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Modification of Bentonite with Nano Silica Oxide (SiO_2) for the Purification Process of Crude Palm Oil (CPO)

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ABSTRACT

The efficiency of β-carotene removal is a critical parameter in commercial refining, as it directly influences the overall process effectiveness; therefore, the selection of appropriate bleaching agents is crucial. The limited effectiveness of Bleaching Earth (BE) in refining crude palm oil (CPO) to meet color standards poses a challenge. To improve BE's performance, natural bentonite was modified with nano-SiO_2 through a facile-mixing method. Bentonite was modified with nano-SiO2 in concentrations of 5, 10, and 15% w/v, to assess the effectiveness of this modified bentonite in the CPO bleaching process. Bleaching was conducted at 90°C with a BE concentration of 0.5% w/v for 30 minutes. Characterization confirmed successful integration of modified Bentonite indicated by enhancing surface area. Bentonite modified with 15% nano-SiO2 showed a significant improvement in bleaching performance, reducing β-carotene content to 553.84 ppm compared to 630.36 ppm with unmodified bentonite. The red/yellow color value also decreased to 1.5/15 from the original CPO value of 2.1/21, along with a reduction in FFA value. The results of this study indicate that modifying bentonite with nano silica oxide offers a solution to reduce the amount of bentonite used in the bleaching process.

Keywords
Bleaching earth, Color standards, Crude palm oil, SiO_2, β-carotene, Innovation

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INTRODUCTION

The growth of the Crude Plm Oil (CPO) industry has driven a significant increase in palm oil production in Indonesia, which reached 45.12 million tons in 2021. This surge in production is closely aligned with the rising national demand, as palm oil remains a crucial source of global vegetable oil and a key raw material for Indonesia's expanding biodiesel sector. Palm oil is naturally red due to its high β-carotene content (500-700 mg/kg), and removing this substance is crucial for achieving commercial quality, including color, free fatty acids, and oxidative stability. Industrial refining of palm oil involves processes such as degumming and bleaching, which are conducted simultaneously to optimize production [1]. The oil refining process consists of three main steps, with bleaching being the most critical due to its ability to effectively remove undesirable component, as it effectively removes unwanted materials, including β-carotene. The efficiency of β-carotene removal is a key parameter in commercial refining, determining the overall process efficiency; hence, the choice of bleaching agents is crucial. The bleaching process of CPO is performed by adding bleaching earth (BE) [2]. Bleaching earth (BE) serves as an adsorbent to achieve standard color quality in the bleaching process of palm oil within the CPO-based refining industry. Bentonite, a common type of BE, also functions as a bleaching agent. Bentonite is primarily composed of 80% montmorillonite mineral, with the chemical formula $(Na,Ca)_{33}(Al,Mg)_{12}Si_4O_{10}(OH)_2 \cdot nH_2O$ [3]. This mineral is distinguished by its softness, exhibiting a hardness of one on the Mohs scale, a specific gravity between 1.7 and 2.7, and a tendency to disintegrate effortlessly. It feels smooth to the touch and swells upon contact with water [4]. The key components of bleaching earth include nano SiO2, Al2O3, bound water, calcium ions, and MgO, making it a highly effective adsorbent. Bentonite typically comprises montmorillonite, sepiolite, and attapulgite groups and contains hydrated silica-alumina along with various intermediate metal ions [5]. The modification of bentonite with nano SiO_2 was carried out to improve its adsorption capacity for Fe in batik wastewater, and it was found that a stirring time of 40 minutes was the optimal condition for Fe adsorption [6]. Bentonite modified with cetyltrimethylammonium bromide (CTAB) was used in the CPO bleaching process, achieving a carotene removal efficiency of 71.04%. At that time, the use of bentonite in the industry ranged from 2–10% for refining capacities between 600–2,500 tons per day. With palm oil production reaching 45.12 million tons in 2021, the demand for Bleaching Earth (BE) was estimated at around 9 million tons per year, resulting in a significant amount of waste generation [7]. Furthermore, the CPO bleaching process was carried out using zeolite modified with Fe. The optimum bleaching process was achieved at a zeolite-Fe concentration of 5% (w/w), a bleaching temperature of 80 °C, and a duration of 30 minutes. The bleached CPO had a chlorine concentration of 25 ± 1 ppb, a carotenoid content of 467.70 ± 13.71 ppm, and a DOBI (Deterioration of Bleachability Index) value of 2.17 ± 0.01 [6].

