Feature Article

Application of Regenerated Spent Bleaching Earth as Adsorbent for Treatment of Palm Oil Mill Effluent

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ABSTRACT

The aim of the present study is to evaluate adsorption capacity of regenerated spent bleaching earth, to decolourise and reduce the biological oxygen demand (BOD) of final discharged of palm oil mill effluent (POME). Different types of spent bleaching earth were used in this study; regenerated using acid and heat treatment after de-oiling (RDSBE-AH), spent bleaching earth (SBE), de-oiled spent bleaching earth (DSBE) and new bleaching earth (NBE). Prior to the study, samples were characterised for their surface area, pore volume and functional groups. RDSBE-AH was found to have the highest surface area and pore volume when compared to the other three types of clays with values of 122.3 $m^2 g^{-1}$ and 68 $cm^3 g^{-1}$, respectively. For the decolourisation of POME, RDSBE-AH exhibited higher efficiency than NBE. Higher BOD reduction efficiency was found for NBE as compared to RDSBE-AH. The results demonstrated that the regenerated SBE, activated using combined acid and heat treatments, capable to decolourise and reduce the BOD of the POME final discharge, to comply with the stringent new proposed limits by Department of Environment (DOE).

Keywords: adsorption; biological oxygen demand (BOD); decolourisation; palm oil mill effluent (POME); regenerated spent bleaching earth

INTRODUCTION

The bleaching process in palm oil refineries helps improve the appearance, flavour, taste and stability of the final palm oil products. Bleaching earth is the common adsorbent used in the bleaching process due to its relatively high adsorption performance for coloured materials and low purchasing cost. The bleaching process generates a large amount of solid waste commonly known as spent bleaching earth (SBE). The SBE normally contains 17% to 30% (w/w) of residual oil, metallic impurities and organic compounds that can cause environmental problems and

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increase the land-fill disposal costs (Cheah and Siew, 2004). Due to these problems, many researchers had attempted to improve the effectiveness of bleaching earth as well as to extract the residual oil and regenerate the SBE (Boukerroui and Ouali, 2000; Tsai *et al*., 2002; Mahramanlioglu *et al*., 2010).

Other than being reused for bleaching process, regenerated SBE offers potential application as an adsorbent in the treatment of palm oil mill effluent (POME). The average effluent production rate from a typical palm oil mill ranges from 65% to 70% of the fresh fruit bunches (FFB) processed. POME is an acidic, thick, brownish colloidal suspension containing 95%-96% of water, 0.6%-0.7% of oil and 4%-5% total solids including 2%-4% suspended solids (Ma, 1998). Recently, due to increasing environmental quality awareness and concern on river water quality, the Department of Environment (DOE) has decided to impose more stringent discharge limits on the effluents from the palm oil mills and other industries. Colour and biological oxygen demand (BOD) of wastewater are amongst the concerned parameters requiring compliance with the revised discharged limits. Wastewater discharged to the water courses such as streams, rivers or the sea with a high level of colouration not only provide undesirable appearance, but can also cause damage to marine lives. This is due to possible deprivation of sunlight to the aquatic species living in the water. This study aims to characterise and evaluate the adsorption capacity of bleaching earths (new bleaching earth (NBE), de-oiled spent bleaching earth (DSBE) and regenerated de-oiled SBE) for polishing treatment of POME.

MATERIALS AND METHODS

Materials

NBE and SBE used in this study were obtained from a palm oil refinery. POME discharge was collected from a palm oil mill. The residual oil in the SBE was removed by Soxhlet extraction method using hexane as solvent. The DSBE was later regenerated by a combination of acid and heat treatment and was labelled as RDSBE-AH. The acid treatment was carried out by impregnating the DSBE with 20 wt% H_2SO_4 (1 M) and stirred for 5 hours at 200 rpm. The treated DSBE was then washed with distilled water, dried in an oven followed by heating in furnace (Naberthem M-7/H) at 500°C for 2 hours.

