/g)	Calculated water uptake (%)*	Wet system (dynamic) (g/g)	Calculated water uptake (%)*
10	1.521±0.255	0.7342±0.371	-5.2	0.796±0.159	-47.6
20	1.721±0.114	0.8598±0.294	-5.0	0.657±0.380	-61.8
30	1.067±0.165	0.8811±0.150	-1.7	0.730±0.111	-31.6
40	1.800±0.093	1.7844±0.093	-0.9	1.079±0.197	-40.1

* Note: negative value represents "no water uptake and equiv. to 0%"

CONCLUSION

The introduction of long alkyl (CH_2) groups onto the SW network *via* esterification has increased the hydrophobic property. In this study, MSW afforded a better sorption capacity on UEO as compared to SW in aqueous environment (wet system). MSW showed excellent affinity for oil and low affinity for water. For oil sorption in the absence of water (dry system), SW was found to be good material.

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