DEOILING EFFICIENCY FOR OIL EXTRACTION FROM SPENT BLEACHING CLAY AND THE QUALITY OF RECOVERED OIL

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ABSTRACT

The disposal and reuse of spent bleaching clay (SBC) from the palm oil processing industry is a problem of growing importance. Although today the only practical way of removing SBC is by disposal, extraction with organic solvents is a well-known method of deoiling contaminated SBC. Various hydrocarbon solvents are used as solvents to extract the residual oil in SBC. In this study, SBC was deoiled by hexane extraction. The content of oil and minor components in SBC was more than 40% by weight. All the extracted oils, irrespective of the solvent used, had poorer quality than crude palm oil (CPO). The outcome of the study showed that the amount of extracted oil using the conventional Soxhlet extraction method was higher than by batch extraction. However, for extraction of the residual SBC using the batch method, a SBC to solvent ratio of 1:7 should be more suitable as more of the impurities are removed. The aim of this study was for a complete separation of the residual oil from SBC. The oil and SBC were analyzed and tested. The results show that SBC still had an activity approximately 80% that of fresh bleaching clay.

Keywords: spent bleaching clay, deoiling extraction, Soxhlet extraction, crude palm oil.

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INTRODUCTION

Refining of vegetable oils, *e.g.* palm oil and rapeseed oil, requires several steps to remove from the raw materials those components that have strong colour or odour or are harmful to health. The traditional process of refining involves degumming, bleaching and deodorization. The purpose of the bleaching step is to remove undesirable substances such as soap residues, traces of heavy metals, phosphorus compounds, as well as coloured matter, *i.e.* carotenoids and chlorophyll pigments. The bleaching clays, *i.e.* activated clay and natural clay, employed for adsorption must be mechanically robust and must possess a high specific surface area by weight (Waldmann and Eggers, 1991).

Malaysia produced 17 million tonnes of crude palm oil (CPO) in 2010 (MPOB, 2010). In the process of refining CPO, clay is used as a bleacher in the bleaching process. The used clay, termed spent bleaching clay (SBC), contains 30%-40% oil, which is estimated at 17 000 t, and SBC is generally disposed off untreated. This disposal constitutes a significant economic waste and an environmental burden. By recovering the oil, the cost of disposal will be reduced effectively, and the recovered oil may be reused for other non-food applications. The solid residue can be further treated and converted to products such as poultry and animal feed and as building material, *i.e.* when added into the cement mixture. Thus, an effective extraction method for maximum recovery of oil from SBC would be desirable.

The method for oil recovery by solvent extraction from SBC resulting from edible oil refining is

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well-known. Laboratory methods for extraction of oil from spent clay have been studied and reviewed (John, 1983; Ooi *et al.*, 1993; Pollard *et al.*, 1993; Lee *et al.*, 2000). Soxhlet extraction has been used for many years in extracting solutes from a solid structure. In this method, the solvent can be distilled off and the solute can be extracted from SBC in a continuous cycle (Rosli *et al.*, 2004). The aim of the present study was to separate the residual oil from SBC using batch extraction as well as to regenerate the bleaching clay in the best possible re-usable condition. The influence of solid to solvent ratio on the residual oil extracted from SBC was also investigated. The result was compared with the conventional Soxhlet extraction method.

MATERIALS AND METHODS

SBC samples were obtained from FELDA Palm Oil Refinery, Kuantan, Pahang. SBC collected from palm oil and palm kernel oil refineries were coded as Sample 1 (S1) and Sample 2 (S2), respectively. Non-polar solvent hexane was used as a standard solvent for the extraction process. This was because the use of hexane is theoretically allowed in extracting edible oil for food utilization. In France, only hexane is allowed for edible oil use (Klein, 1987). The ratio of solid to solvent (wt./wt.) was varied from 1:1 to 1:7. In this study, 10 g of SBC was used for each treatment. The mixture of SBC (solid) and hexane (solvent) was shaken in a water bath for 30 min at 40°C. The hexane layer was then separated off and evaporated using a rotary vacuum evaporator. The extraction was carried out for 8 hr until no further increase in weight of the extracted materials was detectable. After every experiment, the amount of extracted oil was weighed and the percentage of deoiling efficiency was determined after Rosli *et al.* (2004):

$$\text{Deoiling efficiency (\%)} = \frac{W_{be}}{W_{se}} \times 100\% \qquad (1)$$

where W_{be} was the weight of the oil extracted using batch extraction, and W_{se} was the weight of oil extracted using the conventional Soxhlet extraction at a temperature of 60°C for 8 hr. About 10 g SBC sample was placed in the thimble and the top of the sample layer was covered by gauze. Hexane solvent was placed in a round bottom flask. The solvent was evaporated and separated by a rotary vacuum evaporator, and the amount of oil extracted was measured.

