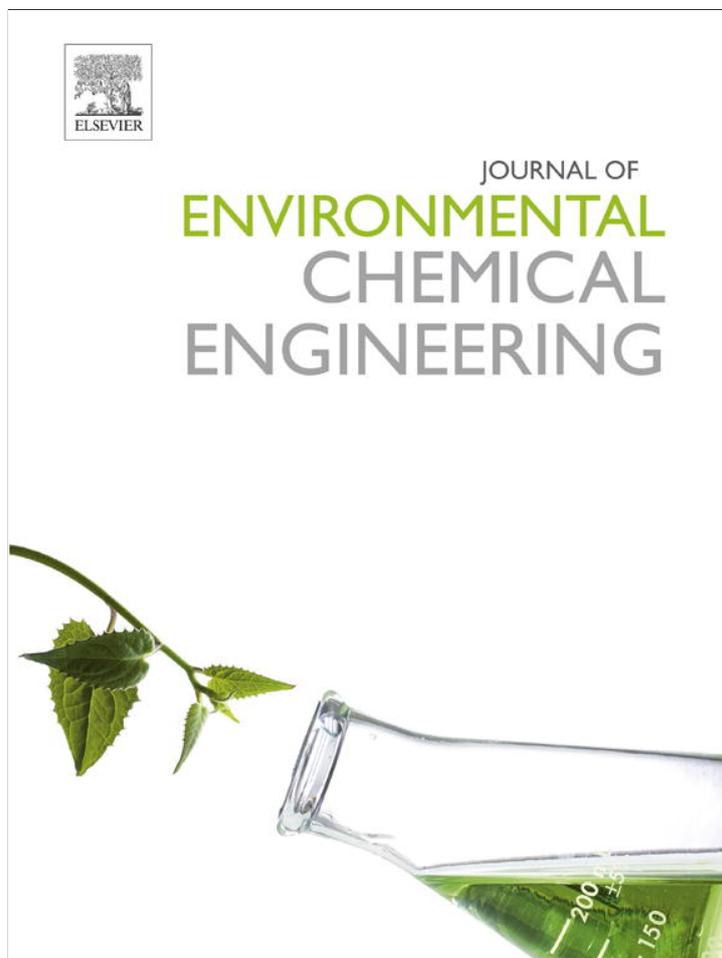


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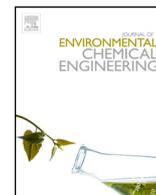
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Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jeceEsterification of *M. sugu* bark as an adsorbent for removal of emulsified oilRafeah Wahi^{a,b,*}, Luqman Abdullah Chuah^a, Zainab Ngaini^b, Mohsen Mobarekeh Nourouzi^a, Thomas Shean Yaw Choong^a^a Department of Chemical and Environmental Engineering, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia^b Department of Chemistry, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia

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ABSTRACT

Sago or *Metroxylon sugu*, harvested in Sarawak, Malaysia, is a low-cost, natural adsorbent. The sago bark (SB) from *M. sugu* was investigated for adsorptive removal of emulsified oil in palm oil mill effluent (POME). Hydrophobicity of this sorbent in aqueous state was improved via esterification process. The esterification of SB was conducted at ratio of sago bark to stearic acid (SA) by 1:1, 4:1, and 7:1; percentage catalyst of 5, 10, and 15; and refluxing time 1, 4.5, and 8 h; respectively. These parameters were analysed using full central composite design (CCD) of response surface methodology (RSM). The adjusted *R*-squared value of 0.9509 showed that the regression model fit the data well. The predicted *R*-squared value (0.9168) also indicated that the prediction of experimental data was satisfactory. Hydrophobicity test, FTIR, and SEM were carried out to characterise the esterified sago bark (ESB). Results showed that esterification process successfully increased the hydrophobicity of sago bark by 42.2% and oil removal efficiency in POME by 50.2%. A developed two-factor interaction (2FI) model showed that the preparation conditions of 1:1 SB:SA, 15% catalyst, and 8 h refluxing time afforded ESB with the maximum oil removal efficiency of up to 95.52% in POME. The esterification of SB successfully improved the oil adsorptivity for the removal of emulsified oil in POME.

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Introduction

Natural organic materials such as lignocellulosic fibres from agricultural residues have been reported as one of the important options of oil sorbents [1]. Some natural sorbents have the ability to absorb significantly more oil compared to commercial sorbents of polypropylene materials [2]. Other advantages of natural sorbents are comparable density with synthetic sorbent, chemical-free, and highly biodegradable [1,3,4].

Numerous natural fibres have been used as oil sorbent, such as kapok [5], barley straw [6], rice husk [7], sugarcane bagasse [8], sawdust [9], wool [10], and grass [11]. These natural sorbents comprise of cellulose and lignin, which are responsible for the oil sorption [8,12]. Despite of their advantages, many natural fibres have low hydrophobicity and low buoyancy, and therefore they are only suitable for oil removal in the absence of water [7]. In response, many studies have been conducted on methods to improve the efficiency of oil removal of natural sorbent by means of alkalisation [5], chloroform treatment [3,5,13], acetylation [2,14], salt treatment [3], surfactant treatment [6,15], combination

of chemical–biotechnological treatment [16], and esterification [8,17]. These studies show that appropriate chemical modification of natural sorbent could improve oil removal efficiency.