Adsorption Experiments

The adsorption studies were performed by batch stirring technique where the bleaching earth was mixed and stirred at the studied conditions. The adsorption experiments were carried out using 200 ml of final discharge of POME. The effect of the dosage of the bleaching earth on the colour and BOD removal was performed by varying the dosage ratio between 5% (wt/vol) and 25% (wt/vol). The contact time and pH for both tests on colour and BOD were maintained at 4 hours and pH 8, respectively. In order to study the effect of pH on the adsorption, trials were carried out using various values of pH ranging from 2 to 10. Adjustment of pH was carried out by using standard alkali (0.1 M NaOH) and acid (0.1 M HCl). The clay dosage and contact time for studies on colour and BOD removal were kept constant at 5% and 4 hours, respectively.

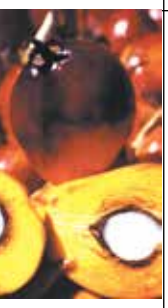
The adsorption percentage (R), was determined as the final removal percentage relative to the initial value of the component, calculated using the following equation:

$$R = \frac{(C_0 - C_e)}{C_0} \times 100\% \qquad (1)$$

where R is the adsorption percentage of components (%), C_o is the initial value of components (mg litre^{-1} for BOD and Pt-Co for colour) and C_e is the final value of components (mg litre^{-1} for BOD and Pt-Co for colour).

Characterisation and Analysis

The surface area and pore volume of the samples were determined by nitrogen gas adsorption at 77K by using a surface area



analyser (Quantachrome Autosorb AS:Qwin Version 3.01, USA). The functional groups of different bleaching earth samples in the range of 4000 – 650 cm^{-1} were carried out with a Fourier transform infra-red (FTIR) spectrometer (Frontier, Perkin Elmer, USA).

The treated POME was analysed for BOD and colour. The colour and BOD concentration were measured by a HACH DR 6000 (Germany) apparatus. All chemicals used in this study were of analytical grade. All analysis were carried out in triplicate and the average values were taken.

RESULTS AND DISCUSSION

Characterisation

An adsorption process depends on the surface area, pore sizes distribution and surface chemistry of the adsorbents (Angin *et al*., 2013). As shown in *Table 1*, the surface area of SBE was substantially reduced from 119.7 $m^2 g^{-1}$ of NBE to 19.4 $m^2 g^{-1}$ and the pore volume was also significantly reduced from 0.0552 $cm^3 g^{-1}$ of NBE to 0.0002 $cm^3 g^{-1}$. The reduction in surface area and pore volume of SBE indicates that the porosity of NBE has been changed after being used in the oil refining process. The removal of residual oil from SBE with hexane (DSBE) has shown slightly increased the surface area and pore volume at 31.2 $m^2 g^{-1}$ and 0.0139 $cm^3 g^{-1}$, respectively. The high increase in the surface area (122.3 $m^2 g^{-1}$) and pore volume (0.0568 $cm^3 g^{-1}$) of RDSBE-AH were possibly due to the acid reaction with the bleaching earth surface and heating temperature which caused the dissolution of retained impurities, thus influencing the surface properties of the adsorbent. Similar effects were observed by other researchers when clays were regenerated with sulphuric acid at high temperature (Noyan *et al*., 2007; Sutcu and Demiral, 2009; Azargohar and Dalai, 2008; Sudaryanto *et al*., 2006). These results also indicate that the micropores would have possibly been regenerated due to the removal of some of the retained substances (acid washed).

TABLE 1. SURFACE AREA AND PORE VOLUME

Sample	Surface Area ($m^2 g^{-1}$)	Pore Volume ($cm^3 g^{-1}$)
NBE	119.7	0.0552
SBE	19.4	0.0002
DSBE	31.2	0.0139
RDSBE-AH	122.3	0.0568

As shown in *Figure 1*, the patterns of the FTIR spectra of NBE, SBE, DSBE and RDSBE-AH are quite similar. All types of bleaching earths exhibited band in the FTIR spectra at 3350–3550 cm^{-1} which indicates the presence of stretching vibrations of O-H of carboxylic acids. The presence of Si-O stretching was observed for all bleaching earths as shown by the band near 980 cm^{-1} - 1010 cm^{-1} (Meziti and Boukerroui, 2011). As compared to other bleaching earths, SBE exhibits additional bands at 2850 cm^{-1} and 2930 cm^{-1} which indicates the presence of

