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NUTRIENT RECOVERY FROM ANAEROBIC PALM OIL MILL EFFLUENT WITH THERMALLY REGENERATED SPENT BLEACHING EARTH USING RESPONSE SURFACE METHODOLOGY

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ABSTRACT

Palm oil mill effluent (POME) and thermally oxidised de-oiled spent bleaching earth (TDSBE) are reusable by-products. This study examined recovery of plant nutrients and biodegradable matter from anaerobically-treated POME using TDSBE. Response surface methodology was used for designing the jar test experiment and optimising the nutrient and colour recovery as a function of TDSBE dosage and mixing time. Phosphorus (P) and ammonia (NH_3) were determined colorimetrically while P, copper (Cu), zinc (Zn), manganese (Mn) and iron (Fe) by atomic absorption spectroscopy. Original, spent, de-oiled (DSBE) and TDSBE were subjected to cation exchange capacity (CEC), Fourier transform infrared-attenuated total reflectance (FTIR-ATR) and Brunauer-Emmett-Teller (BET) (N_2) analysis to determine their adsorption-relevant characteristics. TDSBE (50 g litre^{-1}, 120 min) could recover 3.7% NH_3, 80% P, 7.3% Zn, 30% Mn and 13.6% Fe from POME, but none for colour. Dosage and mixing time had a significant effect on recovery of all five nutrients ($p < 0.0.5$) with interaction occurring only for NH_3 and Zn. Relatively poor performance of TDSBE was due to lack of functional groups, low CEC and BET surface area. However, the recovery of plant nutrients from POME using industrial by-products such as original or modified DSBE is of great importance towards a circular oil palm industry and opens up new avenues for future research.

Keywords: bleaching earth, adsorption, anaerobic treatment, palm oil mill effluent, nutrient recovery.

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INTRODUCTION

The Malaysian palm oil industry has increasingly embraced cleaner technologies to move towards sustainable development (Kushairi *et al*., 2017). However, oil palm plantations still rely primarily on inorganic plant fertilisers consisting of nitrogen (N), phosphorus (P) and potassium (K). Dependency on mineral-based inorganic fertilisers is a drawback since they need to be imported, are not renewable (Teo *et al*., 2010), and causes nutrient runoffs during rainfall that eventually pollutes nearby water resources (Timilsena *et al*., 2015). The usage of inorganic fertilisers is also reported to reduce the quality of fruits produced (Montagu and Goh, 1990). Organic fertilisers, on the other hand, are made from renewable animal or plant-based materials such as manures and dead plant residues. Substituting inorganic- with organic-based fertiliser featuring slow nutrient release is essential which does not only reduce the reliance on imported fertilisers but also minimises excessive nutrient leaching into ground and surface waters.

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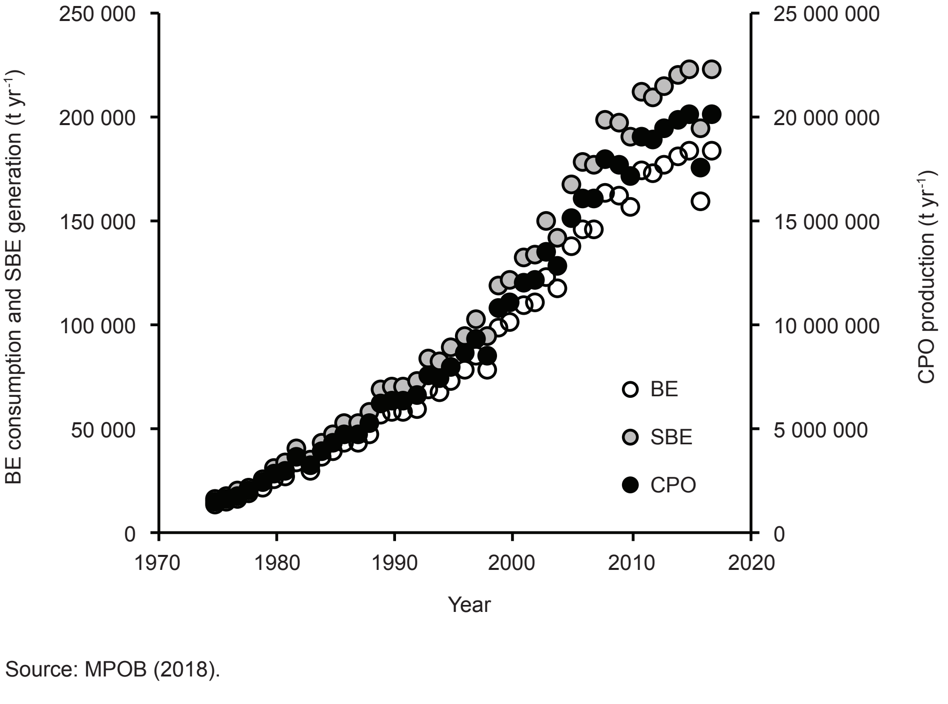
Palm oil milling by-products such as empty fruit bunches (EFB), mesocarp fibre, palm kernel shell (PKS) and palm oil mill effluent (POME) contain valuable macro- and micronutrients (Hadiyanto *et al*., 2012) that should be returned to plantations to substitute inorganic fertilisers (Awalludin *et al*., 2015). However, besides the traditional anaerobic open pond digestion of POME, other treatment practices at mills for effluent standards compliance mainly focus on evaporation (Patel, 2015; Kandiah and Batumalai, 2013), membrane filtration (Liew *et al*., 2015; Tabassum *et al*., 2015; Loh *et al*., 2013a) and physico-chemical treatment (Ahmad *et al*., 2015; Wu *et al*., 2010). For example, Takriff *et al*. (2016) proposed a physico-chemical treatment by combining coagulation and adsorption using rice starch and PKS biochar to reduce suspended solids (SS), chemical oxygen demand (COD) and turbidity of POME. The authors found that optimum dosage for rice starch was 2.5 g litre^{-1}, with 30%-45% reduction of COD, SS and turbidity. POME treatment using PKS char at an optimum dosage of 25 g achieved 78.4%, 79.9% and 70.6% reduction of turbidity, COD and SS, respectively. A more sustainable approach however, is to consider the recovery of energy, for example, biogas trapping (Chin *et al*., 2013; Loh *et al*., 2013a) as well as macro- and micronutrients for use as fertiliser in plantations (Wu *et al*., 2009; Loh *et al*., 2013b).