Esterification is one of the widely used chemical modifications to increase oil removal efficiency of natural fibres [14,17–20]. Many esterification studies on natural fibres via acetylation in the presence of acetic anhydride have been conducted [21]. The hydroxyl (–OH) group in rice, wheat, rye, barley straws, and poplar wood fibre has been successfully replaced with acetyl groups via acetylation [19]. Acetylation of sugarcane bagasse with *N*-bromosuccinimide (NBS) as the catalyst affords oil sorption capacity of 13.5–20.2 g/g on machine oil [20]. Acetylated banana fibre gives high oil sorption capacity (18.12 g/g) for machine oil [18]. Acetylated cotton [2] and acetylated wheat straw [14] show the reduction of the –OH group and the appearance of the three ester bands associated with successful acetylation at 1740–1745 cm^{−1} (C=O stretching of ester), 1369 cm^{−1} (C–H in –O(C=O)–CH₃), and 1234 cm^{−1} (C–O stretching of acetyl group attributed to C=O). However, the drawback in using acetic anhydride is the formation of acetic acid as by-product. Acetic acid causes residual smell, loss in material strength due to acidic hydrolysis of holocellulose, and metal fastener corrosion [21]. An interesting alternative in esterification of natural fibres is using fatty acid derivatives with water as a by-product [17]. Banerjee et al. studied on the esterification of sawdust using oleic acid, stearic acid, and decanoic acid in hexane with H₂SO₄ as the catalyst, at 65 °C

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for 6 h [17]. The results showed that esterification increased the oil sorption capacity of oleic acid-treated sawdust from 3.5 g/g (non-treated) to 6 g/g of crude oil. Stearic acid and decanoic acid, however, showed relatively lower degree of esterification due to lower solubility in hexane compared to oleic acid.

Sago, or scientifically known as *Metroxylon sagu*, is one of the main commodity crops of Sarawak, Malaysia. The bark of the tree is a potential source of natural fibre for oil removal [22]. This is because sago bark (SB) contains phytochemicals namely cellulose and lignin [23] as also found in other natural oil sorbents. Production of SB as a by-product of sago mill industries in Sarawak is more than 20,000 ton/yr. Only less than 15% of the SB are used as fuel in sago processing mill due to the corrosion problem, which can be caused by SB as the compound is acidic in nature [24].

Current practice in managing the overabundant SB poses a serious threat to the environment. Eliminating the SB through open and controlled burning could either cause air pollution or furnace chimney corrosion [24]. Because of its woody nature, SB degrades slowly. Dumping SB into nearby rivers is unacceptable as it could cause the rivers to become shallow [24]. On the other hand, leaving tones of SB to naturally degrade would consume space and time besides unpleasant odour and view. Therefore, there is an urgent need to find ways to systematically utilise SB [25].

Response surface methodology (RSM) is a statistical method used to study the effect of variables and their responses by running minimum number of experiments. The method uses quantitative data from predetermined experiments to obtain regression model equations and operating conditions [26,27]. RSM is more systematic, energy, cost- and time-saving approach compared to the traditional One-Variable-At-a-Time (OVAT) method.

The aim of this work was to enhance the adsorption ability of SB to remove oil from aqueous solution via surface esterification. An RSM model was developed to establish the relationships of various esterification parameters on the ESB oil removal efficiency.

Material and methods

Material

SB was collected from sago processing mill in Mukah, Sarawak. Sample was washed with water to remove debris, sun dried, ground, sieved into particle size of 1.0–2.8 mm, and oven-dried at 105 °C for 24 h. Properties of the SB are presented in Table 1 with fixed carbon content value calculated by weight difference [28].

Raw POME was collected from FELCRA palm oil mill in Kota Samarahan, Sarawak. The sample was cooled to room temperature and filtered through a muslin cloth strainer to remove solid particles of millimetre size. The passing portion of the filtered sample was analysed for its pH, total solid, and oil and grease

Table 1
Properties of SB sample.

	Value
<i>Proximate analysis</i>	
Moisture content (wt%) ^a	10.87 ± 0.20
Volatile matter content (wt%) ^b	72.82 ± 0.26
Ash content (wt%) ^b	3.42 ± 0.33
Fixed carbon content (wt%) ^c	12.89 ± 0.20
<i>Ultimate analysis</i>	
C (wt%)	42.42 ± 0.52
H (wt%)	5.62 ± 0.24
N (wt%)	1.39 ± 1.02
Others (wt%) ^c	50.58 ± 1.62
Apparent density (g/cm ³)	0.314 ± 0.01

^a As prepared sample.

^b Dry basis.

^c Calculated by weight difference [28].

Table 2
Properties of raw POME sample.

Properties	Value
pH	4.18 ± 0.02
Oil and grease content (mg/L)	4850 ± 505.0
Total solid content (mg/L)	15,200 ± 100.00

content. The analysis results are shown in Table 2. The POME sample was stored at 4 °C before use. All chemicals used in this study, namely stearic acid, ethyl acetate, *n*-hexane, and anhydrous sodium sulphate (Merck), were of reagent grade.

Esterification of SB

SB in a quantity of 5 g was placed in 500 mL round bottom flask containing 100 mL ethyl acetate. SA was added according to required SB:SA ratios, 1:1, 4:1, and 7:1. CaO of 5, 10, and 15 wt% of SB mass was added to the mixture as catalyst. The flask was immersed in oil bath and heated at reflux for the required times (1, 4.5, and 8 h). The mixture was then filtered, washed with ethyl acetate to remove unreacted stearic acid, and cooled to room temperature prior to use.

Central composite design (CCD) with 22 experimental runs was used to examine preparation factors that influenced the oil removal efficiency of ESB. The preparation factors of ESB were the SB:stearic acid (SA) ratio (factor A), catalyst percentage (factor B), and refluxing time (factor C). These three factors were chosen to study the response of oil removal efficiency in POME. Each factor was studied at two levels, which were the low level and the high level. The value ranges of SB:SA, catalyst percentage, and refluxing time were chosen based on preliminary experiments. Analysis of the experimental data was conducted using Design-Expert software (version 6.0.6, Stat-Ease Inc.).

