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Column Adsorption Studies for Oil Removal in POME by Using Esterified Sago Bark

(Kajian Penjerapan Turus untuk Penyingkiran Minyak dalam POME dengan Menggunakan Kulit Sagu Terester)

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Abstract

The mixture of residual oil in POME was released into the environment and polluted the environment, affecting the quality of water in rivers and seas. Sago bark (SB) from Metroxylon sagu harvested in Sarawak, Malaysia as a cheap natural adsorbent was investigated for removing POME through the adsorption process. The hydrophobicity of this sorbent in an aqueous state was improved via the esterification process. The esterification of sago bark was conducted at a ratio of sago bark (SB) to stearic acid (SA) by 4 to 1. Parameters of bed height and particle sizes of esterified sago bark (ESB) and flow rate of POME were analysed using full central composite (CCD) of response surface methodology (RSM). Hydrophobicity test, FTIR and SEM were carried out to characterize the ESB. Results showed that the esterification process has successfully increased the hydrophobicity of sago bark by 51.7% and increased the oil removal efficiency of ESB in POME by 53.33%. A developed 2-factor interaction (2FI) model showed that the conditions of ESB in 0.5 mm sizes with 15 cm bed height and at 5 ml/min of flow rate obtained 97.8% efficiency of oil removal in POME. SB esterification has successfully increased the oil adsorption and the removal of emulsion oil in POME.

Keywords: esterified sago bark, palm oil mill effluent, esterification, adsorption, oil removal.

INTRODUCTION

Nowadays environmental issues are increasingly becoming important globally. Palm oil mill discharged waste such as palm oil mill effluent (POME) that contains emulsified oil waste, soil particles and blackish brown suspended solids. Every year, palm oil mill effluent (POME) is generated in large quantities during crude palm oil production (Salihu et al., 2011). Raw or semi-treated POME contains very high levels of decomposed organic matter, due to the presence of unrefined palm oil (Ahmad et al., 2003). This type of oily wastewater is one of the environmental concerns nowadays. In palm oil processing plants, the extraction of palm fruit is carried out using a lot of water. Thus, an alternative adsorbent (or separation technique) is needed to reduce the pollution in the discharge. Due to the environmental impact factors, sago barks have been investigated for their potential in adsorbing POME before being discharged into streams and rivers.

Sarawak has a long tradition in the sago industry of processing flour from the sago palm, *Metroxylon* sagu *Rottboll* (Samiyati, 2010). Although the locals use the bark of the trunk as timber fuel, wall materials, ceilings and fences and sago fibers as components of composite materials, they are much waste material in the sago production industries.

Sago bark or sago waste is a fibrous natural sorbent for oil removal from POME effluent by adsorption and filtration techniques. There are many different methods for treating POME or oily wastewater such as coagulation and flocculation, electrocoagulation, flotation, coalescences membrane filtration, biological treatment, and adsorption. Adsorption has advantages over other methods since it is good oil removal efficiency and is designed with simple operation and low processing cost (Wahi et al., 2013). In this study, POME has been used as oily wastewater for the case study. To treat the oil and grease content in the POME, a suitable sorbent had been selected which is sago bark due to the higher production rate of sago waste in Sarawak, Malaysia.

METHODOLOGY

The material sago bark was collected from Nitsei Sago Mill, Mukah, Sarawak. Sago bark is a fibrous natural sorbent for oil removal from POME effluent by adsorption and filtration techniques. Figure 1 shows the preparation of sago bark (SB) as a sorbent and the esterification of sorbent named esterified sago bark (ESB). The material used to carry out the esterification process of sago bark is by adding stearic acid and thus will chemically modify the performance of the sago bark to esterified sago bark. The ratio of sago bark to stearic acid is 4:1.

