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Reactivation of Spent Bleaching Earth using Acid-Activation and Calcination Treatment for Enhancing Adsorption Abilities and Reducing Environmental Loading in Palm Oil Refining Industries

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Spent Bleaching Earth (SBE) is solid waste categorized as hazardous waste with code number B413 based on the Republic of Indonesian Government regulation number 101/2014 and number 22/2021. Improper processing of SBE can be triggering spontaneous ignition and pose environmental pollution due to the high of oil content which is about 20-30 %. SBE has the potential to be reused as an adsorbent in the crude oil bleaching process. In this research, the reactivation process was carried out using acid activation and followed by calcination. SBE was successfully reactivated using sulphuric acid (H_2SO_4) and hydrochloric acid (HCl) with various concentrations (5-20%), then, followed by a calcination process at 600-700°C for 90 and 120 min. The results showed that the physical appearance color of the bleaching earth (BE) after reactivation and calcination at temperatures above 600 °C resembled color of virgin bleaching earth (light brown). The characterization of reactivated spent bleaching earth (RSBE) product using X-Ray Fluorescence showed that the highest percentage value of silica content is 68.28 % and 74.42 %, under the reactivation condition using 15 % H_2SO_4 (calcination temperature and time at 600 °C and 120 min) and 20 % HCl (calcination temperature at 600 °C, and 90 min), respectively. The characterization results using Brunauer Emmett Teller (BET) analyzer, showed that the surface area of RSBE using HCl 20 % is about 150 m^2/g. However, the surface area RSBE with activator H_2SO_4 15 % (146 m^2/g). These results showed that the RSBE with HCl activator has a larger surface area than activator H_2SO_4, and has good absorption ability. As evidenced by the percentage of bleaching power that the RSBE with activator HCl has 72.92 % higher than RSEBE with activator H_2SO_4 15 % of 70.73 %. The best adsorption capacities of adsorbent were then tested for its performance to purify crude palm oil (CPO). The result shows that the RSBE met the Indonesian Industry standard (SNI 13-6336-2000) for the bleaching of CPO processes.

1. Introduction

Spent Bleaching Earth (SBE) is the main solid waste produced by edible oil industries which are included in dangerous and poisonous waste category 2 with waste code B413. Currently, the most common way to manage SBE is by dumping it in landfills or burning it directly. This processing method, if done incorrectly, can cause fires and pollution due to the decomposition of the remaining oil contained in SBE 20-40 %(w/w) (Pranowo et al., 2020).

To overcome these problems, it is necessary to have proper processing through oil recovery, reactivation, and reuse as an adsorbent. Several researchers have previously attempted to treat SBE waste by regenerating SBE. SBE can be regenerated to obtain an adsorbent with a bleaching efficiency similar to Bleaching Earth (BE)

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(Saputro et al., 2020). Regeneration can be carried out by heating (Tsai et al., 2002) or chemical treatment (Sariğolan et al., 2010) with or without solvent extraction (Al-Zahrani and Daous, 2000), or a combination of these methods (Saputro et al., 2020). The chemical regeneration process is usually carried out by adding strong acids such as H_2SO_4, HCl, and HNO_3 (Meziti and Boukerroui, 2011). This is because strong acids can substitute cations that can be exchanged by protons and solubilize octahedral cations (Boukerroui et al., 2017).
From several studies that have been carried out, it is necessary to reuse the adsorbent in the next process to make it a material with economic value and to reduce the problem of hazardous waste faced by the industry. Therefore, in this study, a solvent extraction process was carried out to remove the oil content contained in SBE, with chemical reactivation followed by calcination. Furthermore, the best reactivation spent bleaching earth (RSBE) is a repeated adsorption process (reuse) to minimize SBE waste and environmental pollution.

2. Material and method

2.1 Materials

SBE is obtained from Tunas Baru Lampung Company and BE from Buma Cima Nusantara Company. Acid activators and solvent extraction, including hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and hexane were purchased from commercial suppliers. Crude Palm Oil (CPO) obtained from PTPN VII Bekri in Central Lampung.