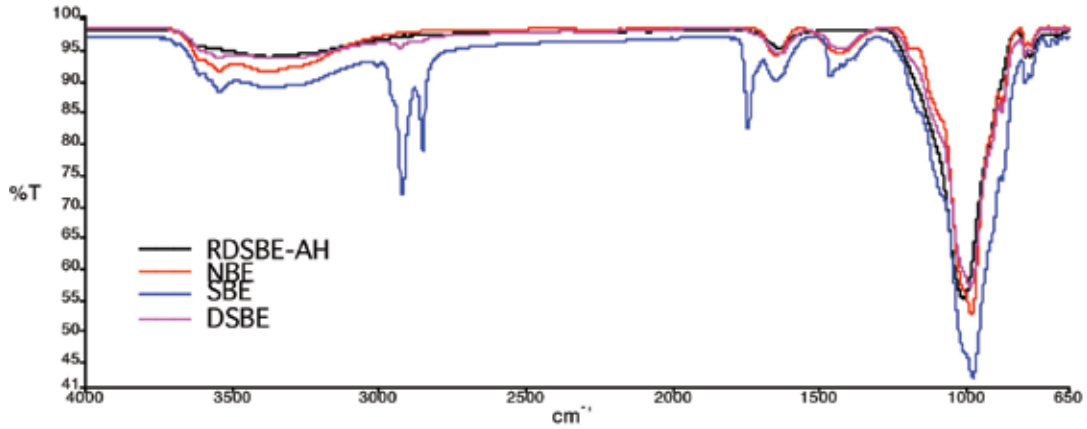


Figure 1. FTIR of various types of clays.

stretching vibration of C–H of carbonaceous chains of oil and the free fatty acids. These bands correspond to the characteristic of residual oil. Another band at 1730 cm^{-1} was also observed for SBE indicating the presence of strong stretching vibration of ester carbonyl of residual oil. After residual oil was removed from SBE, these bands were no longer in existence as indicated in the spectrum of DSBE and RDSBE-AH which suggest that the de-oiling and regeneration processes had eliminated the oil residue adsorbed in the pores of SBE.

Adsorption Study

Effects of adsorbent

A *Figure 2* shows the visual observation on the colour changes from raw POME final discharge to treated final effluent discharge when using different types of bleaching earths. The colours of final effluent discharge treated with NBE and RDSBE-AH were found to be higher than the colour of final effluent discharge treated with SBE and DSBE. The colour that caused pollution is normally due to the presence of organic matter such as synthetic chemical dyes, algae species and natural dissolved organics such as lignin and tannins (www.arviatechnology.com/applications). The decolourisation efficiency of RDSBE-AH is higher at 68.3% as compared to NBE at 51.0% (*Table 2*). SBE shows very low decolourisation efficiency as compared to the other three samples. Differences in the adsorption efficiency were possibly due to the variation in surface area, pore volume and functional groups as presented in *Table 1* and *Figure 1*. The highest to lowest order for the colour removal capacity of the bleaching earths are as follows; RDSBE-AH (68.3%) > NBE (51.0%) > DSBE (24.9%) > SBE (18.8%). The largest specific surface area of RDSBE-AH possibly resulted in the highest colour removal among the clays studied.

The percentages of BOD removal when using various types of clays (NBE, SBE, DSBE and RDSBE-AH) are presented in *Table 2*. The percentage of BOD removal for RDSBE-AH was slightly lower than the NBE with values of 46.4% and 53.0%, respectively. SBE exhibited the lowest value at 2.8% indicating possibly the surface was no longer active and the pores could possibly have been blocked by other components. The slightly higher BOD reduction of DSBE at 13.6% suggesting that removal of residual oil from SBE provides more open pores. On comparing the amounts of BOD adsorbed among the four clays, the following order was found: NBE (53.0%) > RDSBE-AH (46.4%) > DSBE (13.6%) > SBE (2.8%). The results are agreeable with what has been reported by Mudoga *et al*. (2008) that textural and surface properties are related to the ability of an adsorbent to adsorb organic substances. As illustrated in *Table 2*, SBE and DSBE showed very poor performance in terms of the decolourisation efficiency and BOD removal from the palm oil final effluent discharge. Thus, clays of NBE and RDSBE-Ah were selected for conducting subsequent adsorption experiments.