Based on literature studies, the addition of nano silica oxide (SiO_2) can enhance the adsorption capacity of bentonite [8]. Furthermore, stated that during the CPO bleaching process, β-carotene compounds interact with SiO_2 and Al_2O_3. Therefore, this study examines the modification of BE derived from bentonite with varying concentrations of nano SiO_2 (5%, 10%, and 15% w/w) and its application in the CPO bleaching process. The modified bentonite is characterized through Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) analyses. The performance of the modified bentonite as a CPO bleaching agent is evaluated based on parameters such as β-carotene concentration, Deterioration of Bleachability Index (DOBI) value, Free Fatty Acid (FFA), acid number, and moisture content. The objective of this study is to develop a modified bentonite with enhanced performance, reduce BE usage during CPO bleaching, and minimize Spent Bleaching Earth (SBE) waste.

METHOD

Materials

The materials used in this study included Bleaching Earth (BE) of the bentonite type obtained from Padang, and nano silicon dioxide (SiO_2) with a purity of 99.5% and a particle size of 8.6 nm, purchased from Merck (USA). Crude Palm Oil (CPO) was sourced from a CPO factory located in Padang. Analytical-grade n-hexane (85%) and ethanol (90%) were purchased from Merck and supplied by PT. Medisia Sainsindo, Indonesia. Phosphoric acid (H_3PO_4) at a concentration of 40% was prepared at 0.5% v/v and used for the degumming process. Distilled water (aquadest) was also obtained from PT. Medisia Sainsindo.

Fabrication of BE-nano SiO_2

5 grams of bentonite was modified with nano SiO_2 at concentrations of 5; 10; and 15% (w/w) in 150 ml of ethanol, designated as M5%, M10%, and M15%, respectively. The modification process involved stirring the mixture for 3 h at 70°C, followed by filtration and drying at 100°C for 5 hours [8][9]. The CPO was initially degummed by adding 0.5 %v/v H_3PO_4 and stirring for 30 minutes at 70°C [10]. After degumming, the bleaching process was conducted by adding 0.5%w/v of the modified BE to 100 ml of CPO solution and stirring for 30 minutes at 90°C. The performance of the modified bentonite was assessed based on the reduction in DOBI value and β-carotene concentration. The most effective concentration of

nano SiO_2 for bentonite modification was determined based on the performance of nano SiO_2-modified BE in the CPO bleaching process.

Materials characterization

The functional groups of fabricated materials were analyzed using fourier transform infrared spectroscopy (FTIR, Perkin-Elmer UATR Spectrum Two, USA) over a wavenumber range of 4000–400 cm^{-1}. The morphology properties of natural BE and modified BE were investigated using Scanning Electron Microscope (SEM, JEOL JSM-6510LA, Japan).

Free fatty acids (FFA)

A 5 g sample was precisely weighed and placed in an Erlenmeyer flask with 50 ml of 95% ethanol. The mixture was heated to boiling for full dissolution, then a few drops of phenolphthalein (PP) indicator were added. The hot solution was titrated with sodium hydroxide (NaOH) until a brick-red endpoint appeared [11]. The %FFA value was then calculated using Equation 1.

$$\%\text{FFA} = \frac{V_{\text{titration}} \times N_{\text{NaOH}} \times 25.6}{\text{Sample weight}} x\ 100 \quad (1)$$

$$\text{Acid Number} = \frac{V_{\text{titration}} \times N_{\text{NaOH}} \times 25.6}{\text{Sample weight}} \quad (2)$$

DOBI number and β -carotene

A 0.10 g sample was accurately weighed into a 25 ml volumetric flask, filled to the mark with 95% n-hexane, and thoroughly mixed for complete dissolution. The absorbance spectrum was then recorded from 200–500 nm using a Shimadzu 1800 UV-Vis Spectrophotometer [12]. The absorbance measured at 446 nm (A 446) was utilized to determine the concentration of β-carotene according to Eq. 2. Additionally, the absorbance values at both 446 nm (A 446) and 269 nm (A 269) were employed to calculate the DOBI using Eq. 3.

$$\beta\text{-carotene concentration} = \frac{A_{446} \times 283 \times 25}{\text{Sample weight} \times 100} \quad (3)$$

$$\text{DOBI value} = \frac{A_{446}}{A_{269}} \quad (4)$$

CPO color

The color of CPO was assessed using the AOCS Cc 13b-45 method and measured with a Lovibond Tintometer Color scale at 70°C. To ensure optimal accuracy, the analysis was performed using glass cells with a path length of less than 1 inch (25.4 mm) [13]. The color evaluation of CPO was based on the Red (R) and Yellow (Y) readings obtained from the Tintometer.