2.2 Recovery oil of SBE

The recovery stage was carried out by the extraction method using an n-hexane solution. A suspension of SBE in hexane (ratio 1:10 mass/volume) was carried out by heating for 6 h with stirring using a socket extractor. After the extraction process, the samples were dried to constant weight using an oven.

2.3 Reactivation with acid activators and calcination

The reactivation treatment was carried out by contacting the extracted spent bleaching earth (ESBE) with acid in the ratio of the ESBE: Acid 1:5 (m/v). Chemical reactivation was carried out by adding acid activators (HCl and H_2SO_4) with various concentrations (5 %, 10 %, 15 %, and 20 %). Reactivation was carried out for 24 h at room temperature. After 24 h, the RSBE was filtered using filter paper. The solid product of RSBE left on the filter paper was then washed with distilled water until neutral pH. The RSBE was then dried at 105 °C. After the chemical activation, the RSBE was then heated at high temperatures various of temperature 600-700 °C for 90 and 120 min.

2.4 Adsorption performed test of RSBE

The adsorption was carried out following of Indonesian Industry Standard (SNI 13-6336-2000). CPO was heated until the temperature was 105 °C. The adsorbent (RSBE and BE) was added into CPO as much as 2.5 % of the mass of CPO. Heating and stirring were carried out for 30 min while maintained at a temperature of 105 °C. After adsorption, the adsorbent is separated from the CPO oil using filter paper Whattman number 40. BE was used as a reference standard compared to RSBE. The beta carotene value was tested using a UV-VIS spectrophotometer to determine the bleaching power. Bleaching power can be calculated using Eq(1):

$$Bleaching\ Power\ (\%) = \frac{A - B}{A} \times 100\% \quad (1)$$

Where A is the concentration of beta carotene before bleaching (CPO), while B is the concentration of beta carotene after bleaching.

3. Result and discussion

3.1 Characterization of the physical appearance of the adsorbent

From Figure 1 it can be seen that there is a very different physical appearance between BE, SBE, ESBE and RSBE, SBE is the darkest color. This is due to the presence of organic compounds and residual oil which are still trapped in the SBE structure, causing SBE to be darker than BE. The existence of the SBE oil extraction process makes the ESBE adsorbent appear brighter than SBE. From this process it can be seen that the oil content trapped in the SBE sample can be partially recovered. However, the color of ESBE is still very different from BE, so the reactivation process needs to be carried out. The physical appearance of RSBE resulting from the chemical reactivation process shows a color that is not much different from the color of ESBE. RSBE chemical color is lighter than ESBE. Therefore, the chemical reactivation process is still very far from the physical appearance of Bleaching Earth, so it is necessary to carry out further processing using of physics, namely calcination using a furnace at high temperatures.

Figure 1: Physical appearance of (a) BE, (b) SBE, (c) ESBE, (d) RSBE activated with H_2SO_4, (e)RSBE activated & calcinated with H_2SO_4, (f) RSBE activated with HCl, (g) RSBE activated & calcinated with HCl

3.2 Characteristics of BE, SBE, and ESBE

Table 1 shows that the SBE's moisture content was 1.4 wt%, the moisture content in SBE is lower compared to commercial BE because SBE still contains oil. SBE contains accompanying oil trapped in the process of bleaching or bleaching, to reduce SBE's ability to adsorb water molecules around. The volatile content of SBE shows the level of oil residue adsorbed in SBE that is contains 33.12 %, while after the extraction process (ESBE) the VM is 18.41 %. The extraction process is proven to reduce the oil content contained in SBE. The presence of volatile matter content indicates that there is a large amount of oil contained in the volatile SBE. Mark the high ash content is due to the presence of mineral residues carried during the CPO bleaching process.

Table 1: Characteristics of BE, SBE, and ESBE

Composition (wt%)	MC (wt%)	VM (wt%)	Ash (wt%)	FC (wt%)
BE	3.12	5.17	91.44	0.27
SBE	1.4	33.12	64.91	0.58
ESBE	1.3	18.41	78.12	1.57

MC = moisture content, VM = volatile matter, FC = fix carbon

3.3 X-Ray Fluorescence analysis (XRF)

From Table 2 it can be seen that the main content that dominates BE is SiO_2 and Al_2O_3 with a percentage of SiO_2 of 69.92 % by weight and Al_2O_3 of 19.48 % by weight. Other ingredients in BE are 1.86 % CaO and 5.66 % Fe_2O_3 by weight. However, this percentage is lower than 10 %. So,it can be concluded that Si and Al in BE are elements that play a role in forming crystal and pore structures in BE. Table 2 shows that the percentage of Si in SBE has decreased compared to BE.