TABLE 2. TYPES ADSORBENTS

	Adsorption Percentage (R, %)	
	Colour	BOD
NBE	51.0	53.0
SBE	18.8	2.8
DSBE	24.9	13.6
RDSBE-AH	68.3	46.4

Effect of clay dosage

A *Figure 3* presents the influence of clay dosage on colour removal using NBE and RDSBE-AH. It was observed that at 5% dosage of RDSBE-AH, the colour removal was at 69.3%, which was higher than NBE at 5% dosage with those of 40.1%. It was found that gradual increase in the percentage of colour reduction from 69.3% to 92.2% was achieved when the dosage of the RDSBE-AH increased from 5% to 25%, respectively. These results suggesting that the increased in dosage would increase the amount of adsorbent particles which then led to higher available sites binding for adsorption (Wang *et al*., 2010; Angın *et al*., 2013**).** Noorimotlagh

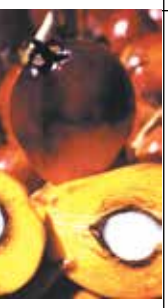


Figure 2. Colour effluent.

et al., (2014) reported a similar trend when conducting research on the use of activated carbon for the adsorption of a textile dye. The highest reduction in RDSBE-AH was observed after treatment with 25% dosage. It is clear that 25% RDSBE dosage produced the highest reduction in colour as compared to NBE when the same amount of clay was used. As for NBE, a 25% dosage resulted in a reduction in colour at 69.2%.

The effect of bleaching earth dosages on the adsorption percentage of BOD of POME discharge is presented in *Figure 4*. It was observed that increasing the dosage of NBE from 5% to 25% gradually increase the percentage BOD removal from 33.0% to 41.3%, respectively. RDSBE-AH also showed an increase in BOD percentage removal from 15.5% to 37.2% when bleaching earth dosage was increased from 5 to 25%, respectively. Similar results were obtained for decolourisation and BOD removal where an increased in adsorbent dosage led to an increase in reduction as observed by other researchers (Kheok and Lim, 1982; Nnadozie *et al.*, 1989).

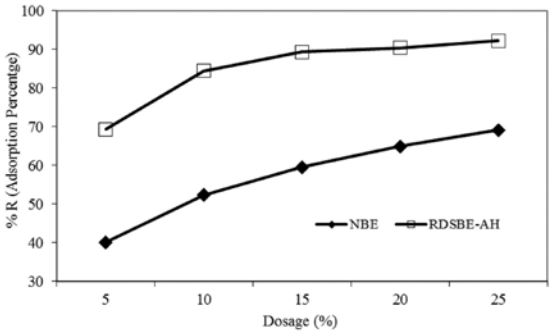


Figure 3. Effect dosage on colour.

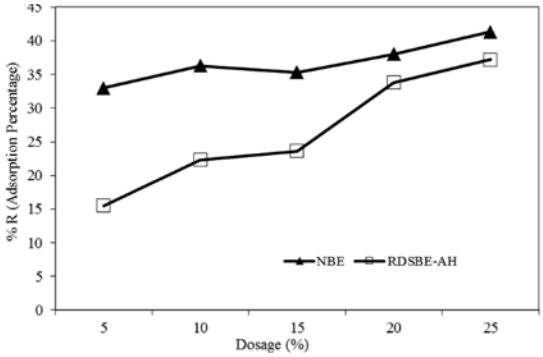


Figure 4. Effect dosage on biological oxygen demand (BOD).

