Reactivating Adsorption Capacities of Spent Bleaching Earth for Using in Crude Palm Oil Industry

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Abstract. The spent bleaching earth from the palm oil refining industries contains various contaminants, including free fatty acids and hazardous material. The conventional procedure is harmful to the environment. In this study, spent bleaching earth (SBE) was successfully regenerated by calcination and acid-activation process. The calcination process was performed at 500, 600 and 700°C for 2, 3 and 4 h. All samples were then mixed with CaCO₃ and lastly activated with aqueous acid. The results showed the SBE color restored at calcination temperature higher than 500°C, even though the decomposition of the volatile compound was removed at 680°C according to thermal gravimetric analysis. Treatment affected the clay structure and mostly removed the impregnated organic matter. The primary phase of regenerated SBE is similar to virgin bleaching earth (VBE), implying the calcination and acid-activation is not alter the phase. Moreover, the adsorbent capacity of regenerated SBE was comparable with VBE, showing the regenerated SBE has promising potential for many applications, in particular for the palm oil refining industry. Regenerated SBE gave significantly larger specific surface area, microporous surface area and total pore volume with smaller the average pore diameter.

Keywords: spent bleaching earth, regenerated SBE, calcination, acid activation

1. Introduction
Palm oil is a highly efficient and yielding source of food and fuel. In 2017, the crude palm oil (CPO) production in a whole nation reached 38.5 million tons with 18 million tons was exported and the remains being consumed domestically [1]. In the long term, the global demand for palm oil shows a growing trend as a ballooning global population, which increases the consumption of food and cosmetic product that contain palm-derived raw material. Moreover, CPO is also a promising source for biodiesel due to abundant resources, especially in Indonesia [2].

The crude palm oil (CPO) through the refining process before it is derived from other products. Traditional palm oil refining processes generally involve four major steps which are degumming, bleaching, neutralization and deodorization [3]. Bleaching is an important process in palm oil refining. The purpose of bleaching processes is to adsorb impurities in crude palm oil mostly both saturated and
unsaturated fats [4]. The bleaching step is realized by using acid-activation clay which known as bleaching clay (usually used is bentonite) because of its high specific surface [5]. The bleaching process generates massive waste of spent bleaching earth. Globally, it is estimated that about 1 million tons or more of SBE are disposed of in the refining process and it expected to grow even further with an increasing global production [6]. The spent bleaching earth contains 20-40 wt. % of the adsorbed oil with a high content of free fatty acids, which is not removed completely during the final filter pressing process. It is typically dumped in the landfill as waste and disposed of. Spontaneous auto-ignition is the main concern with the handling of SBE from the bleaching of unsaturated vegetable oils which can trigger fire hazard [7,8]. If the abundance residues can be converted into a more useful and valuable product, it will be essential for more effective production [9]. Therefore, it is important to develop new economical technologies for SBE disposal and to reduce potential contamination.

Many studies are dedicated to the conversion of these wastes and their reuse in different applications to minimize the contamination risk. The regenerated material (RSBE) has particularly been used as an adsorbent to separate pigments from crude palm oil [3,8,9], hexane micella and from aqueous solution [10], heavy metal ions [11], and to capture the carbon dioxide [5]. Currently, several methods to RSBE are: removed the oil content by the solvent extraction [12–15], acid solutions [16,17], hot alkali solutions [18] and inorganic salt solutions [17,19], thermal activation [16,20] and acid activation [17]. Due to increasingly the high cost of dispose waste to landfills, pretreatment SBE using n-hexane was the best alternative to remove the oil content. It was economically feasible for expensive and relatively stable oils [6]. To our knowledge, however, no study on the reuse of SBE regenerated by using a thermal treatment method in a furnace without chemical additives have been presented.

Hence, the main purposes of this research are as follows: regeneration and reuse spent bleaching earth in the palm oil bleaching, to reduce the production cost of oil refinery and to minimize environmental pollution from this waste. The best regenerated material (RSBE) was characterized by using FTIR, SEM, and XRD methods. On the other hand, measuring some value, such as heavy metals, pore size, and color of the bleached oil, allow us to validate our proposed regeneration method and to conclude on adsorbent capacity.