Table 2: The result of XRF analysis

Sample	Al_2O_3 (%)	SiO_2 (%)	CaO (%)	Fe_2O_3 (%)
BE	19.48	69.92	1.86	5.66
SBE	5.85	40.79	14.15	24.95
RSBE HCl 20%	10.90	72.87	0.88	8.82
RSBE $H2_SO_4$ 15%	5.93	58.54	5.92	14.17
RSBE HCL 20% , T=600°C, t= 90 min	11.82	74.42	0.39	7.80
RSBE $H_2SO_4$15%, T=600°C, t=120 min	10.03	66.03	3.99	7.31

After SBE was reactivated using acid activators (HCl and H_2SO_4) and continued with calcination, the percentage of Si experienced a significant increase from the previous SBE, namely in HCl the Si component was 74.42 % and H_2SO_4 was 66.03 %. This proves that the percentage of Si increases after being reactivated. The higher the concentration used will increase the Si content in the sample which is the active site on the adsorbent in adsorption. This is also supported by the increasing concentration, and the reduction in the percentage of Fe and Ca metals which are the composition of impurities in the adsorbent. The heating or calcination treatment of the adsorbent will affect the physical properties of the sample. There was an increase in the contact surface area of the sample due to the opening of the bentonite pores which were covered with impurities in the form of water, air and acid. This resulted in the cations on the surface of the sample becoming more active.

3.4 Scanning Electron Microscopy-EDX analysis (SEM-EDX)

From Figure 3 (b) it is clear that SBE before reactivated shows that the pore surface has been covered with impurities. Unlike the other samples, it can also be seen in Figures 3 (c, d, e, and f) that the structure is more porous, as well cleaner, because impurities have been removed from the pore surface. As the results of Boukerroui et al. (2017), the SBE surface looked smooth due to the presence of oil residues and other adsorbent substances during the bleaching process.

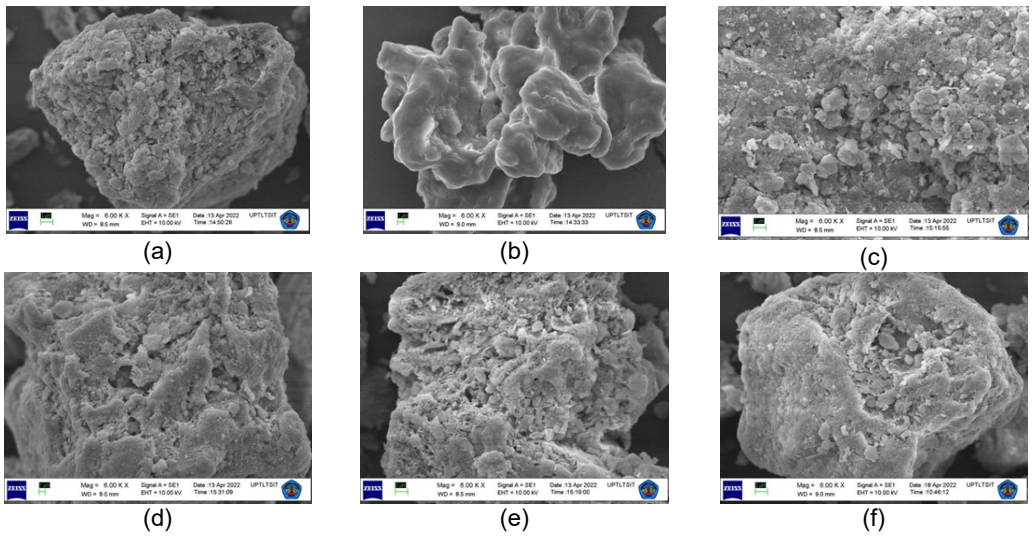

*Figure 3: EDX SEM analysis results of (a) BE; (b) SBE; (c) HCl 20 %; (d) H_2SO_4 15 % (e) HCl 20 % with calcination at 600°C ,90 min (f) H_2SO_4 15% with calcination at 600°C, 120 mi*n