POME nutrients recovery could be achieved by coagulation and adsorption using other generated materials such as spent clay. Clay is also known as bleaching earth (BE) and used in palm oil refineries for degumming and decolourisation of crude palm oil (CPO) (Abd Wafti *et al*., 2011a). From life cycle assessment studies, Tan *et al*. (2010) found that 1 t CPO requires 9.11 kg BE, producing approximately 11.1 kg spent bleaching earth (SBE) per tonne CPO. The 22% increase in weight can primarily be attributed to the sorption of CPO to the SBE. In Malaysia alone, 53 refineries (Kushairi *et al*., 2018) generated 221 000 t of SBE in 2017, the majority of which is de-oiled (DSBE) and either send for disposal, used as a component in organic fertiliser (Loh *et al*., 2013b) or thermally oxidised (TDSBE) for subsequent use in the cement industry. The CPO production statistics along with the estimated consumption of BE and generation of SBE are illustrated in *Figure 1*. The reuse of treated SBE has the advantage of not only potentially recovering nutrients but also returning the material back to plantations as a soil modifier loaded with nutrients. Abd Majid and Che Mat (2017) used different kinds of treated SBE to reduce the colour and biological oxygen demand (BOD) of POME and reported a 90% colour removal efficiency at a dosage of 250 g litre^{-1}. However, recovery of macro- and minor nutrients such as ammonia (NH_3), P, copper (Cu), zinc (Zn), manganese (Mn), iron (Fe) and K from anaerobically-treated POME using TDSBE has not been reported. The aim of this study was therefore to develop models to predict the effect of TDSBE dosage and mixing time on the recovery of these nutrients using response surface methodology (RSM).



Source: MPOB (2018).

Figure 1. Crude palm oil (CPO) production and estimated bleaching earth (BE) consumption and spent bleaching earth (SBE) generation for Malaysian palm oil refineries between 1975 and 2017.

METHODOLOGY

Sample Collection

POME was collected from an anaerobic open pond which receives the effluent of an anaerobic digester (AD) operated by Sime Darby East Oil Mill, Klang, Selangor, Malaysia. POME was stored in white HDPE plastic bottles that have stoppers and caps. The bottles were placed into an ice box to prevent organic matter degradation during transportation and subsequently stored in a freezer prior to analysis. BE and SBE were obtained from Sime Darby Jomalina, Carey Island, Selangor, while DSBE and TDSBE were provided by EcoOils Sdn Bhd, Nilai, Negeri Sembilan, Malaysia. EcoOil recovers the residual oil in SBE and produced DSBE with 4% remaining residual oil in it. TDSBE is the thermally treated DSBE at 1000°C, which is later collected by cement factories as additive in cement production.

Characterisation

POME sampled from AD was characterised using DOE reference method (DOE, 1995) for BOD, COD, pH, ammoniacal nitrogen (AN) and total Kjeldahl nitrogen (TKN). The K and trace elements (Cu, Zn, Mn and Fe) were determined using atomic absorption spectroscopy (AAS) (Perkin Elmer, AAnalyst 400). The P was determined by molybdenum blue method and analysed using a UV-Vis spectrophotometer (Loh *et al*., 2015). *Table 1* shows the characteristics of anaerobically-treated POME used in this study compared to POME collected from the outlet of an AD at Kilang Kelapa Sawit Labu, Sime Darby.

Infrared (IR) spectra were recorded with Fourier transform infrared-attenuated total reflectance (FTIR-ATR) (Perkin Elmer, Spectrum One) for functional group identification of BE, SBE, DSBE and TDSBE at a resolution of 4 cm^{-1} from 650 to 4000 cm^{-1}. Porous texture was observed using a scanning electron microscope (SEM) (Hitachi S-3400) with 1500X magnification, while elemental composition was measured by energy dispersive X-ray (EDX) spectroscopy (Bruker X-Flash 6/10, accelerating voltage = 5000V). The voltage was set at 20 keV, whilst the working distance was 10 mm and the dead time for X-ray acquisition was between 20% and 25%. The Brunauer-Emmett-Teller (BET) surface area of the samples was determined with N_2 gas sorption analysis at -196°C and a relative pressure from 0.05 to 0.2 in an Accelerated and Porosimetry System (ASAP 2010, Micromeritics USA). Prior to BET surface area analysis, samples were degassed for 2 hr at 200°C. The total pore volume was assessed by converting the amount of nitrogen gas adsorbed (expressed in cm^3 g^{-1} at STP) at a relative pressure of approximately 0.97 to the volume of the liquid adsorbate. 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. Cation exchange capacity (CEC) was determined using 1 M NH_4-acetate buffer at pH 7.0 (Loh *et al*., 2015).

TABLE 1. CHARACTERISTICS OF AN OUTLET ANAEROBICALLY-DIGESTED PALM OIL MILL EFFLUENT (POME) IN THIS STUDY COMPARED TO LITERATURE

POME characteristics	This study		Loh *et al*. (2013a)	
	Mean	SD	Mean	SD
pH	6.6	ND	7.4	1.55
COD	2 257	371	2 523	19
BOD	518	145	800	16
SS	1 567	200	2 200	68
AN	261	3.9	220	8
TKN	480	1.4	327	11
P	361	ND	ND	ND
K	28 356	12 360	1 380	2.5
Cu	6.15	0.00	0.23	0.01
Zn	1.82	0.32	0.5	0.03
Mn	4.56	0.04	0.9	ND
Fe	348	1.60	12	2.8

Note: All parameter units in mg $litre^{-1}$ or ppm except pH. SD - standard deviation. ND - not determined.
COD - chemical oxygen demand; BOD - biological oxygen demand; SS - suspended solids; AN - ammoniacal nitrogen; TKN - total Kjeldahl nitrogen.
P - phosphorus; K - potassium; Cu - copper; Zn - zinc; Mn - manganese; Fe - iron.

Analysis of Treated POME

Centrifugation (Hettich, Universal 32R) of POME after treatment with BE and TDSBE was done at 8000 rpm for 15 min to remove BE and TDSBE colloids before further analysis. Preservation of POME supernatant prior to nutrient analysis was carried out in accordance with EPA methods (1983). For K, Cu, Zn Mn and Fe analysis, POME was preserved using 1% nitric acid. A 1% sulphuric acid solution was used to preserve POME for P analysis. Samples were kept in a refrigerator at 4°C. All samples were analysed within a week of storage. The concentration of NH_3 was determined using HACH Salicylate Method 8155 (HACH, 2009). P was measured following the molybdenum blue method and analysed using a UV-Vis spectrophotometer (Loh *et al*., 2015). Samples for K, Cu, Zn, Mn and Fe were analysed using AAS (Perkin Elmer, Analyst 400) by means of the calibration method. Colour was measured with a HACH spectrophotometer (DR 6000) according to HACH ADMI weighted ordinate method 10048 (HACH, 1999). SS was determined based on APHA Method No. 2540D (APHA, 1998).

