Ecological-safe and low-cost activated-bleaching earth: Preparation, characteristics, bleaching performance, and scale-up production

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ABSTRACT

A high acidity extent, as a result of the activation process of bleaching earth, is a major drawback in the production of bleached-palm oil. The high acidity of bleaching earth generates problems for the process equipment as well as the product, which are economically disadvantageous. Addressing this pivotal issue in the manufacture, a more environmentally friendly and efficient activation process of bleaching earth using thermal activation is evaluated. Two types of bentonite-bleaching earth collected from two different locations were used throughout this study; that is from Pacitan and Ponorogo, coded as GS and SS, respectively. The effect of the proportion ratio of GS to SS (1:4, 2:3, 3:2, and 4:1), and variations in thermal activation temperature (150, 250, and 350 °C), to the bleaching performance were investigated. Thermal-activation at 150 °C can efficiently activate the bleaching earth without significant cation exchange capacity decrement. The pilot-scale bleaching process demonstrated that the prepared bleaching earth with GS to SS ratio of 3:2 (coded as M-03) could remove 96% of β-carotene from crude palm oil; which is the best among the investigated samples and also higher than the commercial bleaching earth (only 85−90% β-carotene removal). The feasibility of the production of M-03 at the industrial scale was analyzed by scaling up on the pilot scale. M-03 was able to be produced on an industrial scale by using a fluidized-bed dryer; this result has been adapted by a bleaching earth producing factory located in Madiun, Indonesia. Economic analysis on the factory demonstrated a payout time of 2 years and 10 months and the breakeven point of 21.5%. This paper shows the success of bringing the experimental results in laboratory-scale into the industrial-scale production of bleaching earth.

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1. Introduction

Bleaching earth plays a crucial role in the manufacture of edible palm oil from crude palm oil (CPO). The bleaching earth (BE) is used as the agent in the bleaching process to remove the colorant compounds contained in CPO, which is mainly α and β-carotenes (Ng and Choo, 2016; Ribeiro et al., 2018). The removal of the colorant compound is based on the adsorptive ability of the BE (Silva et al., 2013, 2014). BE can be produced from different types of clay minerals, such as sepiolite, attapulgite, and montmorillonite (bentonite). Due to its abundant availability, bentonite is widely used as the raw material for BE production (Bachmann et al., 2020; Almeida et al., 2019). The activation of bentonite is needed to increase the surface area and hydrophilic properties in the interlayer sites of bentonites (Christidis et al., 1997); the properties enhancement leads to better adsorption capacities of bentonite

Abbreviations

AAB	acid-activated bentonite	FTIR	Fourier Transform Infrared Spectroscopy
AOCS	American Oil Chemists' Society	GE	general expenses
BE	bleaching earth	GS	grey soil
BEP	breakeven point	IDC	indirect cost
BET	Brunauer−Emmett−Teller	M-01	a mixture of 1 GS: 4 SS
CEC	cation exchange capacity	M-02	a mixture of 2 GS: 3 SS
Cf	fixed cost	M-03	a mixture of 3 GS: 2 SS
CPO	crude palm oil	M-04	a mixture of 4 GS: 1 SS
Csv	semivariable cost	POS	profit on sales
DC	direct cost	PSD	pore size distribution
DPC	direct production cost	PV	peroxide value
DFT	density functional theory	ROR	rate of return on investment
DOBI	deterioration of the bleachability index	S	product sales
FA	fatty acid	SS	sandy soil
FC	fixed cost	TCI	total capital investment
FCI	fixed capital investment	TPC	total production cost
FFA	free fatty acid	XRD	X-ray diffraction
		WC	working capital

(Kherroub et al., 2018; Rahimzadeh et al., 2018; Richardson, 1978; Silva et al., 2014). Chemical activation using a strong inorganic acid solution is a standard method for BE preparation; this acid-activated bentonite (AAB) is widely used in many palm oil refineries (Peter, 2016). AAB, however, is not beneficial for the process-equipment because of corrosion caused by its acidity; it also causes loss of some oils (products) due to the catalytic reaction (Essid et al., 2016). The acidity of the surface of AAB is known to catalyze many chemical reactions (including isomerization, degradation, and dehydration), which produce unwanted compounds in the bleached oils (Essid et al., 2016). Furthermore, the use of AAB induces the accumulation of acid waste, which hazardous for the environment. The acid waste originates from the strong acid solution (H_2SO_4) used for the activation process. Often, the wastewater treatment process is more expensive than the activation process itself and make the product is not competitive in the market.

This study specifically highlights the bleaching process in the palm oil industries in Indonesia. Indonesia produces more than 32 million tons of CPO annually, where AAB is the most common bleaching agent used in the bleaching process. Acid-activation, however, is not an efficient process, as mentioned previously. Alkali- and thermal-treatment are other methods for activating bentonite. The acid-treatment altered the octahedral layers of bentonite, while the alkali-treatment altered the tetrahedral layers. Both of alkali-treatment and acid-treatment have a negative effect on the environment because the treatment is involving the hazardous concentrated chemicals. Thermal-treatment, also known as calcination, can be an environmental-friendly alternative for the activation process of bentonite (Chotoli et al., 2015; Komadel and Madejová, 2013).

Similar to chemical-activation, thermal-activation of bentonite also cause alteration in physicochemical properties, such as the pore structure, swelling ability, cation exchange capacity (CEC), plasticity, and the chemical composition of the bentonite (Sarikaya et al., 2000). For ore iron pelletizing or pet adsorbents, the bentonite must be thermally treated (up to 1000 °C), however, for bridge construction, the bentonite should be heated below 600 °C to reduce the swelling capability and harden the bentonite (Souza et al., 2015). However, extremely high activation temperature leads to a decrease of the BET (Brunauer−Emmett−Teller) surface area, pore-volume, and CEC, and subsequently lowering the adsorption capacity (Ismadji et al., 2016). Although thermal-activation of bentonite is a straightforward process, a proper activation temperature is needed to retain the layers structure and maintain the active adsorption sites of bentonite. Thus, it is essential to have a good insight into the thermal activation mechanism of bentonite. The two main events during thermal-activation of bentonite are the evaporation of free moisture and structural water, and the migration of exchangeable cations into the outer tetrahedral sheets or the crystalline structure (Amari et al., 2018; Garg and Skibsted, 2014). Extreme heating causes both events to run out of control, and resulting in the structural breakdown of bentonite; hence the CEC and specific surface area decrease. The two events should be kept in minimum to achieve a sufficient bentonite activation. The correct choice of temperature is the key to the success of the process. In a proper activation temperature, the evaporation of free moisture creates some space between outer tetrahedral sheets and later enhance the percolation of adsorbate molecules into the internal structure of bentonite during the adsorption process. The creation of some pores in the outer tetrahedral sheets while maintaining most of the exchangeable cations and structural water in the 2:1 layer can enhance the adsorption capacity of the BE (Ismadji et al., 2016).

