Journal of Oil Palm Research Vol. 23 April 2011 p. 999-1004

REGENERATION AND CHARACTERIZATION OF SPENT BLEACHING CLAY

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ABSTRACT

Spent bleaching clay (SBC), a solid waste generated from the palm oil refinery, may be recycled rather than being simply disposed off in landfills. The aim of this research was to investigate the heat regeneration of SBC and to evaluate the performance of the heat-treated SBC in bleaching crude oil. Two types of SBC were used, i.e. *(a) acid-activated clay, and (b) natural clay. Two types of regeneration processes were performed,* i.e. *(a) solvent extraction followed by heat treatment, and (b) direct heat treatment. Heat treatment was conducted in a box furnace at temperatures ranging from 400°C to 800°C. Red colour indices of oils were used to determine the regeneration efficiency. Spent bleaching clay produced by the direct heated-regenerated spent bleaching clay (HRSBC) yielded a higher regeneration efficiency than the deoiled-heated-regenerated spent bleaching clay (DHRSBC) produced by solvent extraction and heat treatment. This is because moisture, impurities and dirt were more completely removed by direct heating than by solvent extraction. Specific surface area, total pore volume and average pore size of SBC were measured using the nitrogen adsorption-desorption method. The results show that the HRSBC at 500°C possessed a higher specific surface area and total pore volume and gave a better bleaching efficiency than HRSBC at 400°C and 800°C. All the regenerated SBC samples were mesoporous material.*

Keywords: spent bleaching clay, adsorbent, regeneration, physical properties.

Date received: 13 April 2010; **Sent for revision:** 27 April 2010; **Received in final form:** 15 July 2010; **Accepted:** 6 January 2011.

INTRODUCTION

Oil palm (*Elaeis guineensis*) was introduced into Malaya in 1870, and was commercially exploited in the 1900s. Nowadays, oil palm is the most economically attractive crop in Malaysia. With a total planted area of 4.5 million hectares, it plays a prominent role in the socio-economics and well-being of the country (MPOB, 2009).

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Physical refining of palm oil is a common practice in Malaysia because of its high efficiency, high recovery, low operating cost, low capital input and having less effluent to handle. Three main steps, namely, degumming, bleaching and deodorization, are usually involved in physical refining of palm oil. In physical refining of palm oil, a bleaching clay dosage of 0.5% to 1.0% is generally used. The main task of the bleaching clay is to improve the appearance, flavour, taste and stability of the final product by adsorbing colouring matter and undesirable residues from the crude oil. Bleaching of edible oil is important for producing a light-coloured oil of acceptable quality. Crude palm oil (CPO) contains approximately 1% of minor components, including pigments (*i.e.* carotenoids and chlorophyll), which possess important physiological properties.

Spent bleaching clay (SBC) generated from the palm oil refineries normally still contains 30% to 40% oil by weight, depending on the activity of the bleaching clay and on the processing conditions (Austreng, 1978). SBC is commonly disposed off in a dumpsite without any pre-treatment.

The disposal of SBC in the dumpsite may present environmental issues as the leaching of the residual fat by rain may pollute ground waters, contribute to economic loss in unrecovered oil as well as pose a fire hazard. Malaysia alone generated about 179 000 t of SBC from the production of 17 million tonnes of palm oil in the year 2010. From the environmental, safety and regulatory points of view, recycling is one of the major waste management strategies. The oil retained in SBC, if recovered, may be a valuable product. The residual oil in the SBC may be added to plant waste to make compost. Depending on its quality, this recovered oil may be useful as a component of human foodstuffs or animal feeds, as well as having other technical applications. The mineral residue from SBC can be used for soil improvement. SBC may also be used to construct cement furnaces, or utilized in brickworks and the cement industry (Tsai *et al.*, 2003). The objectives of this study were to establish the optimum heating temperature in the heat regeneration process of SBC, and further to characterize the physical properties and the performance of the regenerated SBC.

MATERIALS AND METHODS

Materials

Two fresh commercial bleaching clays as listed in *Table 1* were used as standard samples. Sample A was acid-activated bleaching clay whereas Sample B was natural bleaching clay. Both fresh bleaching clays were fine white powders.