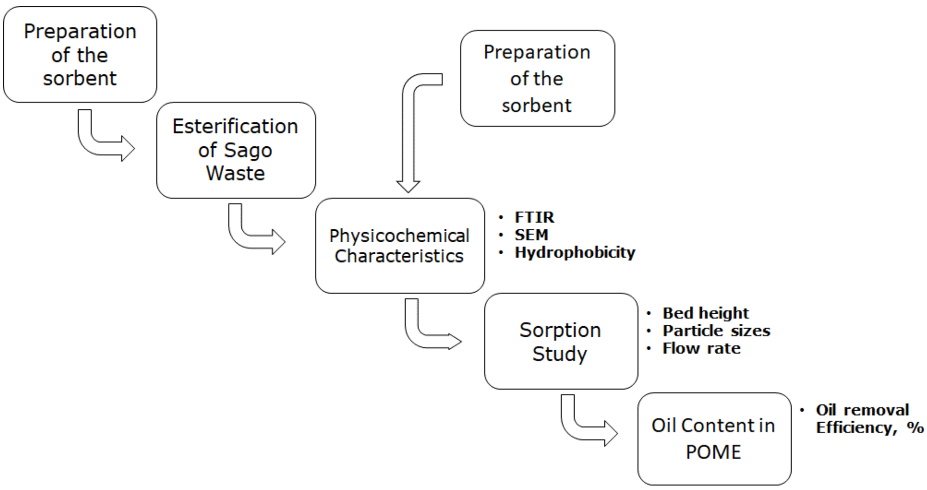


Figure 1. Process flow diagram column sorption study

The hydrophobicity of SB is increased through the esterification process. SB was packed in the bottom of the column containing ethyl acetate. The stearic acid had to be mixed in the ethyl acetate solution to dissolve the solid-state particles of the stearic acid. Calcium oxide is used as a catalyst and the required amount was 10% of the SB mass. The reaction is performed with the addition of ethyl acetate and calcium oxide as the catalyst to enhance the esterification process. Then the preparation of POME stock (sorbate) was stored at 4°C to maintain the concentration of solution before use and to prevent the solution from becoming stale and smelly. At room temperature, an oil adsorption test of POME was conducted by using ESB. The study was conducted by using a chromatography column. POME is filtered with a sorbent that is filled in the column. The sorbent used in ESB was filled in the column based on different bed heights, and different particle sizes and controlled the inlet flow rate of the POME. The parameters relationship such as column height, flow rate and particle size are using RSM Model to determine the efficiency of ESB to remove oil. The minimum numbers of experiments were 9 experiments for the oil adsorption test from experimental and factors (RSM model). This investigation aims to improve the adsorption capacity of sago bark to remove oil from an aqueous solution through esterification. Oil and grease content is determined by the n-hexane solvent extraction method (USEPA: Method 10056). The equation below shows the calculation to determine the efficiency of oil removal:

$$Oil\ removal\ effa\ iciency\ (\%) = \left[\frac{C_O - C}{C_O}\right] x\ 100\%$$

from the formula,
C_O = Initial oil concentration of POME (mg/l)
C = Final oil concentration of POME after filtration with sorbent (mg/l)

Characterization of ESB is conducted by using Fourier Transform Infrared (FTIR) spectroscopy analytical methods, and Scanning Electron Microscope (SEM) to compare the morphology of the SB surface and ESB surface. Also, the characterization of ESB was conducted by hydrophobicity test. It was calculated by using the equation below:

$$Hydrophobicity = \frac{Mass\ of\ sorbent\ in\ hexane\ (g)}{Total\ mass\ of\ sorbent\ (g)} x\ 100\%$$

RESULTS

ESTERIFICATION OF SAGO BARK

The esterification of SB was performed at 80°C for 4 hours using stearic acid in ethyl acetate with calcium oxide as a catalyst. Figure 1 shows the chemical modification of SB to ESB after through esterification of the hydroxyl groups.

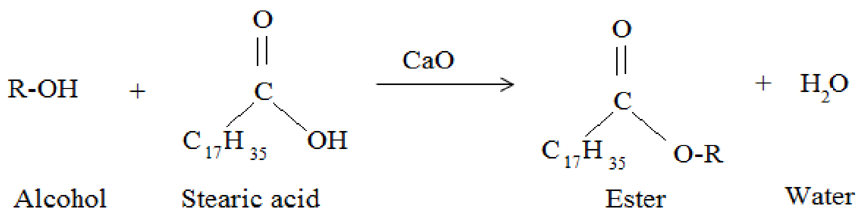


Figure 1. Esterification of SB

Figure 2 shows the physical characteristics of SB and ESB after the esterification process. Due to the reaction in the esterification process, ESB shows a whitish color compared to SB with the original brown color.