Typical bentonite produced in two different mineral sources (Ponorogo, and Pacitan) in East Java, Indonesia, were investigated. Both of those locations are near the BE plant; furthermore, those mining sites produce bentonite with stable characteristics and cheap. The best thermal-activation temperature for producing BE with superior adsorption capacity toward carotene compounds in CPO is being investigated in this work. This investigation aims to demonstrate the potential of thermal-activated bentonite in the bleaching process as an alternative to AAB. The thermal-activation process is considered more environmentally friendly than the acid-activation process. This process also does not require any neutralization of the excess acid; therefore, it is cheaper than the acid activation process. Based on the pilot study with a capacity of 0.5 ton/day, the economic analysis was carried out, and it demonstrates the feasibility for mass-scale production; therefore, scale-up production of the BE was carried out. So far, there is no single study on the BE production using the thermal-activation process, which started with laboratory study until commercial plant development. Currently, a BE plant with a maximum capacity of 450 tons of bleaching earth/month has been established.
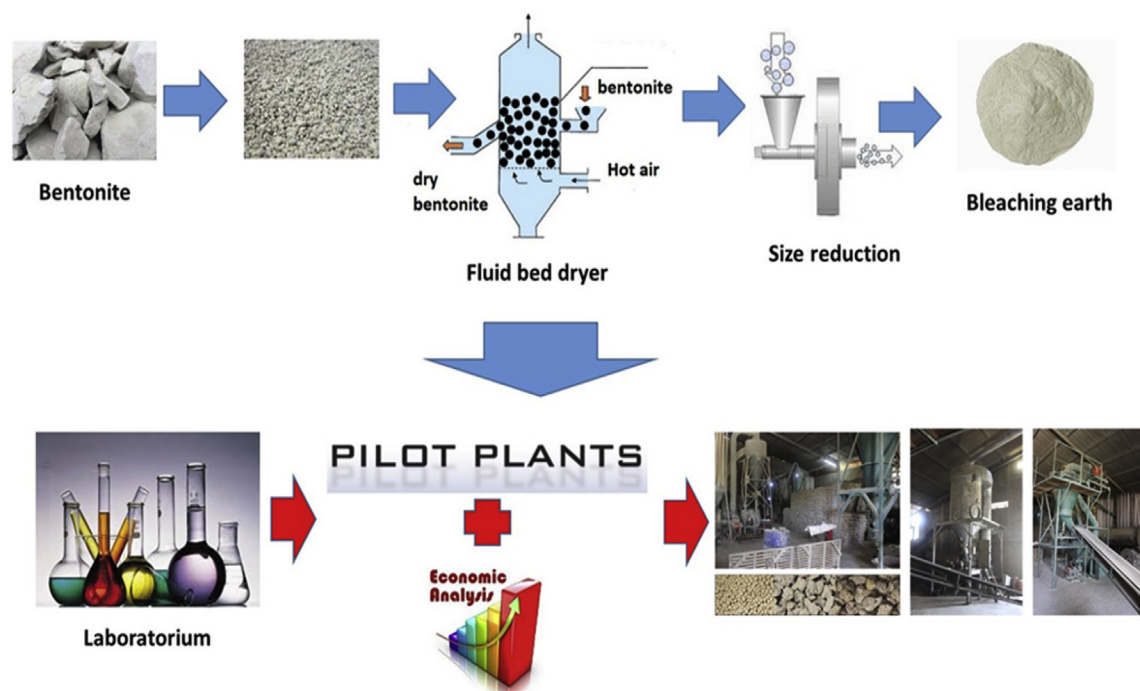
Fig. 1. Schematic diagram of scale-up study.

2. Materials and methods

2.1. Materials

Two bentonite samples were collected from two mineral sources; specifically, Ponorogo and Pacitan (East Java, Indonesia), which abbreviated as SS (sandy soil) and GS (grey soil), respectively. The chemical composition of SS: SiO_2 of 61.48%, Al_2O_3 of 19.31%, CaO of 3.58%, MgO of 1.98%, Fe_2O_3 of 2.48%, Na_2O of 0.94%, K_2O 1.28%, TiO_2 of 0.11% and MnO of 0.22%. The composition of GS: SiO_2 of 60.79%, Al_2O_3 of 20.84%, CaO of 4.77%, MgO of 1.21%, Fe_2O_3 of 0.31%, Na_2O of 0.28%, K_2O of 0.24%, and MnO of 0.07%. Mostly the deposits of bentonite in Indonesia are the Ca-bentonite type. Crude palm oils were collected from three different cooking oil factories in Surabaya. The origin of the crude palm oils from those three cooking oil refineries are Riau (CPO-01 and CPO-02), and Kalimantan (CPO-03), Indonesia.

Phosphoric acid, sodium hydroxide, methylene blue, ethanol, isooctane, and other chemicals used in this study were purchased from Merck, Germany.

Table 1
The physical characteristics of the heat-activated bleaching earth at different activation temperatures.