Preparation of Spent Bleaching Clay (SBC) Sample

Samples of CPO were refined according to the method recommended by the Seed Crushers' and Oil Processors' Association (SCOPA) (Siew *et al.*, 1995). The SCOPA method includes degumming, bleaching and deodorizing steps. In this work, SBC was obtained from the bleaching of oil using fresh bleaching clay. One hundred grams of melted CPO was weighed in a round-bottomed flask. The oil was heated with agitation using a magnetic stirrer under a nitrogen blanket to a temperature of 90°C. Degumming was carried out with 0.5% phosphoric acid with the temperature maintained at 90°C for 10 min. Bleaching clay was then introduced at the end of 10 min, and the temperature was raised to 105°C and maintained for 15 min under a nitrogen blanket. The hot oil and bleaching clay mixture was then filtered under vacuum into a vacuum flask through a Buchner funnel using Whatman No.1 filter paper. SBC collected from the filter paper was used for the regeneration process.

TABLE 1. COMMERCIAL BLEACHING CLAYS

Type	Sample code
Acid-activated clay	A
Natural clay	B

Each sample of SBC was divided into two sub-samples to test the two processes, which were coded as deoiled-heated-regenerated spent bleaching clay (DHRSBC) for the deoiled-heat treatment, and heated-regenerated spent bleaching clay (HRSBC) for the direct heat treatment.

Solvent Extraction and Regeneration by Heat Treatment

This experiment involved solvent extraction followed by heat treatment. In this study, non-polar solvent hexane was used as the solvent for the extraction process. Oil trapped in SBC was extracted using conventional Soxhlet extraction. A sample of about 10 g was placed into the thimble and covered by gauze at the top of the sample layer. Hexane solvent was placed in a round-bottomed flask. Extraction was carried out for 8 hr. The solvent was evaporated and separated by a rotary vacuum evaporator. The deoiled SBC sample was then regenerated by heat treatment. The heat treatment process is discussed in the following section.

Regeneration by Direct Heat Treatment

In this experiment, SBC and deoiled SBC were directly regenerated at a temperature ranging from 400°C to 1000°C for 1 hr. Two grams of SBC sample were heated in a box furnace. The product after heat treatment was then cooled down to ambient temperature before removal from the furnace for further analysis. The regenerated SBC was applied in the refining process, and subjected to SCOPA's bleachability test to determine its performance.

Determination of Physical Properties of Bleaching Clay

Specific surface area, total pore volume and pore size distribution of the samples of fresh bleaching clay and regenerated SBC were determined by measuring their nitrogen adsorption-desorption isotherms at -196°C in an Accelerated and Porosimetry System (ASAP 2010, Micromeritics USA). Brunauer-Emmet-Teller (BET) surface area,

TABLE 2. METHODS AND CORRESPONDING RELATIVE PRESSURE RANGES IN THE DETERMINATION OF POROSITY PARAMETERS

Method	Parameter	Relative pressure range (mesopore analysis)
Brunnauer-Emmet-Teller (BET)	Specific surface area	0.1-0.3
Barret-Joyner-Halenda (BJH)	Mesopore volume	0.05-0.99 (adsorption)
	Mesopore size distribution	0.99-0.05 (desorption)
	Total pore volume	≈0.995

S_{BET}, was calculated using the adsorption data in a relative pressure ranging from 0.05 to 0.20 (Gregg and Sing, 1982). The total pore volume, V_T, was assessed by converting the amount of nitrogen gas adsorbed (expressed in cm^3 g^{-1} at STP) at a relative pressure ≈ 0.97 to the volume of the liquid adsorbate.

Pore size distribution was calculated based on the desorption branch of the hysteresis loop by the Barret-Joyner-Halenda (BJH) model (Gregg and Sing, 1982). The BJH model is based on the Kelvin equation, which relates to the size of pores where capillary condensation takes place (Sing *et al.*, 1985). *Table 2* shows the method used in deriving the porosity parameters in mesoporous material and the relative pressure range selected (Mak, 2003) for data acquisition. The analytical method consisted of three steps, *i.e.* dehydration of samples, degassing of samples under low vacuum pressure and nitrogen gas adsorption at -196°C. In the physisorption, the porous materials can be classified according to the pore widths of the materials. A microporous material has pores of width < 20 Å, a mesoporous material has pore widths in the range 20-500 Å, while a macroporous material has pore widths > 500 Å (Sing *et al.*, 1985).