Oil adsorption test in POME

Batch adsorption study was conducted using ESB (0.35 g) on raw POME (20 mL) at room temperature. The ESB-POME mixture was stirred for 30 min on a magnetic stirrer (IKA C-MAG HS7) before being filtered. Mixture was stirred at stirring scale 0.5 (~125 rpm), the minimum mixing speed for uniform mixing of ESB. The filtrate was analysed for oil content.

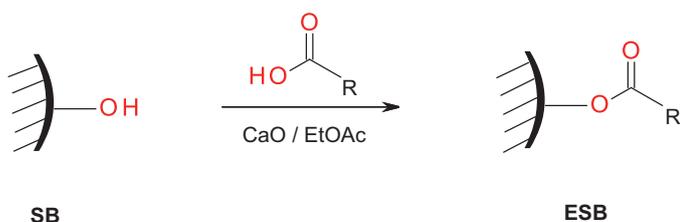
Determination of oil content in POME was conducted by *n*-hexane solvent extraction method (USEPA: Method 10056). 20 mL sample was transferred to separatory funnel. 9 drops of 1:1 HCl:water was added to obtain POME of pH ≤ 2 prior to addition of hexane (3 mL). The separatory funnel was vigorously shaken for 2 min and left for 10 min to form two layers. The combined organic and oil layer was collected onto gravity filtration apparatus and dried over NaSO₄ anhydrous. Hexane in oil was removed using rotary evaporator (Model: Heidolph Hei-VAP Value). Oil sample was oven dried at 103 °C for 15 min, cooled to room temperature and weighed. The measured weight was taken as oil and grease content value. The oil removal efficiency was determined from equation below:

$$\text{Oil removal efficiency (\%)} = \left[\frac{C_0 - C}{C_0} \right] \times 100\% \quad (1)$$

where C_0 and C are the initial oil concentration (mg/L) in POME and the oil concentration (mg/L) in the filtrate, respectively [28].

Chemical characterisation of SB and ESB

The procedure to determine the moisture, ash, and volatile content of the sample was adapted following ASTM D-3173, ASTM D-3174, and ASTM D-3175. CHN analysis was conducted using



Scheme 1. Esterification of sago bark (SB) using stearic acid (SA) and CaO to yield esterified SB (ESB).

CHN Elemental Analyser (Model: CHN Elemental Analyser Flash EA1112 Series). Apparent density was determined by compacting SB and ESB powder in measuring cylinder, and calculated by dividing the mass over the volume of SB and ESB. The BET surface area of all samples was determined by N_2 adsorption at 77.35 K using Quantachrome[®] ASIQwin[™]. All samples were degassed at 90–100 °C for 8 h, prior to the adsorption experiments. The BET surface area was obtained by applying the BET equation. Pore volume was calculated by applying $p/p_0 = 0.99$ to the adsorption data. Hydrophobicity test was conducted using method described in the previous study [29]. Fourier Transform Infra-Red (FTIR) analysis was conducted on SB and ESB in KBr pellet (Model: Thermo Scientific/Nicolet iS10). Scanning Electron Microscopy (SEM) analysis was conducted to compare the surface morphology of SB and ESB (model: JEOL JSM-6390LA).

Results and discussion

Esterification of SB

Chemical modification to increase the hydrophobicity of SB was performed via esterification process. The reaction was performed in the presence of SA and CaO. CaO was used as a base to deprotonate the abundance hydroxyl group available in the SB. The alkoxy group formed subsequently reacted with SA to form ESB (Scheme 1). The presence of peak at 1735 cm^{-1} in ESB was attributed to the formation of ester (Fig. 1). As shown in Table 3, the BET surface area ESB was found lower than SB, while the total pore volume of ESB is higher than SB. This result suggested that esterification cause formation of pore channels and thus, reduced the BET surface area of ESB [15]. Hydrophobicity test of ESB also

Table 3

BET surface area and hydrophobicity of SB and ESB with highest oil removal efficiency (Run 4).

	Multipoint BET surface area (m^2/g)	Total pore volume (cm^3/g)	Hydrophobicity (%)	Oil removal efficiency in POME (%)
SB	1.462	0.002	8.0 ± 5.2	45.36 ± 2.67
ESB	0.000	0.012	50.2 ± 9.7	95.52 ± 6.34

showed that the esterification had successfully increased the hydrophobicity of ESB by 42.2% and increased the oil removal efficiency of ESB in POME by 50.2% (Table 3).

Estimation on the degree of esterification was conducted by calculating the ratio, R , between the intensity of C=O stretching of ester at $1740\text{--}1745\text{ cm}^{-1}$ and the intensity of the C–O stretching vibration of cellulose backbone at $1020\text{--}1040\text{ cm}^{-1}$ [2]. The average R values obtained at different SB:SA, percentage catalyst, and refluxing time are shown in Table 4, and compared to average oil removal efficiency in POME.

Theoretically, lower SB:SA ratio should give higher R value due to the high content of SA, which could be converted into esters in the mixture. However, Table 4 (i) shows that the average R value increased at SB:SA 4:1 before it decreased at SB:SA 7:1. In contrast, the oil removal efficiency indicated consistent trend with the SB:SA ratio whereby the mixture with the highest amount of SA (SB:SA 1:1) showed the highest oil removal efficiency, followed by SB:SA 4:1 and 7:1. The inconsistent R values were attributed to the uneven chemical modification that could also occur on fibre particles of different size and physical shape [19]. Difference in fibre's size and physical shape could lead to uneven swelling of the SB particles. As a result, certain particles tended to be significantly esterified while others were left only partially esterified [19]. Table 4 (ii) and (iii) show that when the percentage catalyst and refluxing time increased, the R value decreased. The inversely proportional relationship between R value and oil removal efficiency was envisaged to result from the reversible nature of esterification process [18]. For instance, in the acetylation of cotton fibre, prolonged acetylation reaction beyond 3 h causes combined acetylation and de-acetylation processes [2].