Code	Heating temperature, °C	pH	CEC, meq/100 g	BET surface area, m²/g	Pore volume, cm³/g
GS	150	2.3 ± 0.4	50.3 ± 2.4	157.8 ± 10.1	0.272 ± 0.03
	250	2.2 ± 0.2	23.3 ± 2.8	143.2 ± 7.0	0.291 ± 0.11
	350	2.5 ± 0.3	6.4 ± 0.3	111.4 ± 8.3	0.321 ± 0.28
SS	150	6.5 ± 0.7	42.1 ± 3.2	123.6 ± 8.5	0.214 ± 0.04
	250	6.3 ± 0.4	15.8 ± 1.7	93.5 ± 5.8	0.221 ± 0.06
	350	6.2 ± 0.5	8.5 ± 0.8	68.1 ± 6.5	0.232 ± 0.05
M-01	150	5.7 ± 0.5	44.5 ± 3.3	124.5 ± 7.8	0.222 ± 0.02
	250	5.2 ± 0.6	14.2 ± 1.1	111.4 ± 3.5	0.239 ± 0.03
	350	5.4 ± 0.3	8.4 ± 0.8	105.6 ± 4.7	0.251 ± 0.04
M-02	150	4.8 ± 0.3	35.7 ± 2.8	130.4 ± 3.6	0.234 ± 0.02
	250	4.9 ± 0.2	16.1 ± 3.2	121.4 ± 5.2	0.248 ± 0.03
	350	4.9 ± 0.4	4.5 ± 0.4	106.7 ± 4.8	0.259 ± 0.03
M-03	150	3.9 ± 0.5	37.5 ± 3.2	140.5 ± 6.9	0.261 ± 0.03
	250	3.8 ± 0.3	10.8 ± 0.9	121.7 ± 5.2	0.277 ± 0.02
	350	4.0 ± 0.3	4.1 ± 0.5	109.6 ± 7.4	0.289 ± 0.03
M-04	150	3.1 ± 0.4	32.8 ± 2.5	131.9 ± 7.2	0.270 ± 0.05
	250	3.1 ± 0.2	16.8 ± 1.1	120.5 ± 5.8	0.288 ± 0.03
	350	2.9 ± 0.1	7.6 ± 0.4	80.6 ± 6.9	0.297 ± 0.02

Note.
GS: raw material natural bentonite from Pacitan, East Java, Indonesia.
SS: raw material natural bentonite from Ponorogo, East Java, Indonesia.
M-01: raw material a mixture of 1 GS: 4 SS
M-02: raw material a mixture of 2 GS: 3 SS
M-03: raw material a mixture of 3 GS: 2 SS
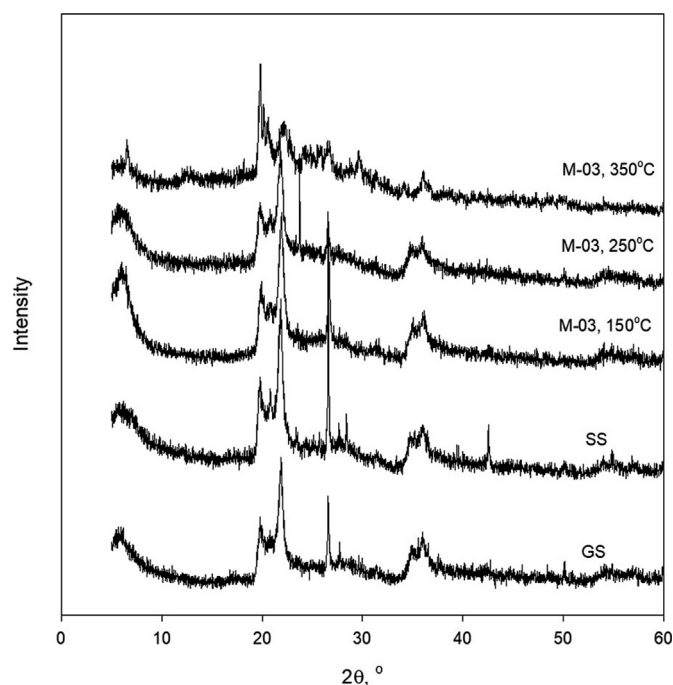M-04: raw material a mixture of 4 GS: 1 SS

Fig. 2. XRD spectra of raw bentonites (GS and SS) and BEs (M-03) prepared under different activation temperatures.

2.2. Thermal activation of bentonite - bleaching earth production

A dry and green process (without using any acids as the activating agents) was employed for the production of bleaching earth, which is the thermal-activation of bentonite. Mixtures of GS and SS bentonite were prepared at a certain proportion; that is 1:4, 2:3, 3:2, and 4:1 (GS: SS). Three heating temperatures of 150, 250, and 350 °C were investigated before the determination of the effective activation process. The heating process was conducted until the moisture content of ~12% achieved. The thermal-activation process was conducted in a tubular furnace. Subsequently, activated-samples was pulverized to the particle size of −100/+200 mesh.

The BEs were prepared from a mixture of two natural bentonites (GS and SS), they are coded as M-01 (a mixture of 1 GS: 4 SS), M-02 (a mixture of 2 GS: 3 SS), M-03 (a mixture of 3 GS: 2 SS), and M-04 (a mixture of 4 GS: 1 SS). In the bleaching of CPO, a thermally stable BE in the term of bleaching capacity is required (Bray et al., 1998; Ismadji et al., 2016). The effect of thermal treatment at different investigated temperatures to the properties of BEs are observed through several characterizations, that is BET surface area, CEC value, pore size, and pore structure, crystallinity pattern, and functional groups.

The pH of BE was determined according to the following procedure: 10 g of BE were added to 100 mL of distilled water (pH 7). The suspension was then stirred for 30 min, covered, and let stand for 1 h. Subsequently, the pH of the solution was measured using a pH meter. Before the pH measurement, the electrode was calibrated with the buffer solution at pH 4, 7, and 10.

2.3. Characterization of the adsorbents

The characterizations were conducted using nitrogen sorption, X-ray diffraction (XRD), and Fourier Transform Infrared Spectroscopy (FTIR) analysis. The nitrogen sorption analysis was carried out at the boiling point of nitrogen gas (−196 °C) using Micromeritic ASAP 2010. The degassing of the sample before nitrogen sorption measurement was conducted at 150 °C under a high vacuum condition. The BET surface area was measured at a relative pressure between 0.05 and 0.3, while the pore volume was obtained at the highest relative pressure (0.998). The pore size distribution of the samples was calculated using density functional theory (DFT) with medium regularization. The DFT program was embedded in a Micromeritic ASAP 2010 software.

The XRD patterns of bentonite and bleaching earth (BE) were obtained using Philips X'pert X-ray Diffractometer. X-ray diffraction spectra of the samples were obtained at 40 kV and 30 mA using monochromatic high-intensity CuKα1 with the wavelength $\lambda = 0.15405$ nm as the radiation source. A step size of 0.01° was used to obtain the XRD chromatograms. Shimadzu FTIR 8400S spectrometer was used to obtain the FTIR spectra of the samples. The KBr method was employed to obtain the FTIR spectra.

The adsorption of the methylene blue method was employed for the determination of the CEC of the sample (Cokca and Birand, 1993).