Laboratory Physical Refining of Oil for Bleachability Test

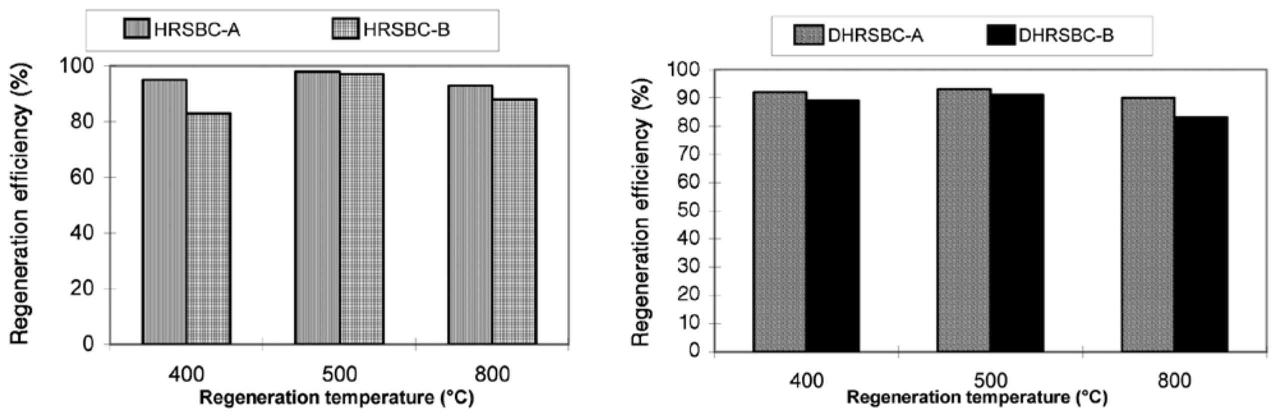
Samples of oil were refined according to the method by SCOPA. Colour is an important quality of refined oil and was used here to determine the regeneration efficiency of SBC. The regeneration efficiency was calculated as:

$$\textit{Regeneration efficiency}\ (\%) = \frac{(R_o - R_r)}{(R_o - R_f)} \times 100\%$$

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

RESULTS AND DISCUSSION

The heat regeneration process was conducted at temperatures of 400°C, 500°C and 800°C. *Figure 1* shows the regeneration efficiency of HRSBC and DHRSBC of acid-activated clay (Sample A) and natural bleaching clay (Sample B) prepared at different temperatures. Generally, the acid-activated bleaching clay was a more efficient adsorbent in physical refining. HRSBC of Sample A had a higher



A = acid activated clay B = natural clay

Figure 1. Regeneration efficiency of heated-regenerated spent bleaching clay (HRSBC) and deoiled-heated-regenerated spent bleaching earth (DHRSBC) of Samples A and B as a function of regeneration temperature.

regeneration efficiency than the HRSBC of Sample B. In general, both acid-activated and natural HRSBC achieved their highest regeneration efficiency at 500°C, *i.e*. 98% for HRSBC-A and 97% for HRSBC-B. However, the regeneration efficiency did not differ much for samples prepared under different temperatures of regeneration, *i.e*. DHRSBC-A and DHRSBC-B. Treatment at a temperature of 800°C decreased the regeneration efficiency slightly.

The colour of refined palm oil using HRSBC regenerated at different temperatures is shown in *Table 3*. The colour of refined oil demonstrates the linkage with regeneration efficiency of HRSBC.

All HRSBC of Sample A, except A800, were able to reduce the colour below 3 R with a bleaching clay dosage of 1%. The colour removal properties of HRSBC of Sample A at 800°C were less efficient compared to those regenerated at 400°C and 500°C. However, HRSBC of Sample A at 500°C was the best regenerated clay, resulting in a refined palm oil colour of 2.3 R. Sintering of HRSBC structures at a regeneration temperature higher than 500°C is thought to be the factor for the decrease in the regeneration efficiency and the quality of refined palm oil (Hu *et al*., 2001).