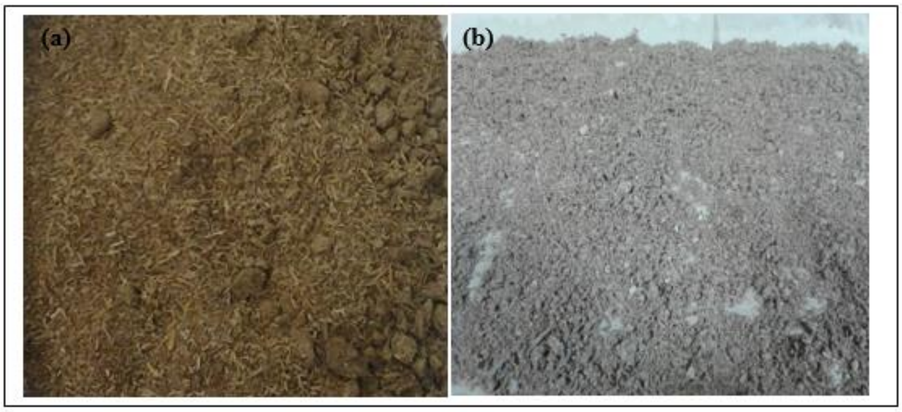
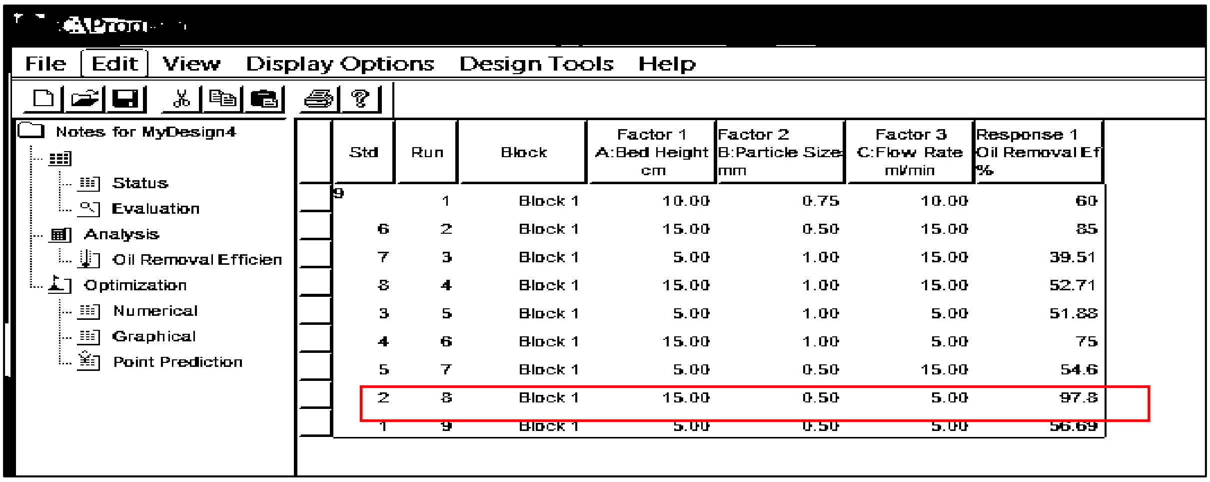


Figure 2. Physical characteristics of (a) sago bark and (b) esterified sago bark.

RSM STUDY

The actual experimental factors and responses are presented in Figure 1. A 2^3 central composite design with 9 experimental runs was employed, and the best model to fit was the 2-factor interaction (2FI) model. Since the target of the esterification study was to increase the quality of SB oil adsorbent, optimization parameters were related to the esterification conditions that could lead to ESB with maximum oil removal efficiency. ANOVA summary by the Design Expert for the response surface 2FI model gives the oil removal efficiency model F-value of 97.80%, which implies the parameters of Run 6 are more significant.



Std	Run	Block	Factor 1 A:Bed Height cm	Factor 2 B:Particle Size mm	Factor 3 C:Flow Rate ml/min	Response 1 Oil Removal Ef %
9	1	Block 1	10.00	0.75	10.00	60
6	2	Block 1	15.00	0.50	15.00	85
7	3	Block 1	5.00	1.00	15.00	39.51
8	4	Block 1	15.00	1.00	15.00	52.71
3	5	Block 1	5.00	1.00	5.00	51.88
4	6	Block 1	15.00	1.00	5.00	75
5	7	Block 1	5.00	0.50	15.00	54.6
2	8	Block 1	15.00	0.50	5.00	97.8
1	9	Block 1	5.00	0.50	5.00	56.69

Figure 1. Experimental factors and response

OIL AND GREASE CONTENT IN POME

Oil and grease content were determined for raw POME (before adsorption) and POME after adsorption. The measured weight is taken as oil and grease content value. Table 1 shows the properties of raw POME before adsorption is conducted.