Effect of pH

One of the important parameters influencing the adsorption of different target pollutants is pH of the solution as it affects the surface properties and binding sites of adsorbents (Lin *et al.*, 2013**).** *Figure 5* shows the variation in the colour adsorption of NBE and RDSBE-AH over a wide pH range from low acidic to high alkaline. It was observed that the colour removal in palm oil mill final effluent discharge treated with RDSBE-AH decreased from 94.2% to 49.7% when the pH of the solution was raised from 2 to 10, respectively. Similar trend was observed for POME discharge treated with NBE where the percentage of colour reduction decreased from 53.4% to 22.5% when the pH was raised from 2 to 10, respectively. Decolourisation seems to be effective when solution was in the acidic condition. Results obtained from *Figure 5* showed that RDSBE-AH was more effective in reducing the colour of palm oil mill final discharge than NBE. The differences in the properties of NBE and RDSBE-AH as indicated in *Table 1* could have resulted in the different activity for colour reducing. The

decline of solute adsorption with increase in pH has also been observed by other researchers (Noorimotlagh *et al*., 2014).

In contrast, *Figure 6* demonstrates an increase in BOD removal efficiency with the increase of pH. Result for RDSBE-AH showed that the BOD percentage removal increased from 12.8% to 46.7% when the pH increased from 2 to 10, respectively. Similar behaviour was observed for NBE where increasing pH from 2 to 10 caused an increase in the BOD percentage removal from 28.6% to 41.3%, respectively. These results suggesting that the repulsion force between the solute molecules and adsorbent was strong which could probably lead to low adsorption removal. Studies by other researchers had shown similar trend where the adsorption removal of methylene blue using activated carbon increased with an increase in pH (Gaedi *et al*., 2014; Kunwar *et al*., 2003).

It was observed from *Figures 5* and *6* that a different pH value for the same solution gave different effects on removal of colour and BOD. The percentage of colour reduction was reduced in between 61% and 59% at moderate pH values of around 6 to 8 treated with RDSBE-AH was used. The BOD reduction was between 27% to 49% when RDSBE-AH with same range of pH (6-8) was used. These results suggested that pH close to 6 to 8 could be used for the adsorption process as it was reported that the normal pH range for irrigation is from 6.5 to 8.4 (www.fao.org/docrep/t0551e03.htm). From the results obtained, it is suggested to use pH 7 for the operation at field, which can reduce both colour and BOD quite effectively.

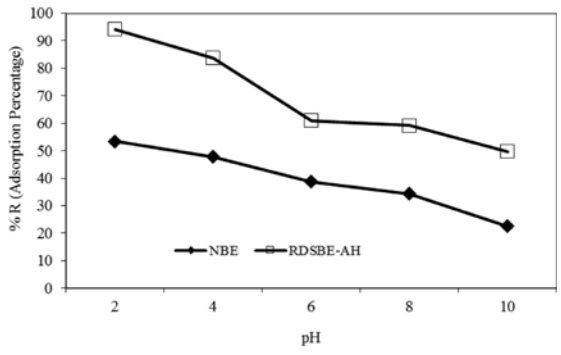


Figure 5. Effect of pH on colour.

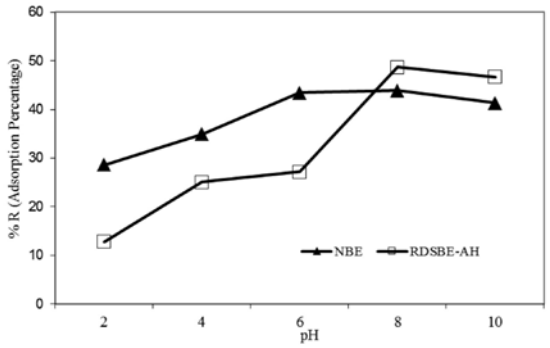


Figure 6. Effect of pH on biological oxygen demand (BOD).

CONCLUSION

SBE regenerated by the impregnation with H_2SO_4 solution followed by heat treatment exhibits a very promising performance in the decolourisation and BOD removal from POME discharge. Regeneration of SBE by acid and heat treatment has cleared the pores of the spent bleaching earth thereby increasing its surface area and pore volume, thus allowing more components/pollutants to be adsorbed.

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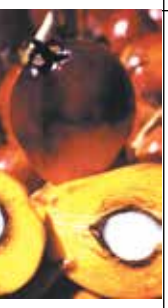
REFERENCES

Angin, D; Köse, T E and Selengil, U (2013). Production and characterization of activated carbon prepared from safflower seed cake biochar and its ability to absorb reactive dyestuff. *Applied Surface Science*, *280*: 705-10.