Moisture content

Moisture content was determined using the gravimetric method with an oven. Approximately 5 grams of the CPO sample were accurately weighed into a dry, pre-weighed crucible. The sample was then heated in an oven at 105°C for 1 hour to evaporate the water content in the oil. After heating, the crucible was cooled in a desiccator until it reached room temperature and then weighed again. The difference in weight before and after heating was calculated as the moisture content of the sample.

$$\text{Moisture Content} = \frac{\text{W1} - \text{W2}}{\text{W1}} \text{ x } 100 \quad (5)$$

W1 represents the weight of the sample before drying, measured in grams. Meanwhile, $W2$ is the weight of the sample after drying, also in grams.

RESULT AND DISCUSSION

Materials characterization

FT-IR spectral analysis was conducted to examine changes in the functional groups of modified BE with the results shown in Figure 1.

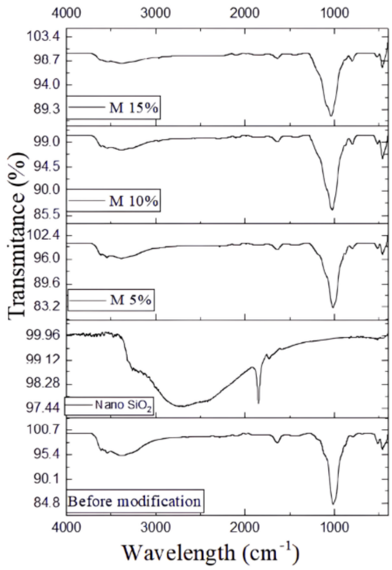

Figure 1. FTIR Spectrum of Modified Bentonite

The Figure 1 displays spectral differences in bentonite before and after modification with varying concentrations of nano SiO_2. The summary of key FTIR peak data for bentonite before and after modification with various concentrations of nano SiO_2 is presented in Table 1.

Table 1. FTIR Peak Data of Bentonite Before and After Modification with Nano SiO_2

Wavelength (cm^{-1})	Assignment	Natural Bentonite	M5%	M10%	M15%
~3434	–OH stretching (hydroxyl groups)	Strong, broad	Decreased	Further decreased	Least distinct
3700–3500	Structural –OH vibration	Present	Reduced	Reduced	Significantly reduced
1111	Si–O stretching	Moderate	Broadened	Broader	Broadest, lower transmittance
1031	Si–O–Si stretching (tetrahedral layer)	Present	Present	Present	Present
520	Al–O–Si bending	Present	Present	Present	Present

Table 1 presents the FTIR peak data of bentonite before and after modification with various concentrations of nano SiO_2, showing the changes in functional group regions. As illustrated, increasing the concentration of nano SiO_2 results in more pronounced changes in the 3700–3500 cm^{-1} range, associated with structural -OH stretching vibrations. At the broad peak around 3434 cm^{-1}, higher nano SiO_2 concentrations decrease transmittance, making the peak less distinct. This decrease indicates a reduction in -OH groups within bentonite due to the extensive substitution of octahedral atoms by nano SiO_2. Additionally, the broadening of the peak at 1111 cm^{-1}, corresponding to Si-O stretching, further supports this observation [14].

The Si-O stretching at 1111 cm^{-1} becomes broader, and the transmittance decreases as the nano SiO_2 concentration increases, particularly at 15% nano SiO_2 addition. These results suggest that Si-O stretching is enhanced with higher nano SiO_2 concentrations, significantly impacting the structural properties of the modified bentonite. Additionally, the Si-O-Si and Al-O-Si stretching peaks in the tetrahedral layer are observed at 1031 cm^{-1} and 520 cm^{-1}, respectively. These findings align with a study, where bentonite modified with chitosan exhibited a peak at 1010 cm^{-1}, corresponding to the characteristic Si-O-Si absorption group of bentonite [15].

The surface morphology of the modified bentonite was analyzed using SEM to evaluate the physical alterations and confirm the incorporation of nano SiO_2. The SEM analysis results showing the surface morphology of bentonite before and after modification with nano SiO_2 can be seen in Figure 2.