The results of the EDX analysis (Table 3) are following with the XRF analysis which shows that the main constituents of bleaching earth are Oxygen, Silica and Aluminum. This composition is a component of montmorillonite minerals. According to a research report by (Merikhy et al., 2018), the presence of abundant silica and a small amount of aluminum in the BE can help lighten the colour of oil in the CPO refining process.

Table 3: The result of SEM-EDX analysis

Composition (wt%)	O	Si	C	Fe	Al	Mg	Ca
BE	40.09	14.72	39.46	0	4.61	0.61	0
SBE	29.3	15.57	49.93	0.26	2.78	1.57	0.6
RSBE HCl 20%	46.45	26.68	20.7	0	4.51	1.65	0
RSBE $H2_SO_4$ 15%	42.01	32.42	10.57	7.34	4.44	2.22	0
RSBE HCL 20% , T=600°C, t= 90 min	37.68	16.02	41.54	0	3.16	1.6	0
RSBE $H_2SO_4$15%, T=600°C, t=120 min	39.69	27.37	19.61	7.57	3.64	1.89	0.22

3.5 Brunaeur, Emmet, and Teller analysis (BET)

Table 4 shows the results of BET analysis for BE, SBE, and RSBE samples which were chemically reactivated with 15% H_2SO_4, 20% HCl and RSBE followed by a calcination process at 600 °C for 90 and 120 min. As shown in Table 4, the surface area of the RSBE substantially increased from 15.94 m^2/g of SBE to 150 m^2/g of RSBE HCl with calcination and pore volume also increased significantly from 0.03 cm^3/g of SBE to 0.11 cm^3/g. Enhancement in the surface area and pore volume of RSBE shows that the oil covering the SBE pores has decreased. From these results, it can be seen that the reactivation process with acid and calcination activators has a larger specific surface area and total pore volume than before activation.

3.6 UV-VIS spectrophotometer analysis

Adsorption was carried out on Crude Palm Oil (CPO). In this study, CPO oil was adsorbed on discoloration based on SNI 13-6336-2000 standards, namely by mixing 2.5 % RSBE adsorbent with the weight of CPO oil. The percentage of bleaching power of RSBE are indicated by the percentage value of the CPO color adsorption efficiency which will be compared with the efficiency value of virgin BE as a standard efficiency for adsorbent.

In this study, the analysis of CPO oil bleaching focused on the bleaching power variable. To be able to determine the bleaching power of the RSBE that has been produced, it can be done by first knowing the concentration of beta carotene, which can be measured using UV-VIS spectrophotometer.

Table 4: Result of BET analysis

Sample	Surface area (m^2/g)	Total pore volume (cm^3/g)
Bleaching Earth	12.24	0.03
Spent Bleaching Earth	15.94	0
RSBE H_2SO_4 15%	56.0657	0.13
RSBE HCl 20%	36.85	0.22
RSBE H_2SO_4 15%,T=600°C, t=120 min	146.269	0.21
RSBE HCl 20%,T=600°C, t= 120 min	150.00	0.11

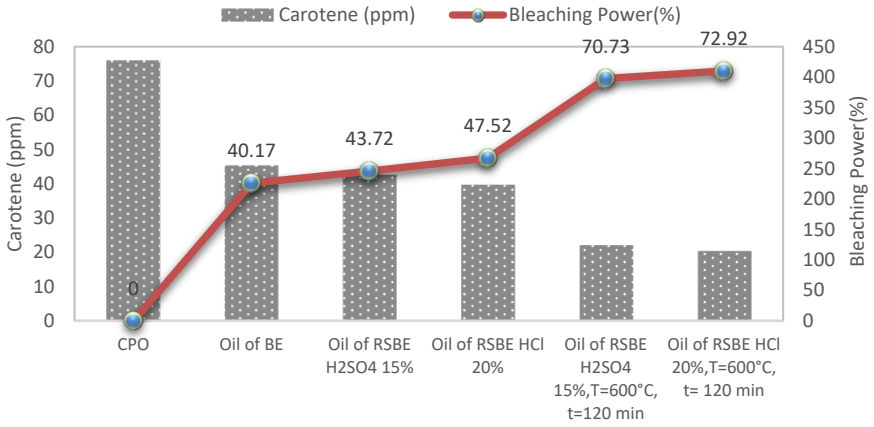

Figure 4: The percentage of bleaching power and carotene content of crude palm oil after bleaching treatment with various RSBE conditions