The effect of various ratios of solid to solvent on the extraction of palm oil and palm kernel oil from SBC was investigated by employing the batch extraction method. A conventional modified Soxhlet extraction was used as reference, in which 100% of the residual oil was extracted. Deoiling efficiency and regeneration efficiency of deoiled spent bleaching clay (DSBC) was determined. Deoiling efficiency was employed to determine the amount of residual oil that can be removed from SBC using solvent extraction. Regeneration efficiency was used to determine the capability of deoiled SBC in removing colour pigments of oil, as compared to fresh bleaching clay. Two types of SBC were used, *i.e.* from the palm oil refinery (SBC-S1) and from the palm kernel oil refinery (SBC-S2).

The quality of oil was determined by parameters which included specific extinction in UV-light, trigylceride composition and fatty acid composition. Deoiled SBC samples were dried at 120°C for 8 hr. The deoiled SBC was used for refining CPO and crude palm kernel oil (CPKO) following the bleachability test of the Seed Crushers' and Oil Producers' Association (SCOPA) (Siew *et al.*, 1995) to determine its performance as shown in *Figure 1*. Colour is an important quality of refined oil, and was used here to determine the regeneration efficiency of SBC. The regeneration efficiency was calculated as:

$$\textit{Regeneration efficiency} \text{ (\%)} = \frac{(R_o - R_d)}{(R_o - R_f)} \times 100\% \qquad (2)$$

where R_o, R_d and R_f were the red colour values of unbleached oil, oil bleached by deoiled SBC and oil bleached by fresh bleaching clay, respectively.

RESULTS AND DISCUSSION

The deoiling efficiency for various ratios of SBC to hexane (1:1, 1:3, 1:5 and 1:7) is presented in *Figure 2*. The SBC to hexane ratio influenced the deoiling efficiency. The deoiling efficiency for both SBC-S1 and SBC-S2 increased as the solid to solvent ratio was decreased. The maximum deoiling efficiency was 90% and 87% for SBC-S1 and SBC-S2, respectively. In contrast, SBC-S1 and SBC-S2 with only 32.6% and 26.8% deoiling efficiency, respectively, was achieved when using a solid to solvent ratio of 1:1. The amounts of oil extracted from SBC-S1 and SBC-S2 using Soxhlet extraction were 2.58 g and 3.47 g, respectively.

Figures 3a and *3b* show the regeneration efficiency of deoiled SBC treated with different solid to hexane ratios. The regeneration efficiency was calculated using Equation (2). The regeneration efficiency of DSBC-S1 and DSBC-S2 in CPO refining was significantly higher compared to refining CPKO, *i.e.* about 80% for CPO and 30% for CPKO. The colour of both crude oils after bleaching using DSBC is shown in *Table 1*.

The basic tests performed for quality control of oil include the determination of the contents of free fatty acids (FFA), specific extinctions at UV wavelengths of 233 nm and 269 nm, deterioration

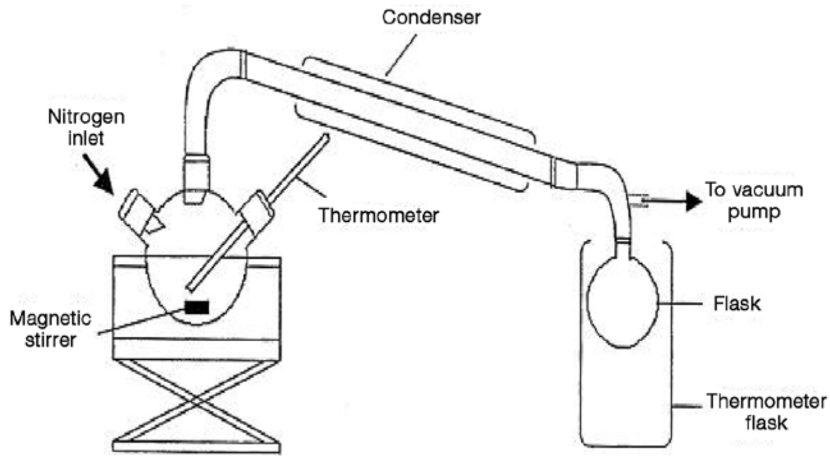

Figure 1. Apparatus set-up for the laboratory bleaching process.