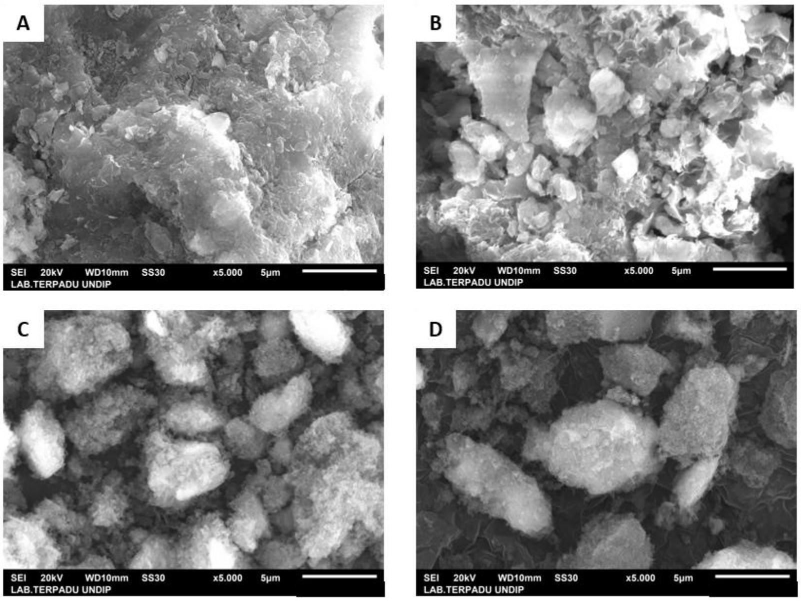

Figure 2. (A) Bentonite without modification, (B) M5%, (C) M10%, (D) M15%

Figure 2 presents the SEM images, highlighting significant changes in the surface morphology of bentonite after modification with varying concentrations of nano SiO_2. In Figure 2 (A), which depicts bentonite prior to modification, the surface appears relatively smooth with some plate-like structures characteristic of natural bentonite. The surface is dense with minimal visible pores. In contrast, Fig. 2 (B), showing bentonite modified with 5% nano SiO_2, reveals notable changes in surface morphology. The surface appears rougher, with increased irregularities and enhanced porosity. The dispersion of nano SiO_2 particles on the surface contributes to these changes. Fig. 2 (C), which represents bentonite modified with 10% nano SiO_2, exhibits an even rougher surface compared to the 5% modification. The irregularities and porosity are more pronounced, indicating a more uniform distribution of nano SiO_2 particles. Finally, Fig. 2 (D), depicting bentonite modified with 15% nano SiO_2, shows the roughest surface, with significantly increased porosity and irregularities. The nano SiO_2 particles are extensively dispersed across the surface, resulting in a highly porous and irregular structure. These observations align with the study, where bentonite modified with nano SiO_2 exhibited greater agglomeration compared to unmodified bentonite due to the incorporation of nano SiO_2 into the bentonite lattice [10].

Performance evaluation of bentonite-nano SiO_2 as bleaching agent

BE-SiO_2 was used as a bleaching agent for CPO to assess its performance in enhancing Bleached Palm Oil (BPO) quality. The concentration of β-carotene and the DOBI value following the bleaching process with bentonite modified at various nano SiO_2 concentrations are depicted in Figure 3.

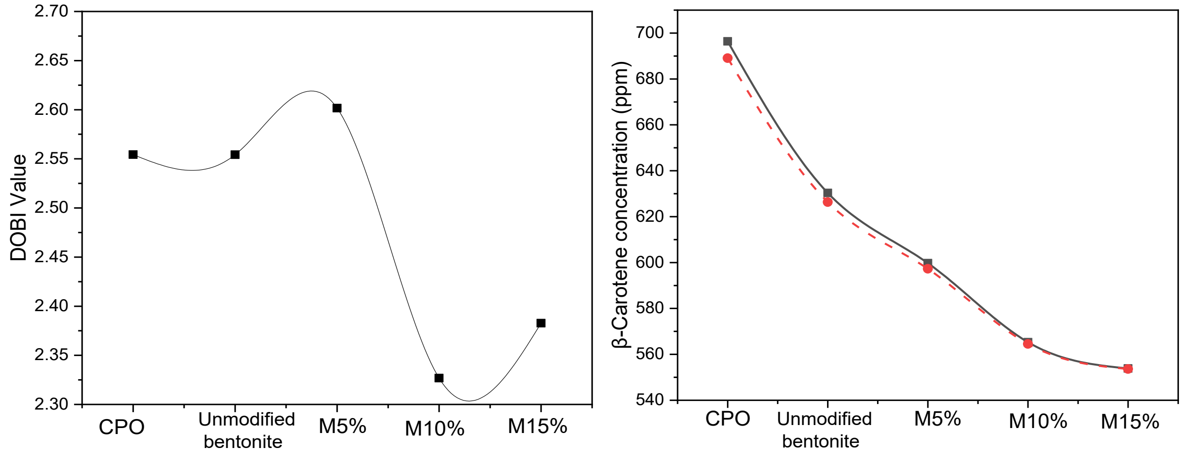

Figure 3. (a) DOBI Value of BPO and (b) β-Carotene concentration after treatment by BE-nano SiO2 with various nano SiO2 embedment concentration