SEM analysis was conducted to compare the surface morphology of SB before and after the esterification process. SEM micrographs in Fig. 2 indicate that esterification at long hours

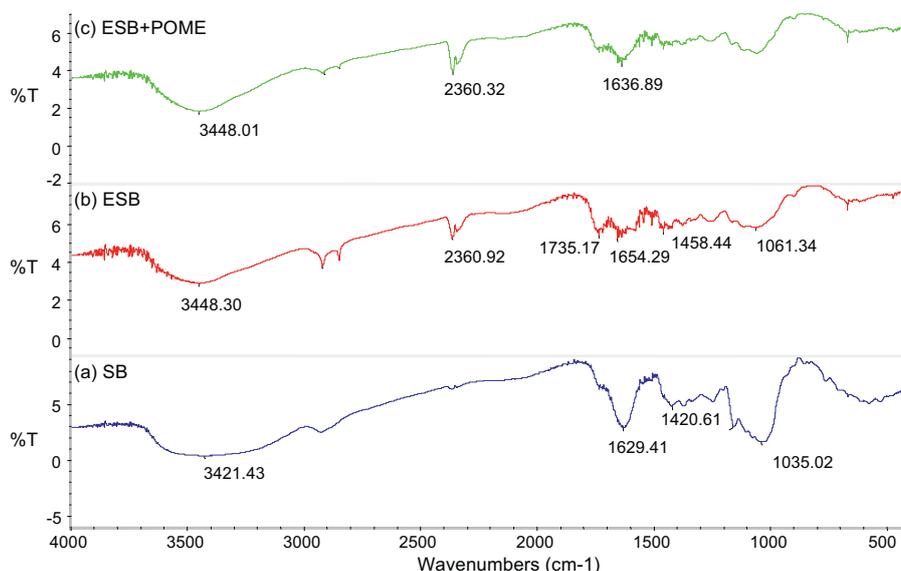


Fig. 1. FTIR spectra of (a) SB, (b) ESB with highest oil removal efficiency (Run 4), and (c) ESB after sorption study. Note: %T = % Transmittance.

Table 4

Average C=O:C–O intensity ratio, R in ESB at different SB:SA, percentage catalyst, and refluxing time.

	Average ratio R	Average % removal
<i>SB:SA</i>		
1:1	1.248 ± 0.333	69.44 ± 5.78
4:1	1.703 ± 0.570	60.06 ± 4.14
7:1	1.051 ± 0.215	50.63 ± 7.46
<i>Percentage catalyst</i>		
5	1.378 ± 0.585	50.02 ± 15.52
10	1.349 ± 0.337	59.68 ± 17.30
15	1.188 ± 0.396	70.34 ± 15.25
<i>Refluxing time, h</i>		
1	1.351 ± 0.620	46.42 ± 11.35
4.5	1.300 ± 0.483	61.48 ± 3.77
8	1.251 ± 0.213	72.59 ± 6.66

resulted in altered surface topography of SB due to removal of fibre's wax and cuticles [18]. The relatively smoother surface of SB compared to ESB (Fig. 2a) was observed rougher in ESB with formation of pores (Fig. 2b). In addition, the internal structure of the SB was revealed, exposing the starch content inside the SB (Fig. 2c and d). This process is referred to as fibrillation, which is the stripping of fibrils on the fibre's surface via mechanical stress on swollen fibres [30]. Alkali pretreatment on plant fibres has been recognised to cause tendency for fibrillation process to occur in plant fibres [31]. In the present study, it was envisaged that the addition of CaO as catalyst in the esterification process may have contributed to the fibrillation process.

RSM study

A central composite design with 22 experimental runs (all in duplicates) were employed, and the best model to fit was the two-factor interaction (2FI) model. The actual experimental factors and average response are presented in Table 5. The central values (zero level) chosen for experimental design were factor A, 4:1; factor B,

Table 5

Experimental factors and response.

Run Order	SB:SA	Percentage catalyst (%)	Refluxing time (h)	Average oil removal efficiency (%)	Standard deviation
1	1:1	5	1	38.19 (36.9)	18.45
2	1:1	5	8	74.84 (77.97)	3.46
3	1:1	15	1	59.18 (64.25)	1.80
4	1:1	15	8	95.52 (97.27)	6.34
5	7:1	5	1	34.00 (31.97)	7.75
6	7:1	5	8	52.99 (51.29)	11.60
7	7:1	15	1	56.65 (53.32)	21.21
8	7:1	15	8	68.17 (64.59)	3.54
9	1:1	10	1	48.80 (49.91)	15.51
10	1:1	15	4.5	89.69 (82.80)	10.21
11	7:1	10	1	38.83 (41.97)	17.62
12	7:1	15	4.5	56.70 (60.99)	5.83
13	4:1	5	8	65.89 (64.54)	13.54
14	4:1	10	4.5	63.18 (60.98)	14.17
15	4:1	15	8	75.84 (80.84)	5.13
16	1:1	10	8	90.11 (86.95)	10.69
17	4:1	5	1	34.70 (34.35)	6.86
18	7:1	10	8	57.38 (57.27)	23.20
19	1:1	5	4.5	59.20 (59.48)	12.95
20	4:1	15	1	61.00 (58.69)	11.59
21	4:1	10	4.5	59.76 (60.98)	15.16
22	7:1	5	4.5	40.35 (43.67)	7.44

Note: Theoretically predicted values are given in the parentheses.