2.4. Bleaching procedure

The CPO was initially degummed using phosphoric acid to remove phospholipid and other impurities from the CPO. The degumming of CPO was carried out by adding 0.2% (wt.) of H_3PO_4 (85%) and heated at 60 °C for 30 min (Liu et al., 2019). One hundred grams of degummed CPO was bleached at a working temperature of 90 °C, with constant stirring (400 rpm) for 15 min. 1−3% of activated-adsorbent was introduced to bleach the CPO. After the bleaching process completed, the adsorbent was removed from the mixture by filtration.

The unbleached and bleached CPO were analyzed according to the standard methods of oil analysis. The standard quality parameters include free fatty acids (FFA) content, color, peroxide value, deterioration of the bleach-ability index, and carotene content. The acid content in the CPO and bleached oils is expressed by the amount of FFA, which determined using the titration method, according to AOCS (American Oil Chemists' Society) Official Method Ca 5a-40. The FFA content was expressed as the % of palmitic acid. The peroxide value (PV) was analyzed based on the AOCS Official Methods Cd 8−53. UV−Vis spectrophotometric was used to evaluate the deterioration of the bleach-ability index (DOBI). The DOBI index is calculated by the following equation:

$$DOBI = (\text{absorbance at 446 nm})/(\text{absorbance at 268 nm}) \qquad (1a)$$

The crude oils which have the DOBI values between 2.5 and 4.0 are categorized as average to good quality oil, while the oils which possess the DOBI index below 2.0 are oils with poor quality (Silva et al., 2014). The carotene content was also determined by UV−Vis spectrophotometric analysis at 446 nm. The oil sample was diluted and homogenized with isooctane. The carotene content in the CPO and bleached oils is expressed as β-carotene. All the measurements were conducted triplicate.

2.5. The scale-up and economic analysis study

The schematic diagram for the scale-up study is depicted in Fig. 1. After the success of the laboratory-scale production of bleaching earth, the experimental data obtained in this stage was subsequently used for pilot-plant scale experiments (100 kg of BE/h, 2 months). Before the installation of the BE production plant, the economic analysis must be conducted to assess the capability of the BE processing plant to operate under certain conditions, which gives a profit. In this case, several factors need to be considered, including profit on sales (POS), rate of return on investment (ROR),
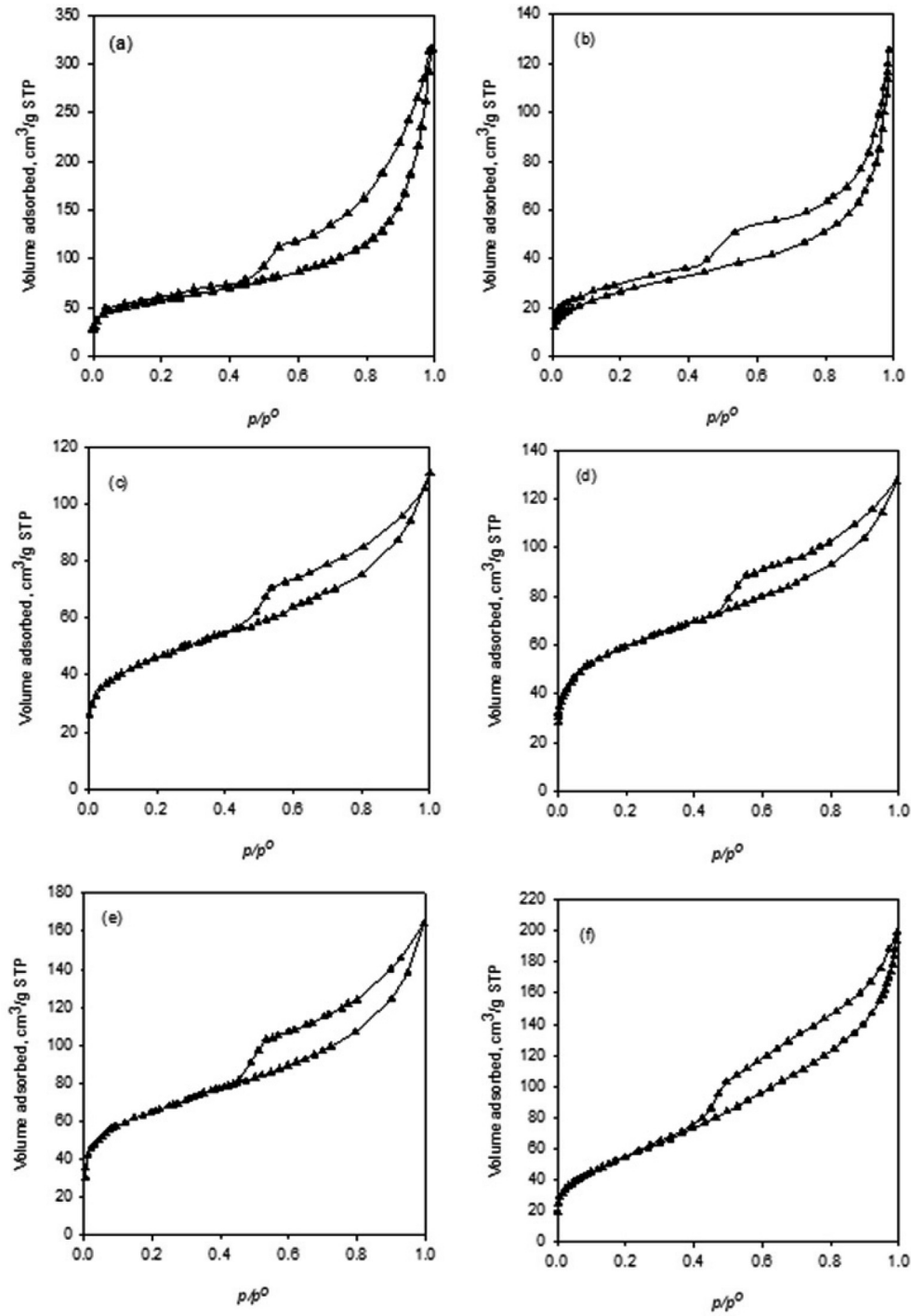
Fig. 3. Nitrogen sorption isotherms of the bleaching earth. The raw-GS, and SS (a, b); and heat-treated (150 °C) M-01, M-02, M-03, and M-04 (c, d, e, and f, respectively).

and breakeven point (BEP).