2. Experimental method

SBE was supplied by PT. SMART Tbk (Palm oil refinery industry in Indonesia). The oil was extracted from SBE by maceration method whereby SBE was mixed with an n-hexane for 4 h at room temperature with 1:5 w/v ratio. This SBE was named deoiled SBE. Then, to activate the deoiled SBE by thermal heating, calcination was performed at 500, 600, and 700°C for 2, 3, and 4 h in the furnace. 0.1 M CaCO₃ solution was added to calcinated SBE and then mixed for 1 h at 105°C. Then the solution was filtered, dried and leached by the acid solution. Furthermore, the SBE powder was chemically activated by mixing with 10% of sulfuric acid (H₂SO₄) for 3 h on a magnetic stirrer. Next, the samples were rinsed with distilled water until the pH 3 – 4 and dried at room temperature. This sample was named regenerated spent bleaching earth (RSBE). Commercial VBE was obtained from PT Clariant AG, Indonesia was also used for comparison with RSBE from this study.

Thermal decomposition of SBE was analyzed by thermogravimetry and differential thermal analysis (TG-DTA, STA PT1600, LINSSEIS, Germany) in an air atmosphere with heating rate 5°C/min from room temperature to 1000°C. Molecular bonding of the SBE, deoiled SBE, RSBE and VBE was characterized by Fourier-transform infrared spectroscopy (FTIR, IRPrestige-21, Shimadzu, Japan). X-ray diffraction (XRD, Rigaku, Japan using CuKa as a source of radiation) was used to observe the phase in VBE, deoiled SBE and RSBE. Microstructure and elemental composition were evaluated by scanning electron microscope (SEM, SU-3500, Hitachi, Japan) equipped with energy dispersive spectroscopy (EDS, Horiba, Japan). The pores of VBE and RSBE, including the surface area, were measured by Brunauer–Emmett–Teller (BET) method using Quantachrome instrument (BET, Nova 4200e, USA).
3. Results and discussion

The decomposition temperature of the oil adsorbed on all samples was determined using TG-DTA before proceeding with calcination (Figure 1). The percentage of calcined products from SBE determined using the muffle furnace and TGA-DTG at 680°C showed about 24.8%. This result is in agreement with previous reports [6,21], that oil retention in SBE of 20–40%. Due to the removal of the hydroxyl group in silica bonding at higher temperatures, the percentage of weight loss for SBE increased by 20–40% [22,23]. The thermogram of SBE (Figure 1) showed three weight loss steps. The first weight between 40 - 200°C loss is caused by the removal of adsorbed water molecules and chemically bonded OH groups [22,23]. The second step showing a substantial endothermal weight loss is primarily associated with the decomposition and burning of the sample organic content and also suggests the carbonization of the residual oils [20]. The third weight loss is observed which corresponds to a subtle endothermic peak due to the loss of structural hydroxyl groups in silica (Si-OH) bonding [22,23].

![Figure 1. Thermogravimetric and DTA plots of SBE.](image)

From our previous study, the amount of oil in SBE is 25%, which is similar to other reports [4,7,15]. Thus, the extraction of oil from SBE by the maceration method was incomplete. To confirm these results, SBE was calcinated at three different temperatures and times, as shown in Figure 2. The color of SBE is a function of temperature and time, which is the darkest color observed at 500°C for 2 h. This is in agreement with TG analysis (Figure 1), whereby the decomposition of SBE is completely at 680°C. The color of SBE powder at 600°C showed lighter color compared to 500°C due to the holding time during calcination. Furthermore, the color of SBE at 600 and 700°C did not change significantly indicating the absence of volatile compounds.