10%; and factor C, 4.5 h. As mentioned earlier, CCD experimental design was employed to optimise the three factors. Since the target of esterification study was to increase the quality of SB as oil sorbent, optimisation parameters were related to the esterification conditions that could lead to ESB with maximum oil removal efficiency.

ANOVA summary generated by Design Expert software for response surface 2FI model gave the oil removal efficiency model the *F*-value of 68.73, implying that the model was significant. There was only a 0.01% chance that a model of such large *F*-value could occur due to noise. Values of Prob > *F* less than 0.05 indicate that

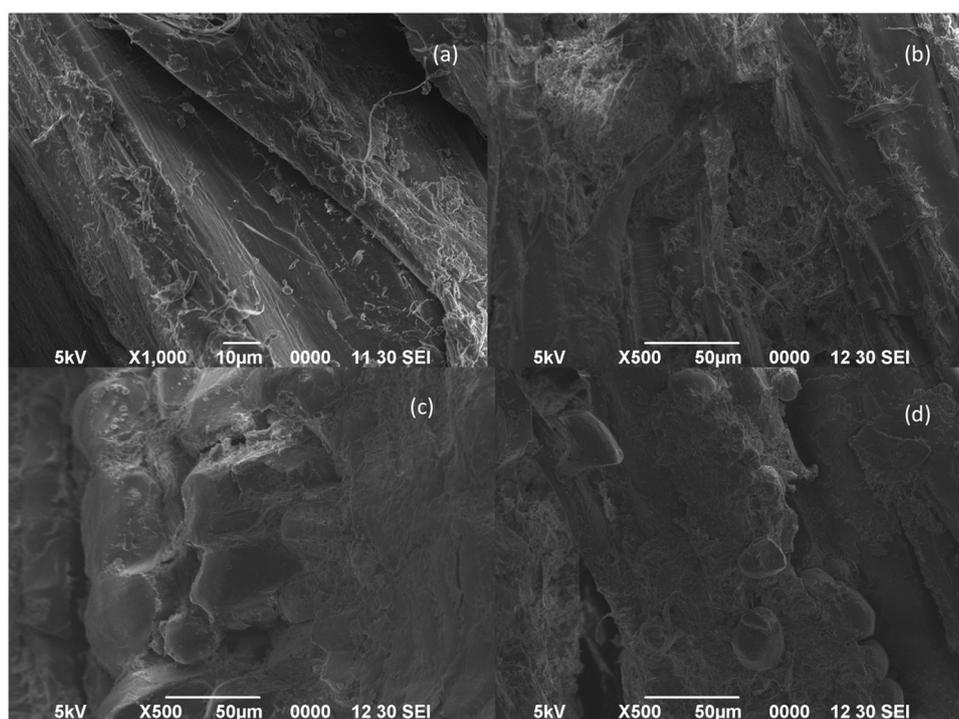


Fig. 2. SEM images of (a) SB and (b), (c), and (d) ESB with highest oil removal efficiency before adsorption (Run 4).

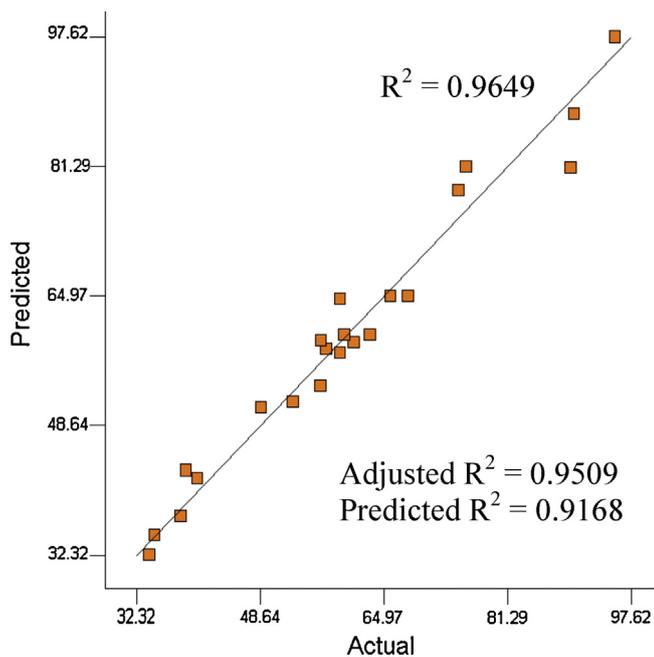


Fig. 3. Predicted vs. actual data for oil removal efficiency (%).

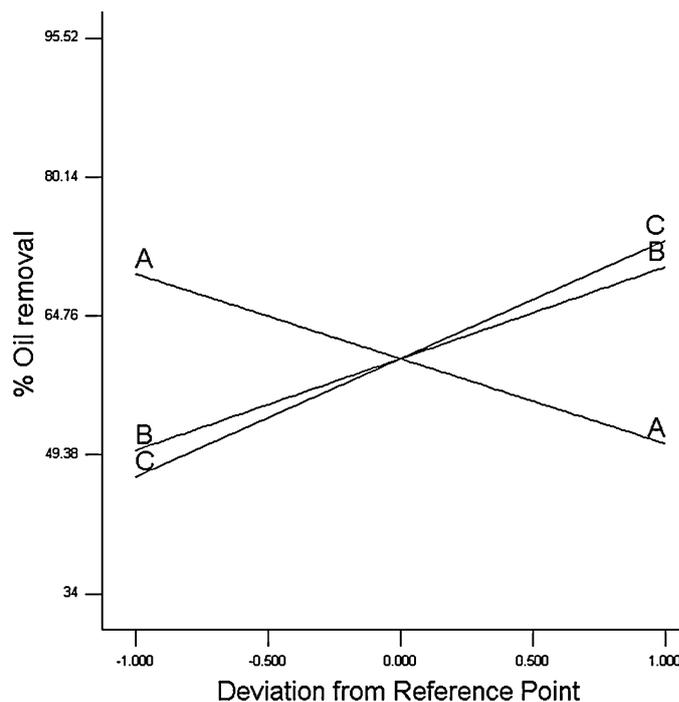


Fig. 4. Effects of individual esterification parameters, (A) SB:SA, (B) percentage catalyst, and (C) refluxing time on the ESB oil removal efficiency in POME (At SB:SA = 4:1, percentage catalyst = 10%, refluxing time = 4.5 h).