From Figure 4 it can be seen that the carotene value is inversely proportional to the bleaching power. This is due to pigment in the oil are absorbed by the adsorbent and make the carotene value decrease over the time. The percentage of bleaching power shows the adsorbent ability of RSBE using activator HCl is better than RSBE activated with H_2SO_4 and virgin BE. The highest percentage of bleaching power of RSBE found under the conditions of activator of 20 % HCl and followed with calcination at 600 °C for 90 min, namely 72.92%. Furthermore, the physical appearance of the RSBE adsorbent which was reactivated using HCl and H_2SO_4 activators accompanied with calcination showed a similarity color of oil as adsorption using virgin BE as a standard. This result suggested that the accumulated problems of SBE can be overcome by the reactivation process.

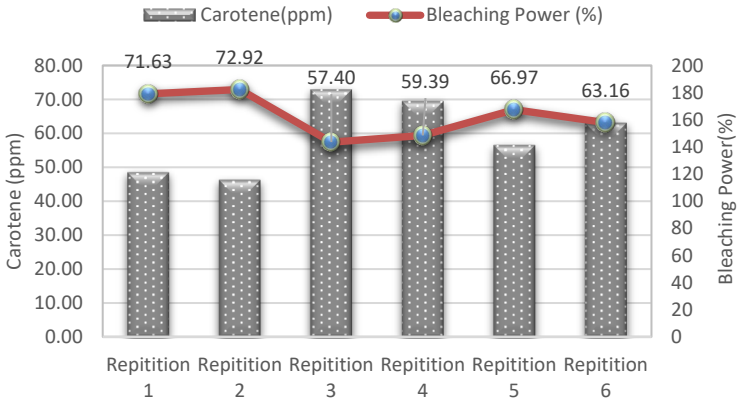

Figure 5: Repetition RSBE performance test using activator HCl 20% 600 °C 90 min, in six cycles of bleaching treatments

3.7 The performance test of RSBE

The repeat performance adsorption test of RSBE was then conducted in order to find out how many times it can be used. The performance test analysis was carried out exactly similar with same condition as the initial stages, which consisted of several treatments such as extraction, reactivation, and adsorption, respectively. Figure 5 showed the performance of RSBE after 6 cycles of bleaching treatments. The percentage of bleaching power values for each reuse from 1 to 6 cycles of reactivation still met the SNI 16-6336-2000 standards, with the ability discoloration efficiency above 40%. This result indicated that the RSBE which is reactivated for six times cycle can still be used again as an adsorbent in bleaching process of CPO. Based on these data it can be seen that RSBE HCl 20% “reuse 2” shows the optimal chemical and calcination reactivation has the best bleaching efficiency compared to the others. The parameter of color in the CPO refinery industry is one of the important things to be able to determine the quality of the oil and is a determining factor for whether it is appropriate or not in world trade.

4. Conclusions

The solid waste refining industries such as spent bleaching earth that has accumulated can be overcome by the reactivation process. The physical appearance of the RSBE adsorbent which was reactivated with HCl and H_2SO_4 acid activators accompanied by calcination showed a similarity performance with virgin BE as a standard. From the results of the reactivation process, it can be seen that the HCl activator has better percentage of bleaching power than H_2SO_4. This is supported by the results of the BET analysis which showed that there was a significant increase in surface area from 0 m^2/g (SBE) to 150 m^2/g (RSBE). The optimal RSBE as an adsorbent performance test was successfully carried out for 6 repetitions and it was found that the reactivation process for 6 repetitions still met the SNI standard to be used as an adsorbent for bleaching CPO.

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