| Sample     | Si  | Al  | Fe  | Ca  | P   | Mg  | S   | O   | C   |
|------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| SBE        | 5.98| 1.44| 0.84| 0.33| 0.3 | 0.21| 0.19| 39.46| 51.25|
| SBE-deoiled| 6.7 | 1.64| 0.97| 0.35| 0.45| 0.26| 0.17| 41.86| 47.59|
| RSBE       | 28.71| 3.09| 1.59| 0.46| 0.14| 0.34| 0.26| 65.4 | -    |
Table 1 shows the elemental composition of SBE, deoiled SBE, and RSBE. The bleaching earth samples represent the expected typical elements such as silicon, aluminum, iron and a small amount of calcium, phosphorus, and magnesium. SBE and deoiled SBE had a significant amount of carbon, while the amount of carbon in deoiled SBE inconsiderably compared to SBE. This result is corresponding with TG analysis of deoiled SBE, whereby decomposing of deoiled SBE observed. Contrary, carbon did not observe in RSBE, which is similar to typical RSBE, as shown in Table 1.

![Image](Image)

Figure 2. Images of SBE after calcination at (a) 700°C for 2 h, (b) 700°C for 3 h, (c) 700°C for 4 h, (d) 600°C for 2 h, (e) 600°C for 3 h, (f) 600°C for 4 h, (g) 500°C for 2 h, (h) 500°C for 3 h and (i) 500°C for 4 h.

Figure 3 presents the FTIR spectra of SBE, deoiled SBE, RSBE and VBE. As shown in Figure 3, a quite strong of stretching vibration of the absorption band CH₂-CH₃ was observed at 2924 cm⁻¹ and 2852 cm⁻¹ in SBE and deoiled SBE. Moreover, a stretch vibration of ester carbonyl (C=O) also appeared at 1747 cm⁻¹. These absorption bands which appeared only in the FTIR spectra of SBE and deoiled SBE is characteristic of edible oil [20]. These absorption bands disappeared in RSBE due to calcination process and acid activation, which removes the volatile compounds. RSBE obtain in this study was comparable to commercial VBE, as shown in Figure 3. The structure of montmorillonite indicated by the presence of absorption bands Si-O and Si-O-Al at 1047 cm⁻¹ and 694 cm⁻¹, respectively. Moreover, stretching bands at 528 cm⁻¹ and 468 cm⁻¹ also suggested the presence of Si-O-Al. The existence of quartz was described by absorption bands ν (Si-O-Si) and δ (Si-O) [24]. A strong band at 3630 cm⁻¹ and 3427 cm⁻¹ showed the possibility of the hydroxyl linkage. However, a broad band at 3427 cm⁻¹ and a band at 1637 cm⁻¹ in the spectrum of SBE suggest the possibility of water of hydration in the adsorbent. A characteristics band reveals the interlayer hydrogen bonding in clay at 3630 cm⁻¹.
The XRD patterns of deoiled SBE, RSBE, and VBE were shown in Figure 4. The presence of montmorillonites observed in XRD patterns for all samples, which confirms the results of FTIR. Although all samples showed partly amorphous phase, the peaks of montmorillonite, quartz, and cristobalite were spotted very clear. These results informed that calcination and acid activation did not change the phases of RSBE, it demonstrates the effectiveness of this method.

Figure 3. FTIR spectra of VBE, SBE, deoiled SBE and RSBE.

Figure 4. XRD patterns of VBE, deoiled SBE and RSBE.

Figure 5. SEM photographs of (a) deoiled SBE and (b) RSBE.

Figure 5 shows the SEM images of the deoiled SBE and RSBE. The microstructure of deoiled SBE and RSBE showed similarity in the shapes and sizes. The calcination and acid activation did not alter the microstructure of RSBE, since it is not different compared to deoiled SBE. Although the particle size of RSBE was very coarse, the surface area of RSBE was very large, as shown in Table 2. The surface area of RSBE was 151.780 m$^2$/g, which is almost twice of VBE’s surface area. This indicates that the particle of RSBE contains a lot of pores. Table 2 shows the average pore size of RSBE and VBE was 29.357 and 56.508 nm, respectively. The pore size of RSBE falls into a mesoporous category according to the International Union of Pure and Applied Chemistry (IUPAC) definition, while VBE had macropores. Moreover, the microporous volume of RSBE and VBE was 0.049 and 0.026 cm$^3$/g, respectively, indicating the VBE only contain a small amount of micropores. These results are evident in the distribution of pores, as shown in Figure 6, which shows very small of micropores in RSBE and
VBE. Figure 6 also shows that the dominant pores of VBE and RSBE were at 60.20 and 36.84 nm, respectively.