Fig. 3 (a) presents the DOBI values for BPO, which were determined by measuring the test solution at A446 and dividing it by the A 269 using a UV-Vis spectrophotometer [16]. DOBI value greater than 2 indicates that the CPO is optimal for bleaching. DOBI value below 2 suggests potential issues in the bleaching process due to the difficulty in removing β-carotene [2]. Ideally, a DOBI value exceeding 2.3 is desired, indicating low levels of oxidation products. The results show a notable decrease in DOBI values with M10% and M15% modifications, with values lower than the original CPO DOBI. The DOBI value gives the palm oil refiner information on what type of bleaching earth to use and how much is required.

In other side, Fig. 3 (b) illustrates the variation in β-carotene concentration in BPO. The data indicate a decrease in β-carotene concentration with increasing nano SiO_2 content in the modified BE. Specifically, unmodified bentonite yields a β-carotene concentration of 630.362 ppm, while bentonite modified with 15% nano SiO_2 (M15%) results in a reduced β-carotene concentration of 553.838 ppm. These findings demonstrate that modifying bentonite with nano SiO_2 enhances the performance of bleaching earth in the CPO bleaching process. The increased nano SiO_2 content contributes to a higher binding capacity for β-carotene, indicating improved bleaching efficiency [7] Bentonite, with its inherent electropositive inorganic cations, typically exhibits hydrophilic properties that attract water to form hydrates. Surface modification is thus necessary to enhance the hydrophobicity of bentonite, improving its interaction with organic substances [17].

Table 2. Analysis of the quality of BPO resulting from bleaching with bentonite modified with nano SiO_2 variations

Parameter	CPO	BPO	BPO Unmodified bentonite	BPO (M5%)	BPO (M10%)	BPO (M15%)
Water content (%)	1.002	1.002	1.002	1.001	1.002	1.002
Acid number	0.0060	0.0064	0.0068	0.0086	0.0072	0.0070

FFA (%)	3.84	4.512	4.352	5.4784	4.608	4.5056
Colour Red/Yellow	2.1/21	1.5/15	1.6/16	1.6/16	1.7/17	1.5/15

Table 2 presents the quality analysis data of BPO, including parameters such as water content, FFA, acid value, and Lovibond color values. The bleaching process using modified bentonite did not induce significant changes in most quality parameters of BPO. However, the color values (red/yellow) obtained after the addition of modified bentonite were substantially lower than those of the CPO baseline (2.1/21), specifically 1.5/15. Despite this improvement, the acid value and FFA increased with both unmodified and modified bentonite. For instance, the acid value reached 0.0086 with the addition of M5%, which also resulted in an increased FFA value. FFA following degumming and bleaching may be attributed to the processing temperature, as well as the effects of oxidation and enzymatic hydrolysis, which lead to the formation of FFA and glycerol [18]. Based on the quality analysis results, DOBI values, and β-carotene concentration, the optimal bleaching earth is M15%. This modification demonstrated the lowest β-carotene content, a color value of 1.5/15 (Red/Yellow), and lower FFA and acid values compared to other modified bentonite samples. Silica-based nanoparticles, such as nano SiO_2, exhibit a higher specific surface area compared to iron-based and alumina-based nanoparticles, contributing to their superior adsorption capacity [17].

CONCLUSION

Based on the research conducted, the modification of bentonite with nano SiO_2 resulted in different characteristics compared to natural bentonite. SEM characterization showed that the surface of unmodified bentonite was relatively smooth with some plate-like structures typical of natural bentonite. Furthermore, FTIR results showed that increasing the concentration of nano SiO_2 led to more noticeable changes in the 3700–3500 cm^{-1} range, which is related to the stretching vibrations of structural -OH groups. Bentonite modified with 15% w/w SiO_2 was the most effective composite, reducing the red/yellow color index to 1.5/15 an improvement of more than 25% compared to unmodified bentonite.

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