As expected, the natural HRSBC of Sample B hardly removed any colour pigments from the oil. The fresh Sample B gave a significantly higher Lovibond colour, *i.e*. 4.5 R. This showed that as regeneration temperature increased from 500°C to 800°C, the value of the red colour index of the refined oil increased as well.

HRSBC of Sample B at the optimum temperature of 500°C achieved a regeneration efficiency of more than 90% with reference to the fresh Sample B. Generally, acid-activated bleaching clays such as Sample A are more effective in removing the colour components than natural bleaching clays such as Sample B (Cheah, 2004).

TABLE 3. MEAN COLOUR OF BLEACHED CRUDE PALM OIL (CPO) USING HEATED-REGENERATED SPENT BLEACHING CLAY (HRSBC)

Bleaching clay	Colour (R,Y)
Fresh Sample A	1.9, 40
HRSBC-A400	2.9, 25
HRSBC-A500	2.3, 30
HRSBC-A800	3.4, 34
Fresh Sample B	4.5, 57
HRSBC-B400	6.9, 79.9
HRSBC-B500	5.1, 61
HRSBC-B800	7.9, 79

Note: Colour of unbleached CPO = 23 R 20Y.
Bleaching clay dosage = 1%.

TABLE 4. MEAN COLOUR OF BLEACHED CRUDE PALM OIL (CPO) USING DEOILED-HEATED-REGENERATED SPENT BLEACHING EARTH (DHRSBC)

Bleaching clay	Colour (R,Y)
DHRSBC-A400	4.1, 45.1
DHRSBC-A500	4, 36
DHRSBC-A800	4.5, 42.1
DHRSBC-B400	4.7, 43
DHRSBC-B500	4.4, 46
DHRSBC-B800	5.9, 60.2

Note: Colour of unbleached CPO = 23 R 20Y.
Bleaching clay dosage = 1%.

The colour quality of CPO after bleaching using DHRSBC is shown in *Table 4*. It was observed that as the surface area in DHRSBC-A and DHRSBC-B decreased, the red colour of the refined palm oil increased concurrent with the increase in the regeneration temperature. This implied that DHRSBC, which was obtained from heat treatment at 500°C, had almost all of the residual oil and impurities removed out of the SBC structure. Thus, the DHRSBC with the highest surface area had a higher bleaching capability, as was evident from the lower red colour index after the bleaching process. Meanwhile, a regeneration temperature of 500°C induced some sintering of DHRSBC which resulted in a lower capability in the bleaching process. As shown by Hou *et al*. (2000), regenerated SBC with a higher surface area gave a higher regeneration efficiency, which was 98% at 600°C. However, the regeneration efficiency decreased with further heating.

Relationship between Physical Properties and Regeneration Efficiency

The relationship between the physical properties of HRSBC and its bleaching performance on crude oil was evaluated. Fresh Samples A and B were used as reference. *Table 5* lists the physical properties of fresh bleaching clay. *Table 6* presents the relationship between regeneration efficiency and the physical properties of HRSBC. The HRSBC produced at different temperatures presented slight differences in physical properties, in terms of specific surface area and total pore volume. The specific surface area of HRSBC at a temperature of 500°C for Sample A was higher than the fresh bleaching clay by about 107%. However, the specific surface area and total pore volume of HRSBC from Samples A and B decreased dramatically at a temperature of 800°C.

The specific surface area of HRSBC of Sample B was lower than that of HRSBC of Sample A. The

TABLE 5. PHYSICAL PROPERTIES OF FRESH BLEACHING CLAY

Bleaching clay	Specific surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Average pore size (Å)
Fresh Sample A	193	0.33	68.5
Fresh Sample B	112	0.24	86.2

TABLE 6. PHYSICAL PROPERTIES OF FRESH AND HEATED-REGENERATED SPENT BLEACHING CLAY (HRSBC) ACID AND NATURAL BLEACHING CLAY

Bleaching clay	Physical properties			Regeneration efficiency (%)
	Specific surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Average pore size (Å)	
Fresh Sample A	193	0.33	68.5	-
HRSBC-A400	186	0.31	61	95
HRSBC-A500	206	0.33	70	98
HRSBC-A800	72	0.20	110	93
Fresh Sample B	112	0.24	86.2	-
HRSBC-B400	53	0.21	136.3	88
HRSBC-B500	62	0.20	154.4	97
HRSBC-B800	3	0.01	127.3	83

specific surface area and total pore volume of all the HRSBC (except for HRSBC of Sample A at 500°C) were lower than those of the fresh bleaching clay. The specific surface area and total pore volume of both HRSBC were maximum at the regeneration temperature of 500°C. The lowest specific surface area and total pore volume were obtained in HRSBC of Samples A and B regenerated by the highest temperature of 800°C.