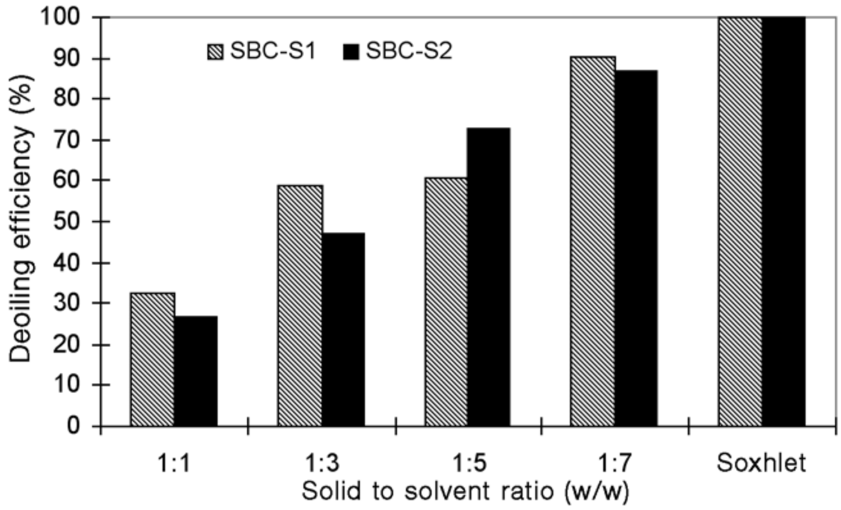

Figure 2. Deoiling efficiency as a function of solid to solvent ratio.

TABLE 1. COLOUR OF CRUDE PALM OIL (CPO) AND CRUDE PALM KERNEL OIL (CPKO) AFTER BLEACHING USING DEOILED SPENT BLEACHING CLAY (DSBC)

Solid to solvent ratio (w/w)	Crude oil			
	CPO		CPKO	
	DSBC-S1	DSBC-S2	DSBC-S1	DSBC-S2
1:1	6.6	6.9	2.0	2.0
1:3	6.4	6.8	2.0	2.0
1:5	6.5	6.8	2.1	2.0
1:7	6.3	6.4	2.0	2.0
Soxhlet	6.3	6.6	2.1	2.3

Note: Colour of refined palm oil using fresh bleaching clay = 2.5.
Colour of refined palm kernel oil using fresh bleaching clay = 0.8.