Preliminary Jar Test Experiments

Aliquots of 250 ml of POME were filled into 500 ml glass beakers to determine the effect of BE dosage, pH and mixing time on colour and turbidity reduction. Adjustment of pH of POME was done prior to experiments using 1 M H_2SO_4 or 1 M NaOH and a calibrated pH meter (Mettler Toledo, FiveEasy FE20). BE was used instead of TDSBE in order to serve as a reference point for comparison. The solution was stirred with a jar tester (VELP Scientifica, FP4) at 100 rpm. After 1 hr of settling time, the colour of supernatant was analysed. Based on the findings, the two most important factors were then chosen for the RSM experiment.

Experimental Design and Data Analysis

The statistical design of experiment and data analysis were carried out using Design Expert software (version 9.0.5) and the circumscribed central composite design (CCD). *Table 2* illustrates the 3^2 full factorial design for dosage and mixing time with further four experimental trials (run numbers 10-13) as replicates of the centre point. The original units of the factors, *i.e.* dosage (g litre^{-1}) and mixing time (min) were used. Mixing was done using the same set-up as described for preliminary jar test experiments, except the sorbent was changed to TDSBE. A negative control (NC) with POME only was included for 0.2, 0.5, 1.3, 2 and 2.3 hr mixing time (*Table 2*). This is to ensure that changes of studied parameters (*e.g.* NH_3, Cu, Zn) that might occur during mixing are considered. This was not taken into account by Abd Majid and Che Mat (2017) who used the initial concentration only to determine the reduction of BOD and colour. The solution was then left to settle for 1 hr followed by BOD analysis or centrifugation to obtain the supernatant. The results were transferred to the RSM software to establish the model for nutrient recovery. The recovery of each nutrient was determined using Equation (1):

$$\%\ \text{Nutrient recovery} = \frac{\text{NC - nutrient concentration after treatment}}{\text{NC}} \times 100\% \qquad \text{Equation (1)}$$

where NC represents nutrient concentration of the negative control.

RESULTS AND DISCUSSION

POME Composition

POME is a highly nutritious wastewater. *Table 1* compares the composition of POME in this experiment to Loh *et al.* (2013a). The N values measured as TKN and AN from both mills are very similar with a mean of 404 mg litre^{-1} and 241 mg litre^{-1}, respectively. N is an important element for plant growth. It is available as nitrate or ammonium ions and used by plants to biologically combine with carbon (C), hydrogen (H), oxygen (O) and sulphur (S) to synthesise amino acids, the building blocks of proteins (Uchida, 2000).

Apart from N, micronutrients such as Fe play an important role for the cultivation of oil palm (Tiemann *et al.*, 2018). However, Fe mean concentration reported by Loh *et al.* (2013a) was 30 times lower than in this study. Overall, micronutrient concentrations in this study were higher than those measured by Loh *et al.* (2013a). The difference observed could be due to open ponding treatment

TABLE 2. CENTRAL COMPOSITE DESIGN MATRIX AND EXPERIMENTAL RESPONSE OF COLOUR, NH_3, P, K, Cu, Zn, Mn AND Fe RECOVERY FROM ANAEROBICALLY-TREATED PALM OIL MILL EFFLUENT

Run No.	Variable		Nutrient recovery (%)							
	Dosage (g litre^{-1})	Mixing time (hr)	Colour	NH_3	P	K	Cu	Zn	Mn	Fe
1	12.5	0.5	-5.0	-7.3	25.7	9.8	-4.68	-86.3	-1.2	7.0
2	50	0.5	1.4	10.1	49.4	2.8	-18.7	12.5	21.8	18.6
3	12.5	2	-3.5	6.3	57.6	1.2	-86.6	-9.7	6.0	3.4
4	50	2	11.0	3.7	79.6	3.9	-48.4	7.3	29.8	13.6
5	4.7	1.3	2.8	2.1	8.75	2.9	-30.0	-12.2	-0.5	1.7
6	57.8	1.3	8.4	6.9	66.6	2.7	-25.1	3.3	25.9	19.1
7	31.3	0.2	2.6	3.5	39.2	0.2	-7.11	-42.5	11.7	26.1
8	31.3	2.3	2.5	7.9	56.0	3.8	-27.7	1.05	23.7	15.5
9	31.3	1.3	6.0	8.5	32.5	5.0	-5.2	-18.8	13.6	17.9
10	31.3	1.3	9.4	7.9	50.4	-1.2	14.5	-14.2	12.8	16.3
11	31.3	1.3	11.8	12.3	58.9	1.8	-10.0	8.8	16.5	12.0
12	31.3	1.3	0.7	6.9	39.6	4.5	-0.03	0.4	17.0	10.8
13	31.3	1.3	7.5	7.9	40.1	2.1	-23.0	-14.0	13.4	11.2

Note: NH_3 - ammonia; Cu - copper; P - phosphorus; Zn - zinc; K - potassium; Mn - manganese; Fe - iron.

with a hydraulic retention time in excess of 100 days as opposed to a closed AD treatment used by Sime Darby East Oil Mill. Furthermore, the pH of anaerobic POME used in this study was about one order of magnitude lower than reported by Loh *et al*. (2013a). An increase in pH from 6.6 to 7.4 can be expected to result in the formation of insoluble metal hydroxide complexes. However, the exact cause is not known and requires further investigation.

Preliminary Jar Test Experiments

BE dosages of 12.5, 25 and 50 g litre^{-1} were used to coagulate 250 ml of POME. The mixing time and pH were fixed at 2 hr and pH 7. Colour recovery from POME was proportional to BE dosage ($R^2 > 0.99$) (*Figure 2a*). In the pH trial, colour recovery decreased from 53% to 42% as pH increased from 3 to 7 (*Figure 2b*). The mixing time trial revealed that most colour was recovered within the first 120 min (*Figure 2c*).