The investments needed to build and operates the BE production plant consist of total capital investment (TCI) and total production cost (TPC). The following equation is used to determine the TCI and TPC of BE plant:

$$FCI = DC + IDC \tag{1b}$$

$$TCI = FCI + WC \tag{2}$$

$$TPC = DPC + Cf + GE \tag{3}$$

FCI is a fixed capital investment, and WC is working capital. Where DC and IDC are direct cost and indirect cost, respectively, the DC includes the purchased equipment, equipment installation, instrumentation and controls, piping, electrical equipment and materials, building, yard improvements, service facilities, and land. IDC includes engineering and supervision, construction expenses, contractor's fee, and contingency. DPC, C*f*, and GE in Equation (3) are direct production costs, fixed cost, and general expenses,
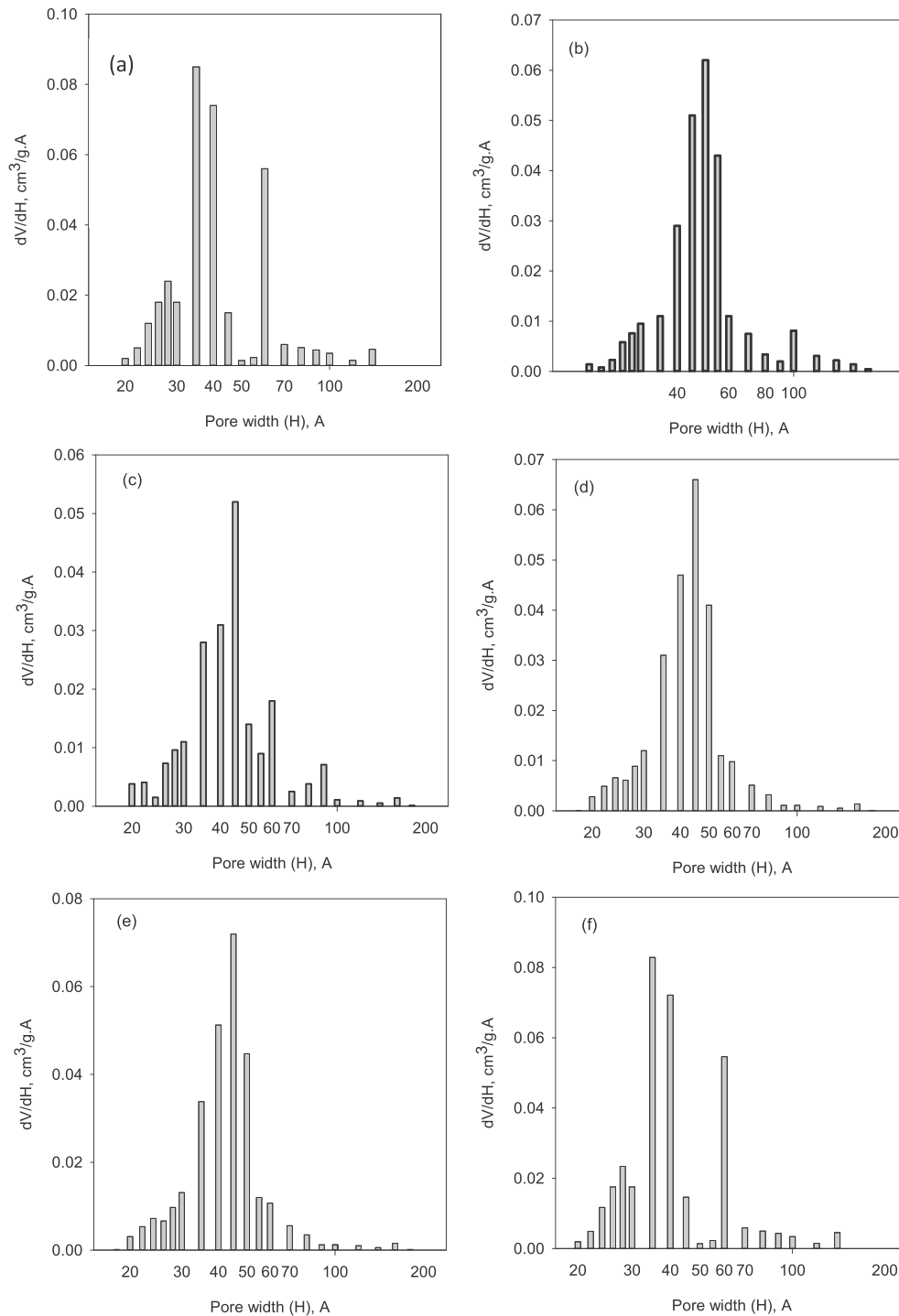
Fig. 4. DFT pore size distribution of the bleaching earth. The raw-GS, and SS (a, b); and heat-treated (150 °C) M-01, M-02, M-03, and M-04 (c, d, e, and f, respectively).

respectively.

The ROR and BEP of the BE plant were determined using the following equations:

$$ROR = POS/TCI \times 100\% \qquad (4)$$

$$BEP = (Cf + 0.3\ Csv)/(S - Cv - 0.7\ Csv) \times 100\% \qquad (5)$$

Where Cv is the variable costs, Csv is semivariable costs, and S is product sales.

3. Results and discussions

3.1. Characterization of the bleaching earth (BE)

The different temperatures of the thermal activation process have a significant effect on the BET surface area of BEs (Table 1); the BET surface area decreases with the increase of activation temperature (detail of the phenomena can be referred to in the introduction section). The XRD diffractograms of BEs (Fig. 2) confirm the influence of temperature on the layered structure of BE (M-03). The

Table 2
FTIR results (wavenumbers) of natural bentonites and bleaching earth.

Functional Group	Wavenumber, cm^{-1}					
	GS	SS	M-01	M-02	M-03	M-04
Al(Mg)−O−H stretching	3622	3620	3619	3625	3621	3618
O−H stretch of silanol (Si−OH) groups	3270	3274	3268	3263	3260	3268
O−H bend, for adsorbed H$_2$O at bentonite interlayer	1664	1648	1661	1665	1658	1665
Si−O−Si stretch of the tetrahedral sheet	1031	1026	1027	1030	1035	1029
O−H bending bounded 2Al^{3+}	926	921	915	925	922	924
Si−O stretching of silica and quartz	669	674	665	667	672	668
Al−O−Si bend (for octahedral Al)	516	511	517	518	518	521
Si−O−Si bend	455	438	441	451	449	453

Table 3
Physical and chemical properties of crude palm oils.