model terms were significant. In this case, the A, B, C, and AC preparation factors were significant model terms. The Lack of Fit F -value of 2.70 implied that the lack of fit was not significant relative to the pure error. Non-significant lack of fit was desirable in order for the model to fit.

Fig. 3 shows the predicted vs. actual plot of oil removal efficiency of ESB for the present study. R -squared was a calculated

value from the sample data and was used to determine the relationship between the actual and predicted oil removal efficiency values. A zero R -squared value indicated that there was no relationship between the actual and predicted oil removal

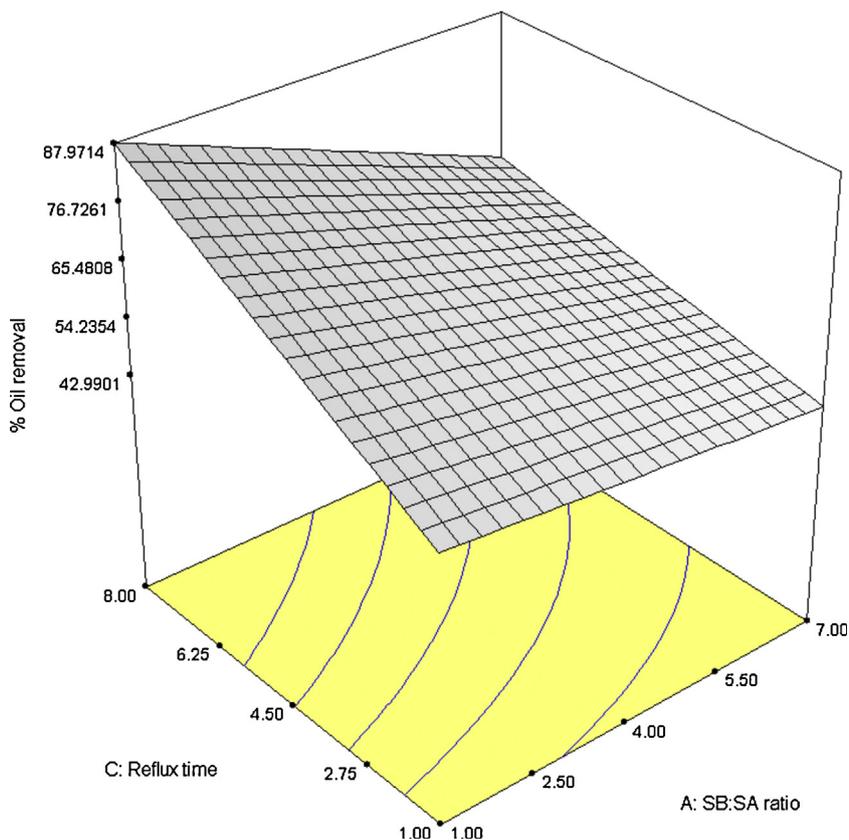


Fig. 5. 3D surface graph and contour plot showing the effect of SB:SA and refluxing time on ESB oil removal efficiency at percentage catalyst of 10%.

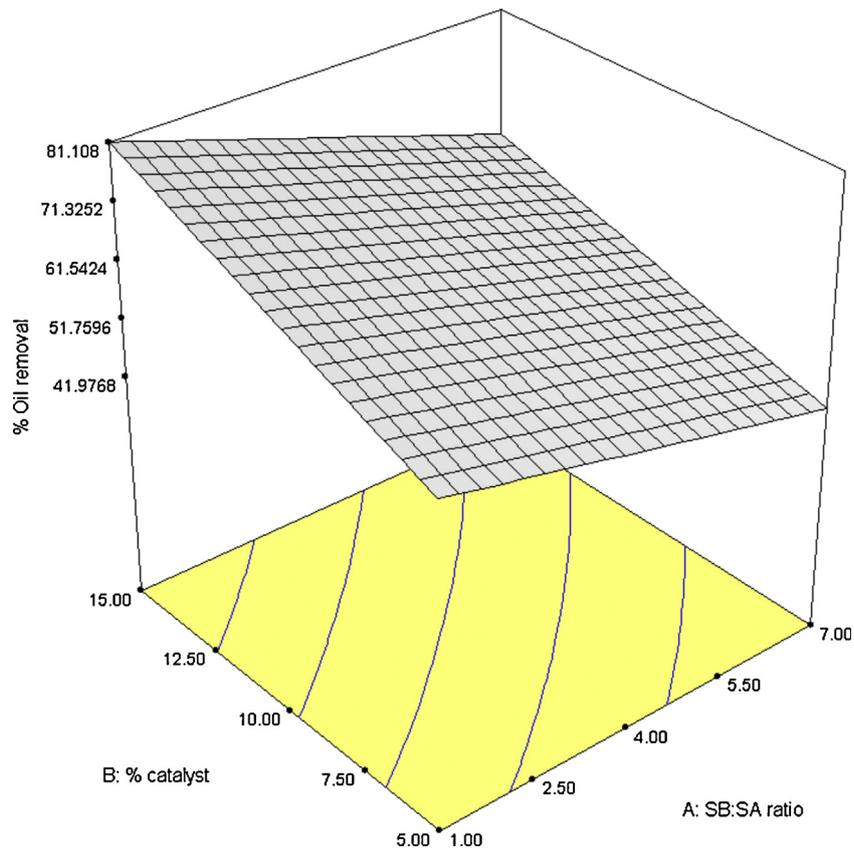


Fig. 6. 3D surface graph and contour plot showing the effect of SB:SA and percentage catalyst on ESB oil removal efficiency at refluxing time of 4.5 h.