The observed linear increase in colour recovery with BE dosage is correlated with the increase in available sorption sites. At a dosage of 50 g litre^{-1}, the colour recovery of 37% was slightly lower compared to that (40.1%) reported by Abd Majid and Che Mat (2017). One of the reasons could be that our experimental design had considered colour reduction over time occurring in the NC. Using the equation provided in *Figure 2a*, a dosage of 128 g litre^{-1} was estimated to fully recover the colour-promoting compounds from anaerobically-treated POME. Assuming that ~170 000 t of TDSBE (complete residual oil removal of about 22%) are available and utilised for nutrient recovery (*Figure 1*), 1.3 million m^3 POME from 5-6 average sized palm oil mills (60 t hr^{-1} processing capacity) could be treated annually. If all nutrients were to be recovered the performance of TDSBE must be improved or additional sorbents or processes used. The adsorbent performance needs to be assessed by integrating with current conventional treatment system with or without advanced polishing technique (Zainal *et al*., 2017). POME treatment with the pH trials revealed that colour recovery decreased with increasing pH caused by deprotonation of the edges of the clay mineral (Tombácz and Szekeres, 2004). The newly formed negative surface attracts cations but repels similarly charged molecules suggesting the colour-inducing substances in POME are negatively charged over the pH range investigated. Abd Majid and Che Mat (2017) also found a decrease in colour removal with increasing pH. Mixing time did not affect the colour recovery of POME as strongly as pH and dosage suggesting that the process was already in equilibrium under the conditions studied. For RSM experiments, it is suggested to use shorter mixing times in order to observe noticeable effects. In terms of SS recovery, dosage and mixing time had no apparent effect. According to Ahmad *et al*. (2005), all types of bentonite clay do not give complete clarification by altering the mixing time due to the fact that while the pollutants are adsorbed onto the surface and removed from the suspension, a fraction of the adsorbent itself forms a colloidal suspension leading to higher level of colour visibility and turbidity of the solution. Hence, colloidal clay could have interfered with the turbidity measurement obscuring potential SS removal effects.

From the preliminary trial, mixing time and dosage were selected as influential factors due to their ease of implementation at industrial scale. The minimum and maximum values selected for dosage were 12.5 g litre^{-1} and 50 g litre^{-1}, respectively. The minimum time for mixing was 0.5 hr while the maximum was 2 hr. The parameter of pH was intentionally neglected since altering the pH of POME requires time and chemicals that incur additional treatment cost while introducing potentially undesirable salts competing for the available sorption sites and requiring removal prior to discharge of the treated POME into the environment.

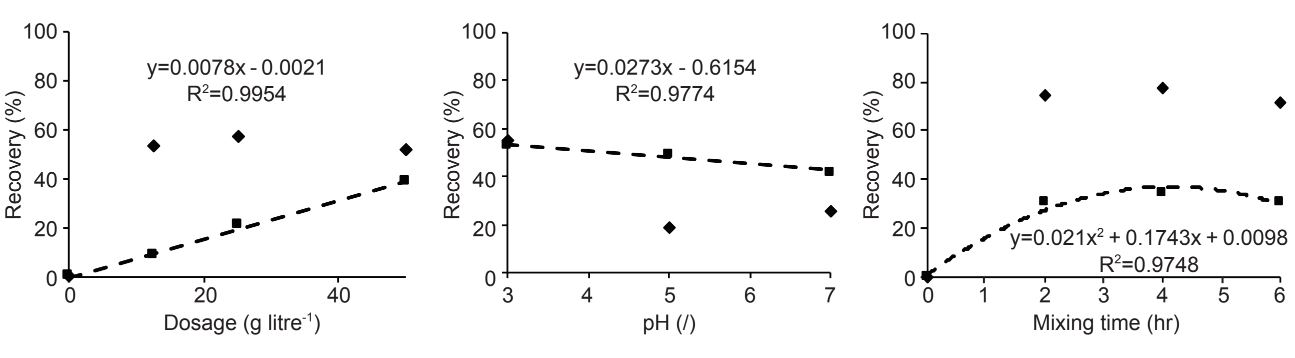


Figure 2. (a) Effect of bleaching earth dosage, (b) pH and (c) mixing time on colour (■) and suspended solids (◆) recovery from anaerobically-treated palm oil mill effluent (n = 2).

Statistical Analysis

Relationship between mixing time, dosage and eight important responses (NH_3, P, Cu, Zn, Mn, Fe, K and colour) during adsorption was analysed using RSM. The design shown in *Table 2* enabled the formation of mathematical equations where recovery was predicted as a function of TDSBE dosage (A) and mixing time (B), and calculated as the sum of a constant, two first order effects (termed A and B), one interactive effect (AB) and two second order effects (A^2 and B^2). The results obtained were analysed using analysis of variance (ANOVA) to assess the 'goodness of fit'. Equations from the first ANOVA analysis were modified by eliminating the terms found statistically highly insignificant.

Table 3 summarises the RSM results of the experiment. Overall recovery of NH_3, P, Zn, Mn, and Fe was significant at $p < 0.05$ level, though *Table 2* shows potential release of Zn at lower dosage of TDSBE. The R^2 values of the models are also >0.5, which indicate that 50% of the observations can be attributed to dosage and mixing time. A higher coefficient indicates that the factor has a higher contribution to the recovery. Contrarily, a negative coefficient indicates there is no desirable effect on final nutrient recovery (Hatami *et al*., 2018). In this study, NH_3 recovery has a high coefficient value for the interaction of dosage and mixing time, while for P, the highest coefficient is observed for dosage. Dosage of TDSBE has a significant effect ($p < 0.05$) on percentage recovery of colour, NH_3, P, Zn, Mn and Fe.

The values of R^2 and R^2_{adj} ensure the quadratic model to be acceptably adjusted to the experimental data. Significant difference between the two values means that there is a chance that insignificant terms have been included in the model which should be eliminated (Hatami *et al*., 2018). In *Table 3*, only Mn has values of R^2 and R^2_{adj} close to each other. It is suggested that effect of mixing time and dosage towards nutrient recovery is to be studied further to determine the range in which nutrient recovery takes place. It may be necessary to increase the dosage to >100 g litre^{-1} in order to reach a point where no further reduction occurs. As for mixing time, the minimum and maximum values may need to be reduced further, while substitution of factors may also be considered.

Figure 3 shows the surface plot of significant responses for NH_3, P, Zn, Mn and Fe. From the surface plot, it is suggested that increasing dosage enhances the recovery of P, Mn and Fe. This is due to the provision of more clay sites for the nutrients to adsorb to (Abd Majid and Che Mat, 2017; Said *et al*., 2015). The NH_3 and Zn have similar surface plots, where increasing mixing time causes a reduction in nutrient recovery.