Table 2. Textural characteristics of VBE and RSBE.

| Sample ID | Surface area (m²/g) | Microporous volume (cm³/g) | Total pore volume (cm³/g) | Average pore diameter (nm) |
|-----------|---------------------|-----------------------------|---------------------------|---------------------------|
| VBE       | 78.157              | 0.026                       | 0.2208                    | 56.508                    |
| RSBE      | 151.780             | 0.049                       | 0.2228                    | 29.357                    |

Figure 6. Pore size distribution of RSBE and VBE.

Figure 7. Nitrogen adsorption-desorption isotherm of RSBE and VBE.

Figure 7 displays the isotherms of adsorption-desorption VBE and RSBE using N₂. These materials (VBE and RSBE) gave the adsorption-desorption isotherm type V. These results revealed the broad distribution of pores, which is in agreement with Figure 6. The isotherm graphics show the reversible isotherm under a lower relative equilibrium pressure, but under higher relative pressure they exhibit a hysteresis loop. RSBE adsorbed more nitrogen than VBE about 144.03 cm³/g, 142.7 cm³/g, respectively, however, it is not notably different. The desorption curves indicated that hysteresis phenomena were rather small with the VBE but were greater in the RSBE.

Table 3 shows the physical characteristics of this studied material. In this test, RSBE were tested with a specific standard of PT. SMART Tbk. The highest bleaching ability for RSBE was 25% belongs to A2. Bulk density, acidity and moisture content have met industry standards. Comparing the results to the VBE, the bleaching performances were 0.2 times higher than the VBE in actual QC procedure. These results suggest that applying RSBE could reduce the application of VBE and the volume of spent bleaching clay treatment, and therefore also reduce the cleanup costs.

The study on adsorption capacities of the RSBE for CPO in commercial refinery site presents interesting reuse for a circular economy. Its efficiency in adsorption-desorption of impurities (including colored pigments, gum and trace contaminants, etc.) during CPO degumming and bleaching cannot be discussed here due to limitations of the study. Further study will be focusing on the targeted impurities removal efficacy, reuse cycle vis-à-vis commercial standards (PT SMART Tbk vs. VBE). Thus, based on the results of textural and physical characteristics, the RSBE provides better performance. This study provides a simple process and procedure to develop sustainable action for spent bleaching clay.
Table 3. Physical characteristics of regenerated RSBE.

| Properties      | A1       | A2       | B1      | B2      | PT. SMART Tbk |
|-----------------|----------|----------|---------|---------|---------------|
| Moisture content| 12.53    | 3.7      | 6.16    | 6.95    | Max. 15       |
| pH              | 2.62     | 2.56     | 2.53    | 2.55    | 2-6           |
| Acidity         | 3.69     | 0.31     | 3.64    | 3.44    | Max. 5        |
| Bleach Ability  | NA       | 25%      | 14%     | NA      | >20%          |

Note: A1. Temperature 500 °C; 2 h, A2. Temperature 500 °C; 3 h, B1. Temperature 650 °C; 2 h, B2. Temperature 650 °C; 3 h.

4. Conclusion

The SBE was successfully regenerated by calcination at 500°C in air atmosphere for 3 hours and followed the acid activation. Although the volatile compounds were completely removed at 680°C, the SBE showed light color after calcination at 600°C, indicating the removal of volatile compounds. The primary phase of RSBE is similar to VBE, implying the calcination and acid-activation is not alter the phase. The characteristic of RSBE was a high surface area (151.780 m²/g) with a mesoporous structure. Moreover, the adsorbent capacity of RSBE was comparable with VBE, in fact, slightly higher, showing the regenerated material (RSBE) have promising potential for many applications, such as palm oil refinery, construction and other fields in large scale for their accessible, cost-effective and high yield.

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