Table 1. Raw POME properties

Properties	Value
pH	4.3
Oil and grease, mg/l	70, 000

Table 2 shows the results of oil removal efficiency after adsorption at the different parameters of bed height, flow rate and particle sizes. The result indicated that at the slow rate of flow of 5 ml/min, 15 cm bed height and 500 μm particle sizes, the maximum oil removal efficiency was 98.69%.

Table 2. The final oil concentration of POME samples (Run 1 – Run 10)

Run Order	Bed Height (cm)	Flow Rate (ml/min)	Particle Size (µm)	Oil Removal Efficiency (%)
1	5	5	500	48.69%
2	5	5	1000	47.71%
3	5	15	500	51.71%
4	5	15	1000	44.00%
7	**15**	**5**	**500**	**98.69%**
8	15	5	1000	75.60%
9	15	15	500	82.80%
10	15	15	1000	69.03%

CHARACTERISTICS OF ESB

1. Hydrophobicity

In Table 3, from the test, it was found that the hydrophobicity of ESB was 59.7%. The result shows the hydrophobicity interaction of ESB is higher compared to the hydrophobicity of SB with only 8.0% (Wahi et al., 2010). The hydrophobicity of ESB is increased by 51.7% successfully by the esterification process. The efficiency of removal of oil by using ESB in POME also increased by 53.33%.

Table 3. Hydrophobicity of SB and ESB (Run 7) with the highest oil removal efficiency

	Hydrophobicity (%)	The efficiency of Oil Removal in POME (%)	Researcher
SB	8.0±5.2	45.36±2.67	Wahi et al. (2013)
ESB	59.7	98.69	Present study

2. SEM Analysis

To compare the SB and ESB morphology of the surface, *Scanning Electron Microscopy* (SEM) analysis was conducted. The relatively smooth surface of SB is due to the removal of fiber wax and cuticles (Teli & Valia, 2013). The SB surface is relatively smooth and is observed to be rougher in ESB with pore formation.

3. FTIR Analysis

The FTIR spectrum of the ESB showed strong bands at 1741.29 cm^{-1}, characteristic of ester structure (due to C=O bending) and ether C-O bending at 1021.82 cm^{-1}. These spectra demonstrate that ester was successfully grafted onto ESB.

4. Sorption Studies

A column adsorption study was conducted to evaluate the performance of ESB in removing oil and grease contained in POME at the minimum and maximum uptakes, 5 and 15 cm of bed height, 500 and 1000 µm of particle sizes and 5 and 15 ml/min of flow rate.

5. Effect of Adsorbent Bed Height

The higher the contact time and adsorbent surface area, the higher the oil adsorption in the column. At the constant flow rate of 5 ml/min and 500 µm of particle sizes, the maximum oil removal efficiency was obtained by the 15 cm bed height of ESB with 98.69% while the lower oil removal efficiency was obtained by the 5 cm bed height with

49.69%. The effect of bed height for oil and grease adsorption in POME was investigated at different bed heights with the constant flow rate and same particle size of ESB as shown in Table 4. At the constant flow rate of 5 ml/min and 500 μm of particle sizes, the maximum oil removal efficiency was obtained by the 15 cm bed height of ESB with 98.69% while the lower oil removal efficiency was obtained by 5 cm bed height with 49.69%.

Table 4. Effects of different bed heights of ESB (500 μm particle sizes) with the low flow rate

Run	Bed Height (cm)	Flow Rate (ml/min)	Particle Size (μm)	Oil Removal Efficiency (%)
1	5	5	500	49.69%
7	15	5	500	98.69%

Table 5 shows the effects of different bed heights of ESB with the high flow rate. The smaller the particle sizes, the higher the oil removal efficiency was obtained by 15 cm bed height of ESB with 82.80% while the lower oil removal efficiency was obtained by 5 cm bed height with 51.71%.