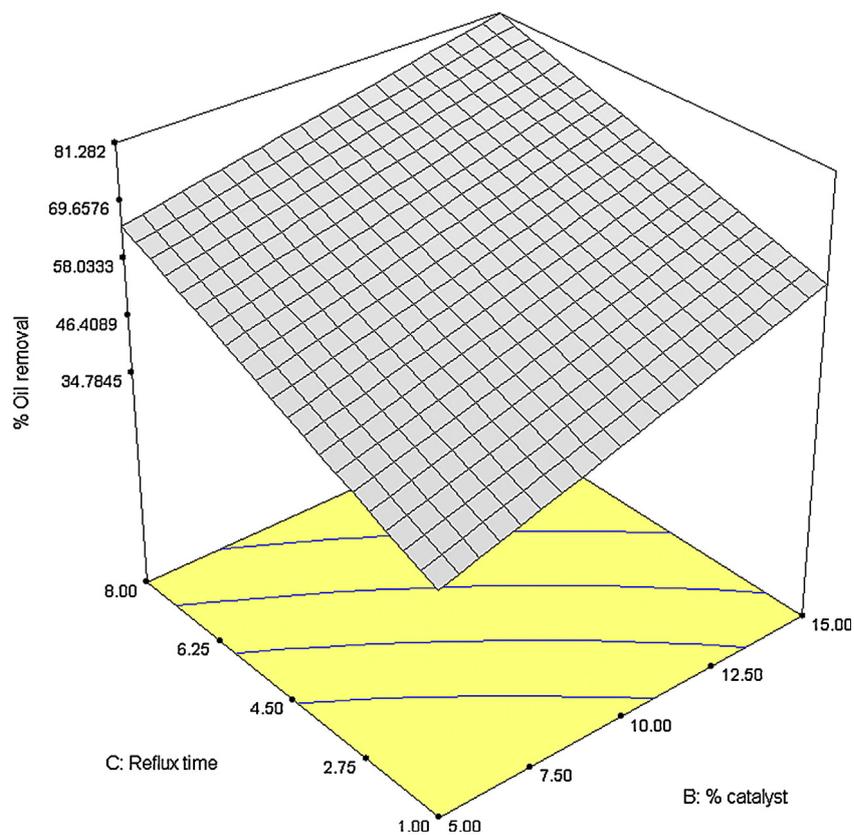


Fig. 7. 3D surface graph and contour plot showing the effect of percentage catalyst and refluxing time on ESB oil removal efficiency at SB:SA of 4:1.

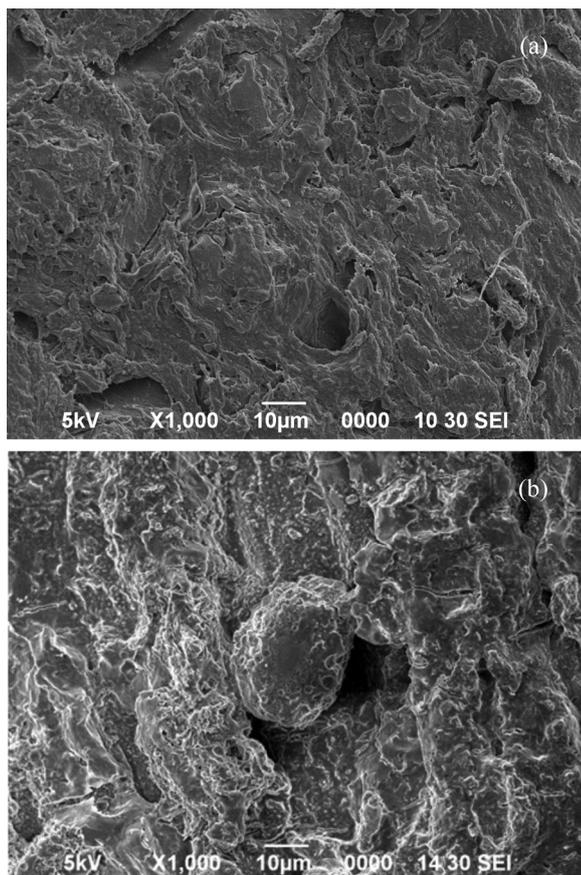


Fig. 8. SEM image of (a) SB and (b) ESB after oil adsorption from POME.

efficiency. The *R*-squared value of 1 showed that the linear regression model fit the data perfectly. In this study, the adjusted *R*-squared value was used instead of *R*-squared value due to the nature of *R*-squared value to decrease when a regressor variable is dropped from a regression model [32]. The adjusted *R*-squared gave an estimate of *R*-squared in the population from which the sample was drawn. ANOVA result showed that the predicted *R*-squared of 0.9168 was in reasonable agreement with the adjusted *R*-squared of 0.9509. The predicted *R*-squared value also indicated that the prediction of experimental data was satisfactory [27].