CPO[a]	FFA, %	PV, meq O$_2$/kg	DOBI	Carotene, ppm
CPO - 01	4.8 ± 0.31	1.25 ± 0.03	2.72 ± 0.3	648 ± 23
CPO - 02	3.7 ± 0.15	1.14 ± 0.01	2.60 ± 0.1	611 ± 15
CPO - 03	4.2 ± 0.3	1.35 ± 0.04	3.16 ± 0.1	558 ± 31

[a] CPOs were obtained from three different edible oil processing industries located in Surabaya, Indonesia.

Table 4
Fatty acid composition (%) of crude palm oil (CPO).

FA	Sample		
	CPO-01	CPO-02	CPO-03
C12:0	−	−	0.11 ± 0.01
C14:0	0.68 ± 0.01	0.75 ± 0.02	0.85 ± 0.01
C16:0	43.16 ± 0.12	42.57 ± 0.07	43.89 ± 0.05
C16:1	0.18 ± 0.01	0.15 ± 0.02	−
C18:0	6.01 ± 0.02	5.84 ± 0.01	5.75 ± 0.01
C18:1	38.99 ± 0.05	39.04 ± 0.08	38.51 ± 0.03
C18:2	9.26 ± 0.04	10.03 ± 0.02	9.58 ± 0.02
C18:3	0.58 ± 0.03	0.31 ± 0.01	0.48 ± 0.01
C20:0	0.79 ± 0.01	0.62 ± 0.02	0.41 ± 0.04

increase of activation temperature reduces the intensity of the 001 reflection, and the alteration of the basal spacing of bentonite due to the evaporation of the structural water is evident (Yao et al., 2014). The XRD spectra of M-01 and M-02 (are not shown in this paper) have similar characteristics to the XRD spectra of M-03.

The deformation of the 2:1 layer of the bentonite was indicated by the decreasing of cationic ions, which measured from the cation exchange capacity (CEC). Thermal-activation of the BEs induced the loss of exchangeable cations, and this reflected from the lower CEC as the samples are heat-treated at the higher temperature (Table 1). For instance, the increase of the activation temperature from 150 °C to 250 °C resulting in a 71.2% decrease of CEC for M-03, which is from 37.5 to 10.8 meq/100 g. Further increase of activation temperature to 350 °C, induce another 17.9% decrease of CEC to 4.1 meq/100 g. Similar CEC reduction events also occur in other investigated samples at almost the same extent. At high activation temperature, the excess evaporation of the structural water gives severe dehydration of BE. The loss of bound water is accompanied by the migration of the exchangeable cations to outer tetrahedral sheets of crystalline structure, and this phenomenon causes the reduction of CEC value (Ismadji et al., 2016).

The characteristics of M-01, M-02, M-03, and M-04 treated at 150 °C as analyzed by nitrogen sorption, and FTIR, were discussed; since the bentonite samples activated at higher temperatures (250 °C and 350 °C) give low CEC value, and bleaching performance (as discussed in next section). The nitrogen sorption isotherms of all the samples (Fig. 3) indicate type IV hysteresis loops, which cause by typical capillary condensation phenomena in a mesoporous material (Almeida et al., 2019). Calculation using Density Functional Theory (DFT) revealed the pore size distribution (PSD) around 2−20 nm for all investigated samples (Fig. 4). The PSD shows the pore size range of mesoporous material. The nitrogen sorption isotherms and PSD analysis indicate that the thermal activation at a temperature of 150 °C does not destroy the mesoporous structure of the mixed bentonite samples.

The FTIR wavenumber of the raw bentonites (GS and SS) and heat-treated BEs (Table 2) show similar functional groups for all of the samples. The absorption band at wavenumber around 3620 cm^{-1} belongs to Al(Mg)−O−H stretching, while O−H stretch of silanol (Si−OH) group is indicated by the absorption band at wavenumber around 3270 cm^{-1}. O−H bend for adsorbed H$_2$O at bentonite interlayer, Si−O−Si stretch of the tetrahedral sheet, and O−H bending bounded to Al^{3+} are indicated by the absorption bands at wavenumbers around 1664 cm^{-1}, 1031 cm^{-1}, and 925 cm^{-1}, respectively. The presence of quartz in the bentonite structure is indicated by the wavenumber of 669 cm^{-1} (Si−O stretching of silica and quartz). The presence of a surface functional group of Al−O−Si bend for octahedral Al is given by spectra bend at a wavenumber of 516 cm^{-1}.

3.2. The bleaching of palm oils

Average quality oil is the oil that has FFA content < 5% and PV value 15 meq O$_2$/kg oil (Almeida et al., 2013). Based on the chemical properties of the oils (Table 3), the quality of CPOs used in this study was categorized as average quality oils. All CPO samples have maximum free fatty acid content less than 5%. The DOBI values above 2.5 indicate that the CPOs are bleachable. All CPOs used in the study contain both unsaturated and saturated fatty acids (FA) (Table 4), such as lauric acid (C12:0), myristic acid (C14:0), palmitic acid (C16:0), palmitoleic acid (C16:1), stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2), γ-linolenic acid (C18:3), and arachidic acid (C20:0). The oleic (C18:1), at ~39% content, is the primary unsaturated fatty acids composition in the CPOs; while palmitic (C16:0), at ~43% content, is found as the primary saturated fatty acids.