Despite the fact that Zn recovery from POME could form a model, it was found to follow similar trend like Cu. Probably, Zn and Cu could only bind loosely to the available clay sites due to a lower transition/oxidation state compared to Mn and Fe, hence, their tendency to be released is greater dependent upon pH condition, type and dosage of clay. At pH 5.33, Loh *et al.* (2015) reported much higher contents of Fe and Mn in SBE compared to Zn and Cu. This together with better adsorption affinity and higher contents of Fe and Mn in POME (*Table 1*) justifies the findings obtained. Suitable pH conditions coupled with deoiling and lower calcination temperature of SBE might enhance its adsorption capability for Zn and Cu and should be pursued in the future.

The K recovery from anaerobically-treated POME did not generate a model probably due to low adsorption capability of TDSBE for K. It was reported that K adsorption onto clay was 50% lower than other nutrients such as N and P, while the loss of K in soil was 1.1- and 14.5-fold that of N and P (Li *et al*., 2014).

RSM could not create a model for colour recovery suggesting that the organic matter in POME such as humic acids could not interact with TDSBE significantly ($p = 0.154$). Humic acid is anionic, phenol-containing recalcitrant organic matter (Kalsom *et al*., 2006) which contributes to colour reading (Zouboulis *et al*., 2004). Since the longest mixing time between TDSBE and POME is 2 hr combined with a low CEC of TDSBE, it is suggested that organic matter such as humic acid could not successfully adsorb to the TDSBE surface.

Bleaching Earth Characterisation

It was expected that TDSBE has better adsorbent properties compared to BE, SBE and DSBE due to the thermal treatment. However, TDSBE has a relatively poor performance from the experiment. This contradicts with Abd Majid and Che Mat (2017), who reported that highest colour removal by 68.3% was obtained using regenerated DSBE. Abd Wafti *et al*. (2011a) also observed highest removal of colour from CPO using regenerated SBE. In order to elucidate the relatively poor performance of TDSBE, it was subjected to FTIR, CEC, BET (N_2) and SEM-EDX analysis and compared with BE, SBE and DSBE. FTIR analysis of BE, SBE, DSBE and TDSBE revealed a similar spectrum at band 1089-1042 cm^{-1} which indicates the presence of Si-O stretching (*Figure 4* and *Table 4*). The presence of Si was confirmed by EDX (*Figure 5*). The Si-O is one of the main components in BE with composition up to 57% and more, depending on its type (Loh *et al*., 2013b). Abd Majid and Che Mat (2017) also reported the presence of Si-O for BE, SBE, DSBE and acid regenerated DSBE.

Falaras *et al*. (1999) stated that acid activated Ca-montmorillonite shows Si-O at bands of 1089 and 1042 cm^{-1}. It is suggested that neither thermal nor acid treatment affects the composition of Si-O in BE. SBE and DSBE possess two unique peaks at 2930 and

TABLE 3. SUMMARY OF RESPONSE SURFACE MODEL RESULTS FOR THE RECOVERY OF MACRO- AND MICRONUTRIENTS FROM ANAEROBICALLY-TREATED PALM OIL MILL EFFLUENT USING THERMALLY OXIDISED SPENT BLEACHING EARTH (TDSBE)

Response	Final equation in terms of coded factor	p-value of regression	Dosage A	Mixing time B	AB	A^2	B^2	Lack of fit	R^2	R^2_{pred}	R^2_{adj}
Colour	_	0.154	0.048	0.399	0.372	0.381	0.102	0.451	0.62	0.00	0.35
Ammonia	$2.695A+1.672B-2.579A^2-1.967B^2-4.997AB+8.688$	0.004	0.01	0.065	0.002	0.016	0.047	0.427	0.88	0.51	0.80
Phosphorus	$15.9371A+10.7346B+44.3060$	0.04	0.007	0.038	0.947	0.88	0.377	0.294	0.76	0.00	0.58
Potassium	_	0.588	0.581	0.752	0.125	0.529	0.79	0.307	0.36	0.00	0.00
Copper	_	0.229	0.153	0.330	0.101	0.316	0.379	0.00	0.56	0.00	0.25
Zinc	$17.2042A+16.6138B-20.4422AB$	0.023	0.018	0.02	0.036	0.991	0.212	0.162	0.79	0.00	0.65
Manganese	$10.5271A+4.0193B+14.6414$	<0.001	0.00	0.001	0.866	0.153	0.150	0.402	0.97	0.88	0.95
Iron	$5.7737A-2.9429B-2.8614A^2+13.6411$	0.015	0.003	0.06	0.861	0.082	0.141	0.292	0.82	0.16	0.69

Note: A – TDSBE dosage.
B – mixing time.
AB – interactive effect between A and B.
A^2, B^2 – second order effects.
R^2 – coefficient of determination.

TABLE 4. CHARACTERISTIC FTIR BANDS FOR BLEACHING EARTH (BE), SPENT BLEACHING EARTH (SBE), DE-OILED SPENT BLEACHING EARTH (DSBE) AND THERMALLY OXIDISED DE-OILED SPENT BLEACHING EARTH (TDSBE)

	Wavenumber (cm^{-1})										
	3 624	3 549	3 476	3 239	2 930	2 850	1 730	1 634	1 439	1 089, 1 042	875
Functional group	*O-H stretching	*O-H stretching	*O-H stretching, intermolecular bonded	*Aliphatic primary amine, stretching	‡C-H stretching, aliphatic hydrocarbons	‡C-H stretching, aliphatic hydrocarbons	‡C=O stretching, aldehyde	‡C=O stretching, alkene/ HOH deformation	O-H bending, carboxylic acid	‡SiO stretching	§Al-Fe-OH bending
BE	✓	✓	✓	✓	–	–	–	✓	✓	✓	✓
SBE	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
DSBE	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓
TDSBE	–	–	–	–	–	–	–	–	–	✓	–

Note: * Falaras *et al*. (1999).
‡ Abd Majid and Che Mat (2017).
§ Ashtiani (2012).
FTIR - Fourier transform infrared.