The 2FI models for the oil removal efficiency (%) with coded and uncoded factors are shown in Eqs. (2) and (3), respectively. In both equations, the coefficients with one and two factors represent the single factor effect and the two factor interaction effect, respectively. The positive and negative signs in front of the terms show synergistic and antagonistic effects, respectively.

$$\begin{aligned} \text{Oil removal efficiency (\%)} = & +60.04 - 9.40A + 10.16B \\ & + 13.09C - 1.5AB - 5.44AC \\ & - 2.01BC \end{aligned} \quad (2)$$

$$\begin{aligned} \text{Oil removal efficiency (\%)} = & +16.94642 + 0.19431A \\ & + 2.94900B + 6.95927C \\ & - 0.099889AB - 0.51778AC \\ & - 0.11490BC \end{aligned} \quad (3)$$

Based on experimental runs described in Table 5, effects of individual esterification parameters on the ESB oil removal efficiency in POME were summarised in Fig. 4. Results showed

that, in general, a lower SB:SA (factor A) generated ESB with higher oil removal efficiency. The results also indicated that an increase in catalyst amount (factor B) and refluxing time (factor C) during esterification resulted in the production of ESB with higher oil removal efficiency. An increase in the amount of CaO as catalyst enabled excellent deprotonation of hydroxyl group in SB particles, consequently gave rise to more reaction between stearic acid and SB.

ANOVA result revealed that the most dominant preparation factor influencing the oil removal efficiency of ESB was AC (the combination of SB:SA and refluxing time factors). Fig. 5 shows that as SB:SA was increased, longer refluxing time was needed in order to obtain ESB with high oil removal efficiency. The result was supported by optimisation of esterification process using Design Expert. It was found that at SB:SA ratio 1:1 and 10% catalyst, only 2.5 h refluxing time was needed to obtain ESB with oil removal efficiency of 58.86. When SB:SA was increased to 7:1 at 10% catalyst, 8 h refluxing time was needed to obtain ESB with oil removal efficiency of 58.29%. Combination of low SB:SA (1:1) and high refluxing time (8 h) resulted in ESB with maximum oil removal efficiency of 87.97%. Lower SB:SA means more stearic acid was used per gram SB, giving rise to more opportunities for esterification reaction. Long refluxing time allowed exposure of internal surfaces of SB, which in turn increased ester formation sites. The AC interaction effect afforded ESB with high oil removal efficiency.

Figs. 6 and 7 illustrate the interaction effects of factor AB and BC. At the refluxing time of 4.5 h with SB:SA 1:1 and 15% catalyst, the maximum oil removal efficiency of ESB was 81.108% (Fig. 6). It was

Table 6

Comparison on performance of different sorbent for removal of oil from POME.

Sorbent	Oil removal efficiency in POME	Sorption condition	Author(s)
(i) Chitosan (flake)	99%	Adsorbent dosage: 2 g/L Sorption time: 30 min Mixing rate: 100 rpm pH: 4.0–5.0	[33]
(ii) Chitosan (powder)	99%	Adsorbent dosage: 0.5 g/L Sorption time: 30 min Mixing rate: 100 rpm pH: 4.0–5.0	[34]
(iii) Commercial activated carbon	99%	Adsorbent dosage: 8 g/L Sorption time: 30 min Mixing rate: 150 rpm pH: 4.0–5.0	[34]
(iv) Bentonite	99%	Adsorbent dosage: 10 g/L Sorption time: 30 min Mixing rate: 150 rpm pH: 4.0–5.0	[34]
(v) Palm shell activated carbon	90%	Adsorbent dosage: 80 g/L Sorption time: 24 h Mixing rate: 150 rpm pH: 4.5	[28]
(vi) Palm shell activated carbon magnetic composite	85%	Adsorbent dosage: 80 g/L Sorption time: 24 h Mixing rate: 150 rpm pH: 4.5	[28]
(vii) SB	45.36%	Adsorbent dosage: 17.5 g/L Sorption time: 30 min Mixing rate: 125 rpm pH: 4.18	Present study
(viii) ESB	95.52%	Adsorbent dosage: 17.5 g/L Sorption time: 30 min Mixing rate: 125 rpm pH: 4.18	Present study

also observed at the SB:SA 4:1 with refluxing time of 8 h and 15% catalyst, the maximum oil removal efficiency of ESB was 81.28% (Fig. 7).

Oil removal efficiency of ESB

The SEM image of SB and ESB after oil adsorption from POME (Fig. 8) shows that the surface of both SB and ESB was covered by a layer of oily substance, indicating successful attachment of oil on both samples. The results were consistent with previous study in which the attachment of emulsified oil in POME onto sorbent surface could be seen in the SEM images of sorbent after adsorption [33]. In the present study, the oil removal efficiency was found greater in ESB. The relatively higher oil removal efficiency of ESB than SB was attributed to the presence of hydrophobic groups (Fig. 1 and Table 3) and the rougher surface topography in ESB (Fig. 2(b)–(d)).

Table 6 shows the performance of ESB for the removal of oil from POME. The ESB had relatively better oil removal efficiency (95.52%) compared to palm kernel activated carbon and its magnetic composite in Table 6 (v–vi) [28] with less adsorbent dosage and sorption time. Although ESB required slightly more adsorbent dosage to achieve comparable oil removal efficiency with some natural sorbents, as shown in Table 6 (i, ii and iv) [33,34], ESB showed potential real application as the ESB was synthesised from a renewable and locally abundant source.

Conclusions

In summary, a locally abundant waste material from sago has been successfully utilised for the removal of oil from POME. The esterification has successfully increased the hydrophobicity of SB by 42.2% and the oil removal efficiency in POME by 50.2%. The ESB produced at the operating condition of SB:SA 1:1, 15% catalyst, and 8 h refluxing time gave the highest oil removal efficiency in POME (95.52%). The two most dominant influencing factors for ESB preparation were SB:SA and refluxing time. Future works include the regeneration studies and treatment of the waste SB and ESB.

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