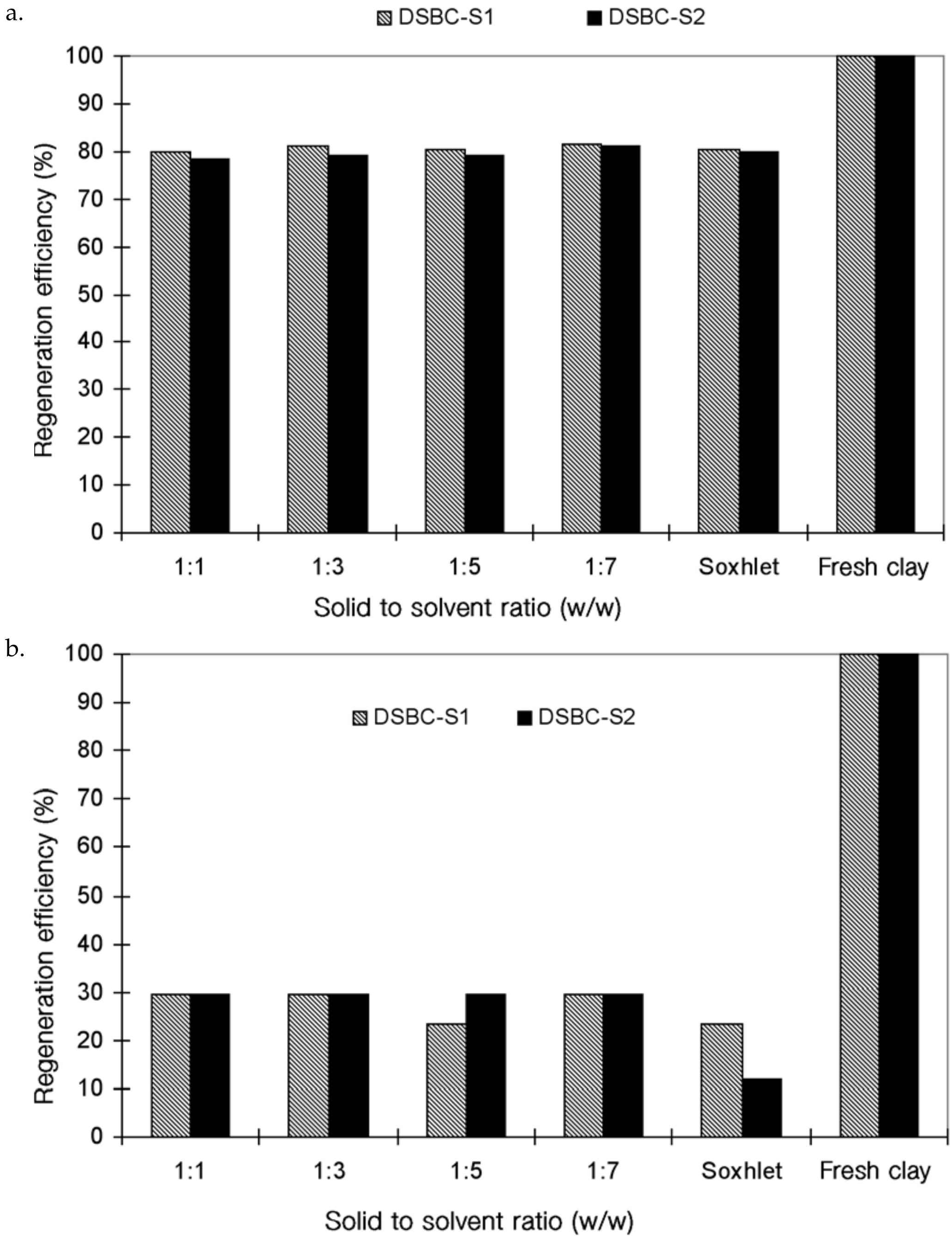

Figure 3. Regeneration efficiency as a function of solid to solvent ratio in the refining of (a) crude palm oil (CPO) and (b) crude palm kernel oil (CPKO) with fresh bleaching clay as reference.

of bleachability index (DOBI), iodine value (IV), fatty acid and trigylceride compositions, and minor constituents such as chlorophyll and carotenoids. Information on FFA content and DOBI are required in the trading of oil. *Table 2* shows that the FFA content, primary and secondary oxidation products of oils extracted from SBC were higher compared to values found in crude oils. The FFA is the most important parameter of crude oil quality used in the refining process. The FFA in CPO and CPKO were 3.26% and 2.47%, respectively, which are within the typical values of FFA in Malaysian CPO and CPKO, *i.e.* 3.2% (Siew, 2000) and 2.5% (Siew and Berger, 1980), respectively. The oil extracted from SBC had much higher FFA, *i.e.* 20.5% and 13.49% in extracted palm oil (EPO) and extracted palm kernel oil (EPKO), respectively. This deterioration of quality arose because of hydrolysis of the residual oils. The FFA content and the degree of oxidation products (*i.e.* conjugated dienes and conjugated trienes) of the oil were higher, while the DOBI value was lower and the oils were deep brownish for EPO and yellowish for EPKO in colour appearance. An increase in FFA content had similarly been observed earlier in palm oil extracted from SBC with a different solvent (Lee *et al.*, 2000).