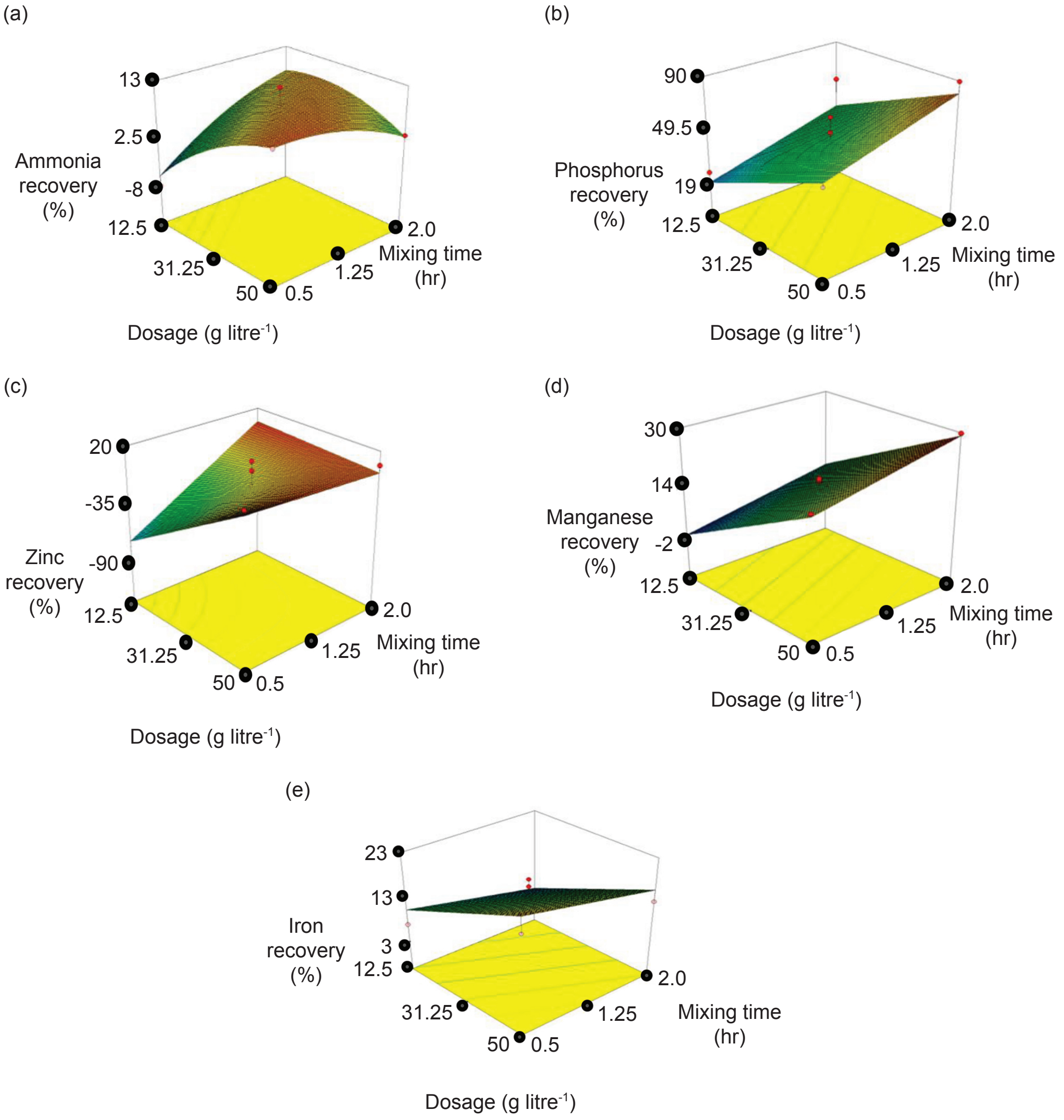


Figure 3. Surface plots representing percentage recovery of (a) ammonia (NH_3), (b) phosphorus (P), (c) zinc (Zn), (d) manganese (Mn) and (e) iron (Fe).

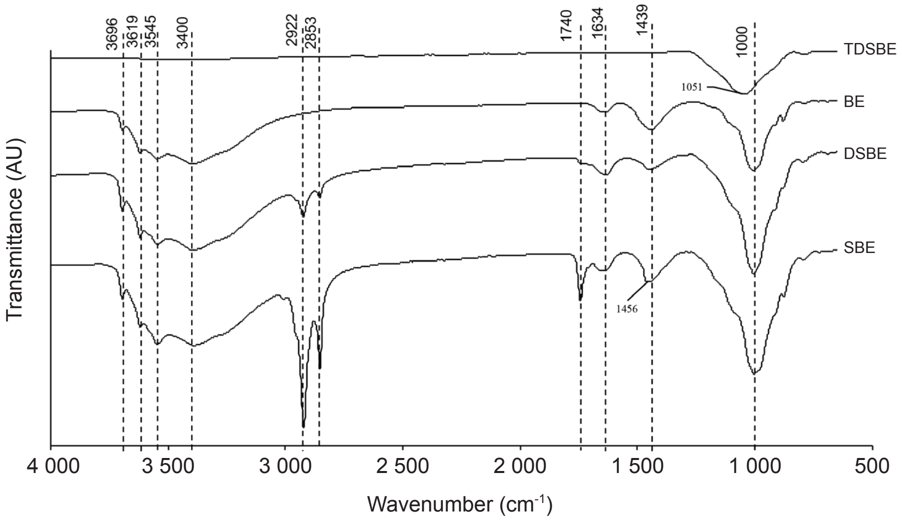


Figure 4. Fourier transform infrared (FTIR) analysis of bleaching earth (BE), spent bleaching earth (SBE), de-oiled spent bleaching earth (DSBE) and thermally oxidised de-oiled spent bleaching earth (TDSBE).

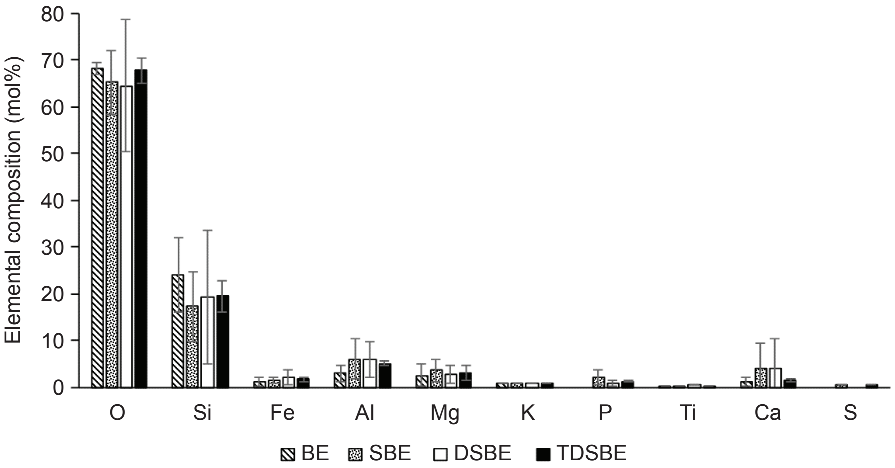
2850 cm^{-1}. These peaks reflect the C-H stretching of aliphatic hydrocarbons which indicates the presence of residual palm oil (Abd Majid and Che Mat, 2017). Presence of residual oil on SBE is plausible since BE adsorbs not only impurities but also CPO during the refining process.