The M-01, M-02, M-03, and M-04, treated at a high temperature of 250 °C and 350 °C are revealed to have low CEC value (Table 1); they also show poor performance on color removal in the preliminary experiments. Therefore, only BEs produced at 150 °C were used for the bleaching process. The bleaching process performed by introducing the different amounts of BE into the prepared CPO. Higher BE loading into CPO significantly decreases the amount of β-carotene from CPO (Fig. 5) since there are more adsorption sites available to adsorb the carotene as the adsorbent particles increase. The BE coded as M-03 gave the best performance on the removal of β-carotene from all of CPOs. At low loading (0.5% loading), the M-03 able to remove 118.0, 120.2, and 152.6 ppm of carotene from
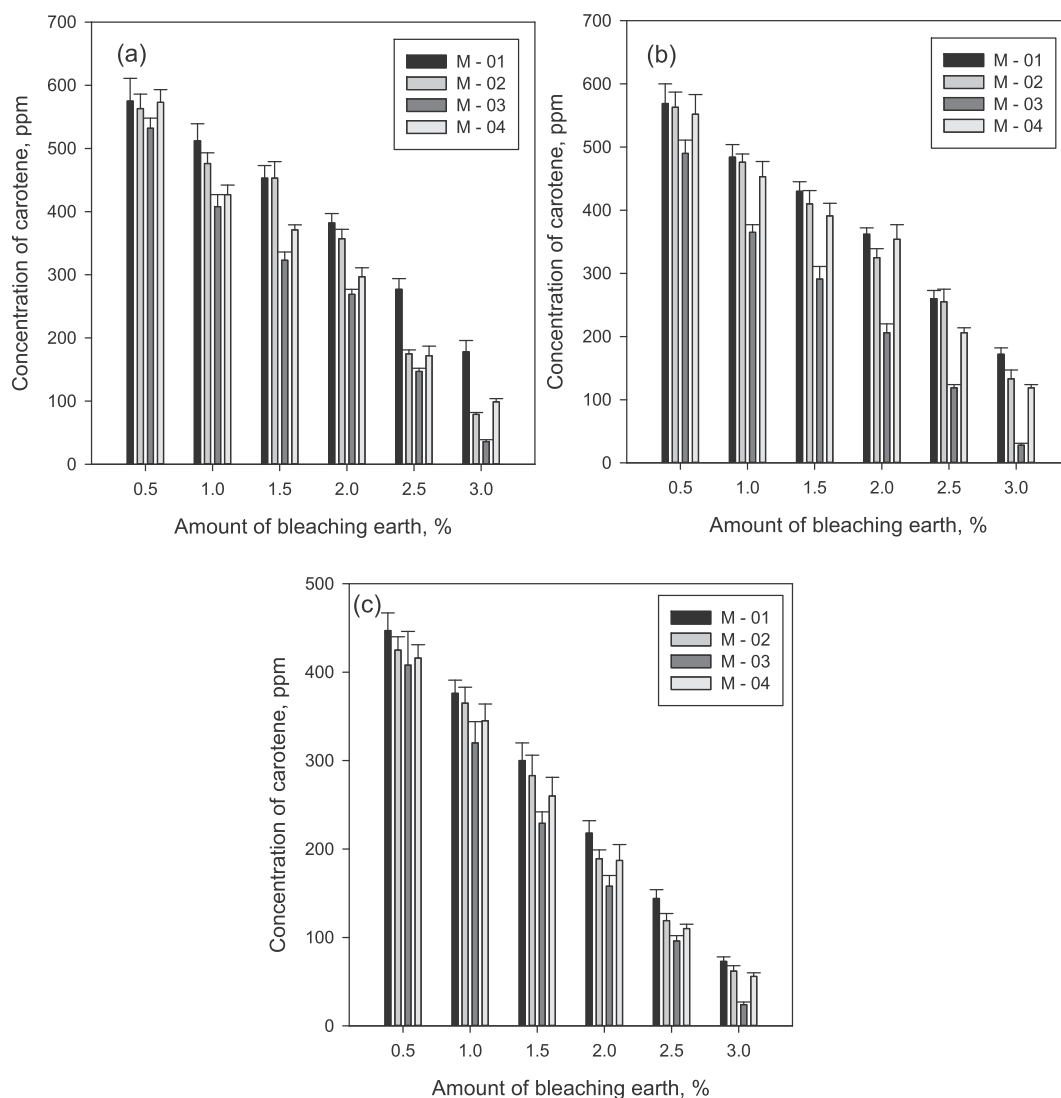
Fig. 5. Effect of BEs amounts on the removal of β-carotene from (a) CPO-01, (b) CPO-02, and (c) CPO-03.

Table 5
Comparison of bleaching capability for various BE.

No	BE	Bleaching capacity (mg/g)/bleaching removal (%)	Reference
1	Tonsil OPT 210 FF (acid activation of calcium bentonite)	18.72/-	Almeida et al. (2019)
2	Pure Flo B 80 (neutral bentonite)	14.93/-	Almeida et al. (2019)
3	Tonsil	-/57.7	Chakroun et al. (2017)
4	Acid activated Eocone Ca-bentonite	-/84.9	Chakroun et al. (2017)
5	M-03	18.41/95.9 (CPO-01)	This study
6	M-03	17.69/97.3 (CPO-02)	This study
7	M-03	16.34/98.4 (CPO-03)	This study

initially 648 (CPO-01), 611 (CPO-02), and 558 (CPO-03) ppm of carotene, respectively. At high loading (3% loading), a significant amount of carotene was removed from CPOs by M-03, leaving only 27.5 (CPO-01), 16.6 (CPO-02), and 9.0 (CPO-03) ppm of carotene at the end of the bleaching process.

A comparison of the bleaching capacity of M-03 with other commercial bleaching earth is summarized in Table 5. The bleaching capacity of M-03 towards CPO was calculated according to the following equation:

$$\text{Bleaching capacity} = (C_o - C_e) \cdot V/m \qquad (6)$$

where C_o is the initial concentration of carotene in CPO, C_e is the concentration of carotene in CPO after the bleaching process, V is the volume of CPO (100 mL), and m is the mass of BE (3 g). Since the unit of carotene concentration in ppm, it should be converted first to mg/L. The density of CPO is 890 g/L, and the initial concentration of carotene in the unit of mg/L is 576.72 mg/L (CPO-01), 545.54 mg/L (CPO-02), and 498.21 mg/L (CPO-03). The final concentration of

Table 6
The FCI of BE plant.

No.	Item	Unit cost, USD	Total, USD
DC			
1	Processing equipment	98,000	
2	Equipment installation	21,000	
3	Instrumentation and control	11,500	
4	Piping and electricity	12,750	
5	Yard improvement	15,000	
6	Land and building	125,000	
	Total DC		283,250
IDC			
7	Engineering and supervision	15,000	
8	Construction	30,000	
9	Contractor's fee	30,000	
	Total IDC		75,000
10	FCI = DC + IDC		358,250

Table 7
The TPC of BE plant.

No.	Item	Unit cost, USD	Total, USD
DPC			
1	Raw materials (5400 ton/year of GS and 3600 ton/year of SS)	81,000	
2	Salary	75,000	
3	Maintenance and operating supplies	30,000	
4	Utility (fuels, water, etc.)	150,000	
	Total DPC		336,000
Cf			
5	The depreciation of equipment (10%/year),	9800	
6	The depreciation of building (5%/year)	6250	
7	Local tax	5000	
8	Insurance	6450	
	Total Cf		27,500
GE			
9	Administration expenses	2500	
10	Distribution and marketing expenses	6000	
11	Packaging	2500	
12	Research & Development (R&D)	1500	
	Total GE		12,500
	TPC		376,000

utilization of GS in the bleaching process is its high price and acidity. The cost of raw GS (40–50% moisture) is USD 11/ton, while for SS (30–40% moisture) only USD 6/ton. Another disadvantage is due to the high acidity of GS, which causes the FFA content of the bleached oils to increase to 1% (after two months of storage). Based on the economic and technical considerations, the use of GS as the sole BE is not advantageous.