Heat treatment with increasing temperatures in HRSBC caused the decrease in specific surface area as a consequence of pore collapse and damage in the structure. It can be seen that the optimal regeneration temperature was 500°C for both acid-activated and natural bleaching clays.

The Lovibond Red colour was lowest at 2.3 R and 5.1 R for HRSBC of Samples A and B, respectively (*Table 3*), while having the highest specific surface area. An interesting result observed here is that although the specific surface area of regenerated SBC reduced drastically at high temperature, the regeneration efficiency still achieved more than 80%. This suggests that specific surface area may not have been the only factor that affected the regeneration efficiency of SBC. It was observed that as specific surface area decreased, average pore size increased.

As the cross-sectional dimensions of monomeric carotene pigments in the palm oil are about 7×31Å (Taylor *et al.*, 1989), an increase in average pore size may facilitate the entrance of the carotene molecules to the active site. This helps to explain the rather high regeneration efficiency of HRSBC-B800 even when its specific surface area was only about 5% of its fresh sample.

The physical properties of DHRSBC-A and DHRSBC-B at different regeneration temperatures are shown in *Table 7*. The results show that DHRSBC-A500 and DHRSBC-B500 achieved the highest regeneration efficiency, *i.e.* 93% and 91%, respectively. Specific surface area, total pore volume and regeneration efficiency were maximum at the regeneration temperature of 500°C. The specific surface area of the regenerated SBC increased initially as more adsorbed water and residual vegetable oil were driven off as the regeneration temperature increased. The structure of the bleaching clay may collapse at high temperature as suggested by Wang and Lin (2000) in a study on heat regeneration of SBC (over 300°C-650°C).

According to the results above, the specific surface area of regenerated SBC decreased at high temperature thus reducing the regeneration efficiency for adsorbing colour pigments and impurities in the crude palm oil. The highest total pore volume of DHRSBC-A and DHRSBC-B at 0.15 cm^3 g^{-1} and 0.18 cm^3 g^{-1}, respectively, was attained at 500°C. Higher regeneration temperature leads to a collapse of some of the bleaching clay structure (Seng *et al.*, 2001).

TABLE 7. PHYSICAL PROPERTIES OF DEOILED-HEATED-REGENERATED SPENT BLEACHING EARTH (DHRSBC)-A AND DHRSBC-B

Bleaching clay	Physical properties			Regeneration efficiency (%)
	Specific surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Average pore size (Å)	
DHRSBC-A400	19	0.07	173	92
DHRSBC- A500	21	0.15	160	93
DHRSBC- A800	11	0.05	200	90
DHRSBC- A1000	3	0.01	201	88
DHRSBC-B400	21	0.08	149	89
DHRSBC- B500	36	0.18	151	91
DHRSBC- B800	17	0.09	199	83
DHRSBC- B1000	3	0.02	203	82

CONCLUSION

Two regeneration methods were carried out, *i.e.* (a) SBC pre-treated by solvent extraction followed by heat treatment; (b) SBC directly regenerated by heat treatment. Experimental results indicate that regeneration by direct heat treatment was more efficient than solvent extraction followed by heat treatment.

Generally, specific surface area and total pore volume of DHRSBC, which was produced from the solvent extraction and heat regeneration process, were lower than those of HRSBC. It can be concluded that the impurities present in CPO were still retained in the pores of the spent bleaching clay after deoiling of SBC. The regeneration efficiency of heat-treated SBC was dependent on the temperature of the regeneration process, which was found to be optimum at 500°C. Regeneration efficiency decreased at a temperature higher than 500°C. The physical properties of the regenerated SBC at the regeneration temperature of 500°C were better than regenerated SBC at 400°C and 800°C, and as compared to fresh clay.

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