Loh *et al*. (2006) and Abd Wafti *et al*. (2011b) reported that SBE contains up to 40% of residual palm oil that could be recovered using solvent or supercritical CO_2 extraction, for example. The presence of C-H peaks at 2930 and 2850 cm^{-1} in DSBE indicates that the SBE de-oiling process was not complete. From the peak height reduction of DSBE (*Figure 4*), we estimated a recovery of 79% of residual oil from SBE. Abd Wafti *et al*. (2010) used a solvent-to-clay ratio (SCR) of 7:1 and reported a 90% de-oiling efficiency of SBE with hexane, while Al-Zahrani and Daous (2000) reported a de-oiling efficiency of 42% for a SCR of 5:1 using hexane at 25ºC with a 5-min extraction time. A peak at 1730 cm^{-1} was observed for SBE and DSBE, which indicates the presence of ester carbonyl from residual oil (Abd Majid and Che Mat, 2017). The peaks between 3624-3239 cm^{-1} represents the O-H stretching mode which can be attributed to the adsorption characteristics of montmorillonite, where the adsorption occurs at the interlayer water and stretching vibrations of structural hydroxyls (Mana *et al*., 2008). This region is also a characteristic for strong hydrophilic interactions (Ashtiani, 2012). The peak at 1634 cm^{-1} indicates the bending vibrations of interlayer water hydroxyls (Mana *et al*., 2008; Ashtiani, 2012). TDSBE has only Si-O stretching, which suggests that thermal treatment oxidised the residual palm oil as well as destroyed most of the functional groups and bonds present on BE. Our findings agree with Al-Zahrani and Daous (2000) who reported that OH-O bonds between the layers of the clay are destroyed during heating at high temperatures. Peak at 875 cm^{-1} represents the functional group of Al-Fe-OH. Aluminum is one of the main components of BE (Loh *et al*., 2013b; Krzysko-Lupicka, 2013), and its presence is in agreement with EDX results (*Figure 5*).

CEC represents the capability of a material to hold positively charged ions. A high CEC indicates that the material, for example soil, can retain positively charged plant nutrients more effectively. SBE has a much reduced CEC compared to fresh BE since it is loaded with residual oil and impurities removed during CPO refining. De-oiling increased the CEC of DSBE by 26% compared to BE, while thermal treatment reduced the CEC by 85%.

It is suggested that de-oiling removes impurities from the clay's ionic structure. Low CEC in TDSBE suggests that the octahedral sheet in the clay is devoid of OH-O as a consequence of the thermal treatment process. For slow-release fertiliser production with TDSBE, it is proposed to reduce the temperature to 500°C during thermal treatment, or use DSBE directly which appears to be more favourable since it has a greater CEC and water holding capacity as well as slower release of nutrients in soil (Loh *et al*., 2013b). Acid activation of TDSBE may also be considered. However, Falaras *et al*. (1999) observed that acid activation of montmorillonites using 8 N H_2SO_4 decreased the CEC from 100% to 64%. In addition, acid activation may also affect the anion exchange capacity due to the removal of octahedral cations such as Mg^+ and Fe^+. However, thermal treatment had no effect on Mg and Fe content of DSBE and TDSBE as was evidenced by EDX analysis (*Figure 5*).

Surface area analysis revealed that BE has the largest BET surface area followed by DSBE and SBE. Pore volume of BE is also highest followed by DSBE



Note: O - oxygen; Si - silicon; Fe - iron; AI - aluminium; Mg - magnesium; K - potassium; P - phosphorus; Ti - titanium; Ca - calcium; S - sulphur.

Figure 5. The elemental composition of bleaching earth (BE), spent bleaching earth (SBE), de-oiled spent bleaching earth (DSBE) and thermally oxidised spent bleaching earth (TDSBE) as determined by energy dispersive X-ray spectroscopy.

and TDSBE. Pore volume of TDSBE and DSBE is almost the same with only 0.01 cm^3 g^{-1} difference. The reduction of BE surface area and pore volume after CPO refining indicates that the CPO and impurities have occupied the pores of BE. The de-oiling process using hexane removes these components from SBE, hence, there is a slightly greater surface area and pore volume of DSBE (*Table 5*). This trend was also observed by Abd Majid and Che Mat (2017). Ng *et al*. (1997) stated that the surface area of montmorillonite clay was modified after de-oiling, and further heat treatment caused some regeneration of smaller pores. However, TDSBE in this study had the lowest surface area and low pore volume (*Table 5*). Thermal treatment has possibly caused surface destruction to the clay considering the high temperature used (900°C). It is reported that thermal treatment coupled with acid activation causes dissolution of impurities, hence, influences the surface properties of the clay (Abd Majid and Che Mat, 2017). Abd Wafti *et al*. (2011a) thermally treated DSBE at temperatures of 400°C to 1000°C and observed highest reduction in surface area at 1000°C. The authors also reported that higher regeneration temperatures caused a collapse of BE's pore structure. This correlates well with the properties of TDSBE used in this study. Tsai *et al*. (2002) found that there was no significant change in SBE surface area, pore volume and porosity at 660°C-770°C during thermal regeneration, and the surface area of thermally regenerated SBE was less than BE. Al-Zahrani and Daous (2000) reported that calcination of de-oiled clay at 500°C increased the surface area by a factor of 3.9 from 44 to 175 m^2 g^{-1}. The findings reported in literature demonstrate that thermal activation at lower temperatures preserves the sorptive features of BE and should be used in future thermal treatments of TDSBE as an adsorbent. A high surface area and pore volume enhances adsorption capacity of clay (Hussin *et al*., 2011), therefore for adsorption purposes, high treatment temperature of SBE or DSBE is not advisable.