Table 5. Effects of different bed heights of ESB (500 μm particle sizes) with the high flow rate

Run	Bed Height (cm)	Flow Rate (ml/min)	Particle Size (μm)	Oil Removal Efficiency (%)
3	5	15	500	51.71%
9	15	15	500	82.80%

From the results, the best oil removal efficiency was performed by 15 cm bed height compared to 5 cm bed height by considering the constant flow rate and same particle sizes. It was reported that higher bed height gives rise to higher oil removal efficiency. These available binding sites increase adsorption in higher adsorbent doses (Ahmad et al., 2003). The study shows the higher the bed height, the higher the sorbent dosage being used giving higher oil removal efficiency.

- Effect of Adsorbent Particle Sizes

The results obtained show that the size of the ESB affects the oil adsorption process. The adsorption capacity of oil by 500 μm ESB particle size is much higher compared to 1000 μm of particle sizes. In a balanced state, the adsorption capacity will be higher if the adsorbent particle size is small and the surface area is larger (Amode et al., 2013).

- Effect of Flow Rate

In this experiment, the effect of flow rate on the uptake of oil in POME by ESB was explored using two flow rates of 5 and 15 ml/min. The oil removal efficiency of bed height (15 cm) and small particle sizes (500μm) were investigated at the different flow rates as tabulated in Table 6. The oil removal efficiency obtained was 98.69% by conducting the low flow rate (5 ml/min) compared to the high flow rate (15 ml/min) which obtained a slightly different value of 82.80%. The pressure will drop if the flow rate is high across the adsorbent bed column (Shin et al., 2004).

Table 6. Comparison between low flow rate and high flow rate for oil adsorption in POME at the constant bed height and same particle sizes.

Run	Flow Rate (ml/min)	Bed Height (cm)	Particle Size (μm)	Oil Removal Efficiency (%)
7	5	15	500	98.69%
9	15	15	500	82.80%

CONCLUSION

Sago bark as a sorbent named esterified sago bark (ESB) was successfully produced by esterification to obtain higher oil removal efficiency in the adsorption of grease and oil in the palm oil mill effluent (POME). The ESB is found to effectively adsorb oil in POME at the slower flow rate of 5 ml/min with the smallest particle size of 500 μm and the highest bed height of 15 cm with 98.69% oil removal. This study showed the small particle sizes of ESB play an important role. This study also showed the higher the bed height of ESB, the slower the flow rate. Therefore, the low flow rate of 5 ml/min and a bed height of 15 cm was selected as the optimum condition. This experimental study is quite useful in developing appropriate technology for treating POME in the palm oil industry before being discharged into water courses. Besides the sago waste from the agriculture industry also can be commercialized as a sorbent of oil content in POME.

REFERENCES

Salihu, A., Alam, M. Z., Abdul, M. I., & Salleh, H.M. (2011). Suitability of using Palm oil mill effluent as a medium for lipase production. Afr. J. *Biotechnol*., *10*(11), 2044-2052.

Ahmad, A., Ismail, S., Bhatia, S. (2003). Water recycling from palm oil mill effluent (POME) using membrane technology. *Desalination*, 157, 87-95.

Ahmad, A. L., Sumathi, S., & Hameed, B. (2005). Adsorption of residue oil from palm oil mill effluent using powder and flake chitosan: Equilibrium and kinetics studies. *Water Research,* 39(12), 2483-2494.

Wan, S. (2010). Sago craft paper: A potential solution to sago industry pollution: *UiTM.*

Wahi, R., Chuah, L.A., Choong, T.S.Y., & Ngaini, Z. (2013). Separation and Purification Technology. *Elsevier B.V.* 113, 51-63.

Wahi, R., Devagikanakaraju and Ashikin, Y.N. (2010). Preliminary Study on zinc removal from aqueous solution by sago wastes. *Global Journal of Environmental Research, 4* (2), 127-134.

Teli, M.D., Valia, S.P. (2013). Acetylation of banana fibre to improve oil absorbency, Carbohyd. Polym. 92(1), 328-333.

Amode, J.O., Santos, J.H., Mirza, A.H., & Mei, C.C. (2013). Sorption of toxic cations onto sago waste 1: Investigation of sorption capacity. *The Third Basic Science International Conference.* C19-1.

Shin, C., & Chase, G.G. (2004). Water-in-oil coalescence in micro-nanofiber composite filters, *AIChE J, 50*(2), 343–350.