Azargohar, R and Dalai, A K (2008). Steam and KOH activation of biochar: Experimental and modeling studies. *Microporous and Mesoporous Materials*, *110*: 413-421.

Boukerroui, A and Ouali, M S (2000). Regeneration of a spent bleaching earth and its reuse in the refining of an edible oil. *J. Chem. Technol. Biotechnol*. *75*: 773-776.



Cheah, K Y and Siew, W L (2004). Regeneration of spent bleaching clay. *MPOB Information Series* 230.

Ghaedi, M; Golestani Nasab, A; Khodadoust, S; Rajabi, M and Azizian, S (2014). Application of activated carbon as adsorbents for efficient removal of methylene blue: Kinetics and equilibrium study. *J. Industrial and Engineering Chemistry*, *20*: 2317–2324.

Kheok, S and Lim, E (1982). Mechanism of palm oil bleaching by montmorillonite clay activated at various acid concentrations. *J. Amer. Oil Chem. Soc*, *59* :129-131.

Kunwar, P S; Dinesh, M; Sarita, S; Tondon, G S and Devlina, G (2003). Color Removal from Wastewater Using Low-Cost Activated Carbon Derived from Agricultural Waste Material. *Ind. Eng. Chem. Res, 42* :1965-1976.

Lin L; Zhai, S R; Xiao, Z Y; Song, Y; An, Q D and Song, X W (2013). Dye adsorption of mesoporous activated carbons produced from NaOH-pretreated rice husks. *Bioresource Technol*ogy *136* :437–443.

Ma, A N (1998). Environmental management for the palm oil industry. Paper presented at 'Seminar Mesra Alam Kilang Sawit', 12 October 1998, Lahat Datu, Sabah.

Mahramanlioglu, M; Ozgen, O; Cinarli, A and Kizilcikli, I (2010). Adsorption of pyridine by acid treated spent bleaching earth. *Asian J. Chem*, *22 (2)* :1428-1434.

Meziti, C and Boukerroui, A (2011). Regeneration of a solid waste from an edible oil refinery. *Ceramics International*, *37* :1953-1957.

Mudoga, H L; Yucel, H and Kincal N S (2008). Decolourisation of sugar syrups using commercial and sugar beet pulp based activated carbons. *Bioresource Technol*. *99* :3528-3533.

Nnadozie, N; Arowolo, T and Akpan, H (1989). Quality of Nigerian palm oil after bleaching with local treated clays. *J. Amer. Oil Chem. Soc*, *66* :218-222.

Noorimotlagh, Z; Darvishi Cheshmeh Soltani, R; Khataee, A R; Shahriyar, S and Nourmoradi, H (2014). Adsorption of a textile dye in aqueous phase using mesoporous activated carbon prepared from Iranian milk vetch. *J. the Taiwan Institute of Chemical Engineers*, *45* :1783-1791.

Noyan, H; Userref, O and Yuksel, S (2007). The effect of sulphuric acid activation on the crystallinity, surface area, porosity, and bleaching power of a bentonite. *Food Chem*, *105* :156-163.

Sudaryanto, Y; Hartono, S B; Irawaty, W; Hindarso, H and Ismadji, S (2006). High surface area activated carbon prepared from cassava peel by chemical activation. *Bioresource Technol*, *97* :734-739.

Sütcü, H and Demiral, H (2009). Production of granular activated carbons from loquat stones by chemical activation. *J. Analytical and Applied Pyrolysis*, *84* :47-52.

Tsai, W T; Chen, H P; Hsieh, M F; Sun, H F and Chien, S F (2002). Regeneration of spent bleaching earth by pyrolysis in a rotary furnace. *J. Analytical and Applied Pyrolysis*, *63* :157-170.

Wang, L; Zhang, J; Zhao, R; Li, C; Li, Y and Zhang, C (2010). Adsorption of basic dyes on activated carbon prepared from *Polygonum orientale* Linn: Equilibrium, kinetic and thermodynamic studies. *Desalination*. *254* :68-74.

Waste water characteristics and effluent quality parameters. www.fao.org/docrep/t0551e03.htm.

Waste water colour removal. www.arviatechnology.com/applications/wastewater-colour-removal.