TABLE 2. CHARACTERISTICS OF CRUDE OIL AND OIL EXTRACTED FROM SPENT BLEACHING CLAY (SBC)

Parameter	EPO*	CPO	EPKO**	CPKO
Oil recovery (%)	8-26	-	9-35	-
FFA (%) max	20.57	3.26	13.49	2.47
$E^{1\%}_{233}$ max	3.2	1.83	2.0	1.28
$E^{1\%}_{269}$ max	1.5	0.80	0.50	0.25
Carotene content (ppm)	41	555.09	13	20
DOBI	<0.1	2.80	<0.05	0.06
IV	≈53	54.6	14	19.8

Note: *Extracted palm oil (EPO) = oil extracted from SBC at a palm oil refinery.
**Extracted palm kernel oil (EPKO) = oil extracted from SBC at a palm kernel oil refinery.
FFA = free fatty acid.
IV = iodine value.
DOBI = deteriorating of bleachability index.

TABLE 3. FATTY ACID COMPOSITION OF CRUDE OIL AND OIL EXTRACTED FROM SPENT BLEACHING CLAY (SBC)

Sample	C8:0	C10:0	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C20:0
CPO	0	0	0.2	1.2	42.6	3.8	40.4	10.8	0
EPO*	0	0	0.2	1.1	43.4	4.2	39.2	10.1	1.2
CPKO	3.8	3.4	47.0	15.7	8.3	2.1	16.2	2.8	0
EPKO**	3.6	3.7	50.0	15.5	7.7	2.0	13.4	2.4	0

Note: CPO = crude palm oil.
CPKO = crude palm kernel oil.
*Extracted palm oil (EPO) = oil extracted from SBC at a palm oil refinery.
** Extracted palm kernel oil (EPKO) = oil extracted from SBC at a palm kernel oil refinery.

The specific extinction coefficients at 233 nm and 269 nm correspond to the presence of primary and secondary oxidation products, respectively, with a higher value of absorbance indicating a larger amount of oxidation products. *Table 2* shows that the specific extinction coefficients at 233 nm and 269 nm of EPO were 3.2 and 1.5, respectively, which were higher than for CPO being 1.83 and 0.80, respectively. These results indicate that EPO contained a larger amount of primary and secondary oxidation products than CPO. A similar conclusion can be reached for CPKO.

The DOBI value, carotene content and IV of CPO were higher than the corresponding values of the oil extracted from SBC. CPO had a DOBI value of 2.8, while the values for EPO and EPKO were less than 0.1 and 0.05, respectively. According to Siew (2000), CPO samples having DOBI values between 3 and 4 are easily bleached to a light colour oil, whereas samples having DOBI values less than 2 are difficult to be refined. A poor quality of crude oil required a higher dosage of bleaching clay to produce acceptable FFA and colour in the refined oil (Lal and Antony, 1991).

CPO contains typically 555 ppm of carotenoids, and appears orange red in colour. On the other hand, CPKO is deep yellow in colour with approximately 20 ppm of carotenoids. The carotene contents in EPO and EPKO were found to be 41 ppm and 13 ppm, respectively, which were obviously much lower than in the crude oil. The carotene compounds could be bounded strongly in the pores of SBC. The IV is a measure of unsaturation of fats and oils. The IV of EPO was 53 and of EPKO was 14, which were lower than the values of 54.6 for CPO and 19.8 for CPKO, respectively. However, the difference in IV between extracted oil and crude oil was not obvious. The extracted oil from both SBC samples was slightly more saturated than for CPO and CPKO.

Palm oil is characterized by its high level of palmitic acid (C16:0), approximately 39.2% to 45.8% (Siew, 2000). Palm kernel oil is richer in lauric acid (C12:0) at about 48% (Siew and Berger, 1980). *Table 3* shows the fatty acid composition of both crude oils and extracted oils. The results indicate no evident difference in fatty acid composition of the crude oils and extracted oils. It can be seen that the bleaching process had very little effect on the fatty acid composition of the oils. This is consistent with the findings of Siew (2000) that the refining process has negligible effect on the fatty acid composition of the oil.

CONCLUSION

The quality of the oil extracted from SBC was inferior to crude oil. The results indicate that the oil extracted from SBC may be difficult to be refined to a good quality and stability. The amount of extracted oil and deoiling efficiency for both SBC samples increased as the solid to solvent ratio was decreased. However, the regeneration efficiency of deoiled SBC treated using different solid to solvent ratios gave almost similar regeneration efficiency, *i.e.* about 80%, for bleaching CPO, and not more than 30% for bleaching CPKO. This shows that deoiled SBC was not good enough for use in the bleaching process.

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