The elemental compositions of BE, SBE, DSBE and TDSBE do not vary noticeably from one another except for P and S. The presence of P in SBE is probably due to the phospholipids present in CPO. During bleaching, phospholipids are adsorbed onto the surface of BE. Loh *et al*. (2006) detected only 18.7 mg kg^{-1} of P in residual oils recovered from SBE using solvent extraction. The de-oiling and thermal treatment do not appear to remove P from the clay's surface. It is therefore suggested that P has chemically bonded to the surface of BE during thermal treatment.

Krzysko-Lupicka *et al*. (2014) proved that the presence of S in SBE was in the form of sulphates (1650 mg kg^{-1}). Reappearance of S in TDSBE might be due to diffusion of S from the pores to the surface during thermal regeneration.

TABLE 5. CATION EXCHANGE CAPACITY (CEC), BET (N_2) SURFACE AREA AND PORE VOLUME OF BLEACHING EARTH (BE), SPENT BLEACHING EARTH (SBE), DE-OILED SPENT BLEACHING EARTH (DSBE) AND THERMALLY OXIDISED DE-OILED SPENT BLEACHING EARTH (TDSBE)

Sample identity	CEC [Cmol (+) kg^{-1}]	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})
BE	22.4	194	0.31
SBE	8.03*	156	0.13
DSBE	30.3	186	0.30
TDSBE	3.47	126	0.14

Note: *Loh *et al.* (2013b).

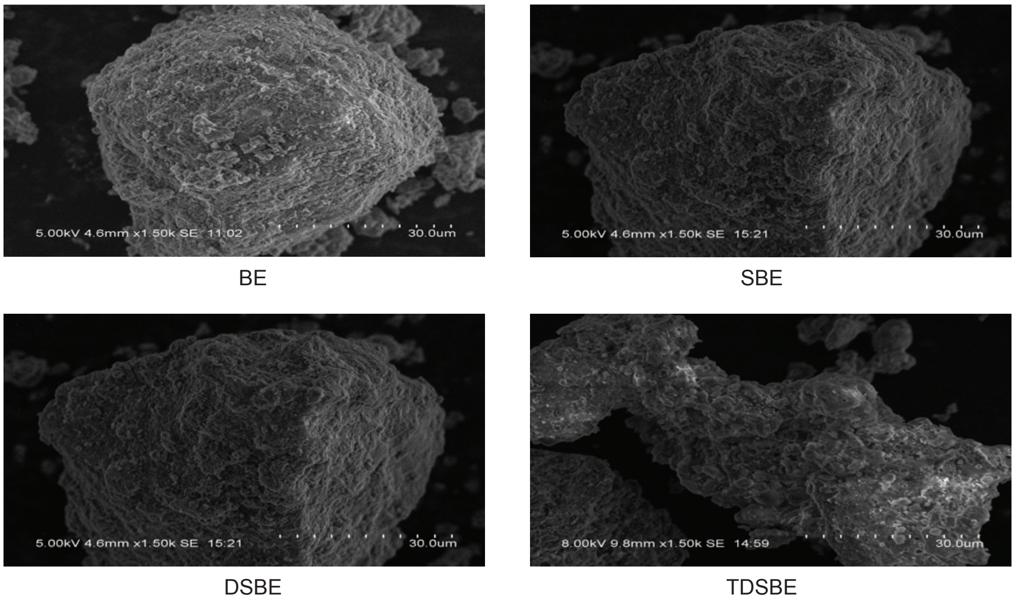
Table 6 summarises the elemental composition of various BE from this study and compares them with literature. It was observed that the elemental composition reported here is of similar order of magnitude with values reported in literature.

TABLE 6. COMPARISON OF ELEMENTAL COMPOSITION OF BLEACHING EARTHS CHARACTERISED IN THIS STUDY WITH LITERATURE

Clay type	Source	Elemental composition (wt%)									
		O	Si	Fe	Al	Mg	K	P	Ti	Ca	S
BE	This study	53.9	33.3	w3.5	3.8	3.0	1.9	0.0	0.7	2.4	0.0
	Falaras *et al.* (1999)	NA	35.7	0.3	4.4	2.3	0.1	NA	NA	1.3	NA
SBE	This study	49.7	22.9	3.8	7.6	4.1	1.2	3.1	0.6	7.9	1.0
	Loh *et al*. (2013b)	NA	26.6	2.9	2.4	2.6	0.8	2.1	0.5	2.8	NA
DSBE	This study	49.1	24.8	5.1	7.6	3.1	1.4	1.3	1.1	8.2	0.0
TDSBE	This study	53.0	26.6	4.5	6.7	3.5	1.4	1.8	0.7	2.8	1.0
	Tsai *et al*. (2002)	NA	NA	1.0	1.9	0.5	0.2	NA	0.1	0.2	NA
	Eliche-Quesada and Corpas-Iglesias (2014)	NA	38.4	0.8	0.8	0.2	0.2	0.1	0.3	0.5	NA

Note: BE - bleaching earth, SBE - spent bleaching earth, DSBE - de-oiled spent bleaching earth (DSBE) and TDSBE - thermally oxidised spent bleaching earth.

O - oxygen; Si - silicon; Fe - iron; AI - aluminium; Mg - magnesium; K - potassium; P - phosphorus; Ti - titanium; Ca - calcium; S - sulphur; NA - not available.



BE SBE DSBE TDSBE

Figure 6. Scanning electron microscope (SEM) micrographs of bleaching earth (BE), spent bleaching earth (SBE), de-oiled spent bleaching earth (DSBE) and thermally oxidised de-oiled spent bleaching earth (TDSBE).

Figure 6 illustrates surface irregularities of BE, DSBE and TDSBE. The surface of SBE appears to be smoother, which might due to the presence of residual palm oil. The surface of DSBE is similar to BE, while in TDSBE, pores appear at the surface.

CONCLUSION

Selected nutrients could be recovered from anaerobically-digested POME using TDSBE. From ANOVA in RSM, NH_3, P, Zn, Mn and Fe recoveries by TDSBE were significant. However, TDSBE was unable to recover all nutrients due to lack of functional groups, a low BET surface area and CEC. Characterisation of BE, SBE, DSBE and TDSBE proved that de-oiling produces clay (DSBE) that has surface area and CEC similar to BE. FTIR results confirmed that SBE has residual oil present on the surface. Nutrient recovery of POME by TDSBE in an integrated approach provides a new perspective to palm oil millers on viewing POME as a valuable resource instead of a wastewater that requires treatment to meet legislative requirements.

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