The trial on industrial-scale production of M-03 was performed. Based on the laboratory results, the pilot plant production of bleaching earth was conducted at a temperature of 150 °C. The capacity of the pilot plant trial was 100 kg of M-03/h. The pilot plant runs were conducted for two months using several types of dryers (tray dryer, fixed bed dryer, and semi-fluidized bed dryer). The trial production of M-03 using tray dryer produced M-03 with high moisture content (>15%); 15 h drying was required to achieve a

carotene after the bleaching process is 24.55 mg/L (CPO-01), 14.82 mg/L (CPO-02), and 8.04 mg/L (CPO-03). From Table 5, it can be seen that the BE produced in this study has comparable or even better bleaching performance with commercial BE.

3.2.1. Industrial-scale production of M-03 bleaching earth and economic analysis

M-03 is prepared from a mixture of GS and SS at a weight ratio of 3:2. GS naturally has a stronger acid property than SS, which is reflected in the measured solution pH after contact with GS or SS (Table 1). After contact with GS, a solution pH of 2.3 is measured; while, solution pH of 6.5 is measured after contact with SS. The bleaching property of GS itself is very excellent; 2% of GS could remove 98% of the β-carotene content in CPO. The bleaching ability of SS much lower than GS; 2% of SS only could remove less than 50% of the β-carotene. However, the main disadvantage of the sole

product with the moisture content of 12%. The M-03 produced gave inferior bleaching performance, which is <40% β-carotene removal. For large scale production of BE, the heat distribution in the tray dryer is poor, therefore longer drying time was required. Similar results were also obtained for a fixed bed dryer, the M-03 produced using a fixed bed dryer also gave a poor performance on the β-carotene removal. Finally, a semi-fluidized bed dryer with the direct heating process was employed; the M-03 produced by this dryer could remove more than 85% of β-carotene using 3% BE. A full industrial scale BE factory Madiun, East Java, Indonesia, was constructed based on this pilot plant results. Currently, the factory can produce the BE with the following technical specification:

- Particle size: 200/300 mesh
- Moisture content: 10–13%
- Apparent bulk density: 570 kg/m^3

Table 8
Sensitivity analysis of the production of BE.

The increase in the cost of raw materials, %	BEP, %	the increase in the utilities, %	BEP, %	The increase in the cost of raw materials and utilities, %	BEP, %
0	21.5	0	21.5	0	21.5
10	22.2	10	22.8	10	23.7
20	22.9	20	24.4	20	26.4
30	23.8	30	26.2	30	29.8
40	24.7	40	28.3	40	34.3
50	25.7	50	30.8	50	40.3

- pH (10% suspension): 4.0
- Filtration time: 60 s

The factory in Madiun is located 160 km west of Surabaya (the capital city of East Java province). The total area of the factory is 4600 m^2, and the BE processing area is 1000 m^2. The production capacity of the factory is 450 tons/month. All of the processing equipment was designed and locally fabricated. The maximum capacity of the BE processing plant is 450 tons/month. The number of employees is 15 persons (1 factory manager, 2 salespersons, 1 administrative staff, 1 process engineer, 10 processing staff).

The FCI of BE factory is calculated using equation (1), and detail of the components are listed in Table 6.

The WCI was 30% of FCI and equal to USD 107,475, and based on equation (2), the TCI of this plant was USD 465,725.

The TPC of BE consists of DPC, FC, and GE. The TPC was calculated using equation (3), and detail of the components are summarized in Table 7.

The BE is sold USD 100/ton. Therefore the annual sales (S) of the BE product are USD 540,000, with the gross profit 164,000. The net profit on sales (POS) after tax is around USD 120,000. The ROR of the company (calculated using Equation (4)) was 25.77%. Based on the discounted cash flow method, the payout time of this factory is 2 years and 10 months, and the breakeven point (BEP) calculated from equation (5) was around 21.5%. The variable cost (Cv) consists of raw materials, utilities, and packaging, while the semi-variable cost (Csv) consists of the salary of employees. Administration, distribution, marketing, and R & D.

The sensitivity analysis study was also conducted to determine the influence of the cost of several variable processes (cost of raw material and utilities) on the BEP value. The influence of the increase in the cost of raw materials and utilities on the BEP value (without increasing the selling price) is given in Table 8. From this table, it is evident that the BEP value is not sensitive to the increase in the cost of raw materials or utilities. However, the increase of utilities (especially fuel) usually followed by the increase of raw materials. As indicated in Table 8, the company still survives with the 50% increase in the cost of raw materials and utilities without increase the selling cost of the product.

The BE factory began its production in early 2012, and the payout time was achieved in August 2017 (double the predicted time using a discounted cash flow method). The main reason for the delay in the payout time due to tough competition in BE sales in the last 4 years. Currently, there is a big bleaching earth company (Clariant) operates in Indonesia with an estimated annual production capacity of around 300,000 tons/year. With the operation of this company, the sales of BE in the Indonesia market become tougher.

4. Conclusion

A simple and green process for producing bleaching earth is developed. The mixing of bentonite from Pacitan (GS) with bentonite from Ponorogo (SS) at wt.% weight ratio of 3:2 and heating the mixture at 150 °C until its moisture content around 12% to yield a BE with high adsorption capacity. The resultant BE could remove more than 85% of β-carotene using 3% BE. Importantly, it can be scaled-up in the industry, as demonstrated that a bleaching earth factory has been established and operates at the production capacity of 450 tons/month. The theoretical payout time for the factory is two years and ten months, and real payout time is around five years.

CRediT authorship contribution statement

Felycia Edi Soetaredjo: Doing experiment, providing funding, drafting the manuscript. **Livy Laysandra:** Doing experiment and characterization. **Jindrayani Nyoo Putro:** Doing experiment and characterization. **Shella Permatasari Santoso:** Characterization, economic analysis, drafting, manuscript. **Artik Elisa Angkawijaya:** Characterization, economic analysis, drafting, manuscript. **Maria Yuliana:** Doing experiment, economic analysis. **Yi-Hsu Ju:** providing research facility, corrected the manuscript. **Chun-Hui Zhou:** providing research facility, corrected the manuscript. **Suryadi Ismadji:** Providing funding, concept the idea.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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