



BENTONITE-BIOCHAR COMPOSITE FOR BLEACHING OF CRUDE COCONUT OIL

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ABSTRACT

CNO (Crude Coconut Oil) is oil extracted from coconut flesh that is orange or brownish yellow. Usually, CNO refining process is done through bleaching process or blanching to remove color. In general, this oil blanching process using bleaching earth or bentonite as an adsorbent. In this study, bentonite was combined with biochar to improve its adsorption ability. The purpose of this research is to investigate the process of making bentonite-biochar composite from cassava peel and its application in CNO bleaching process. The variables studied in the manufacture of bentonite - biochar composite for CNO blanching process were the ratio of bentonite: biomass, and the influence of temperature on the composite manufacturing process. The maximum color removal was 99.2 %.

Keywords: CNO, bentonite- hydro-char, adsorption.

1. INTRODUCTION

Cooking oil is one of the world's largest commodities traded globally. Indonesia is a country that accounts for 80-85% of world's cooking oil production. The high production of cooking oil is also accompanied by high consumption of cooking oil in Indonesia. According to data obtained by Indonesia Statistical Centre in 2014 consumption of cooking oil in Indonesia reached 1, 120, 000 MT. The high consumption of cooking oil in Indonesia needs to be accompanied by increasing production of cooking oil. Therefore, to obtain quality cooking oil, a series of oil purification processes are required. One of the most critical stages in the oil purification is bleaching or oil blanching using adsorption method.

In general, in the cooking oil industry used bentonite or known as bleaching earth and activated carbon as an adsorbent on oil blanching process. This bleaching process takes place in two stages: adsorption with bentonite followed by adsorption using activated carbon. The result of adsorption using bentonite depends on the quality of bentonite used. To improve the efficiency of this oil purification process, a biomass-bentonite composite has a high adsorption capacity so that the oil purification process can take place once.

Agricultural wastes which abundantly available are promising raw material for the production of the adsorbent. One of these agricultural wastes is cassava peel. Cassava peel has considerable carbon content found in the form of cellulose, hemicellulose, and lignin. This high carbon content can be utilized as the raw material of adsorbent by converting into hydro-char. Hydro-char is a carbon produced from the process of hydrothermal carbonization (HTC) that is the thermochemical conversion of biomass as its raw material (Funke & Ziegler, 2010; Guiotoku *et al.*, 2011).

In this study, the bentonite-hydro-char composite was made as an adsorbent for oil purification process. By combining bentonite with hydro-char made from biomass into a composite, a new adsorbent with a larger adsorption

capacity was obtained. With higher adsorption capacity than commercially available adsorbents, higher removal efficiency was achieved. The composite prepared in this study was used as the adsorbent for bleaching of low-quality crude coconut oil.

2. MATERIALS AND METHODS

2.1 Materials

The bentonite used in this study was obtained from Ponorogo, East Java, Indonesia. Before use, the bentonite was purified using 30 % of hydrogen peroxide solution. The purification was conducted at room temperature for 24 hours under continuous stirring. The purified bentonite was then separated from the solution and dried at 105 °C for 24. The dried bentonite was pulverized until its particle size around 100/200 mesh. Crude coconut oil (CNO) was purchased from a local company near Surabaya, Indonesia. Cassava peel was obtained from Semarang, Central Java, Indonesia. Before use, the cassava peel was dried under the sunlight and pulverized until its particle size around 100/200 mesh.

2.2 Bentonite - biochar preparation

Bentonite - biochar composite was prepared by the following procedure: a mixture of bentonite and cassava peel powder with the ratio of 1:1, 1:2, 1:3, and 1:4 was placed in a tubular furnace. Nitrogen gas with a volumetric flow rate of 3 liters/min was introduced into the tubular furnace. Subsequently, the furnace was heated at 450°C under a continuous flow of nitrogen gas. After 30 min of the heating process, the flow of nitrogen gas was switched by the flow of carbon dioxide with a flow rate of 1 liter/min for 10 min. Detail of the procedure can be seen elsewhere (Ismadji *et al.*, 2016).

2.3 Characterization of bentonite - biochar composite

The bentonite - biochar composites were characterized using nitrogen sorption, Scanning Electron Microscopy (SEM), and Fourier Transform Infra-Red



(FTIR) methods. The nitrogen sorption measurement was carried out on an automated Micromeritics ASAP 2010 adsorption analyzer at -196°C . Before the nitrogen sorption measurement, all of the samples were degassed under high vacuum condition at 150°C . The BET surface area was calculated at relative pressures of 0.05 to 0.3, while the pore volume of the adsorbent was obtained at the highest relative pressure (0.995). The surface topography of bentonite - biochar composites were acquired with a JEOL JSM-6500F SEM. The samples were coated with thin layer platinum before the SEM analysis. The FTIR analysis was conducted in FTIR using SHIMADZU 8400S using the KBr method. The FTIR spectra were obtained at wavenumber range of $4000 - 500\text{ cm}^{-1}$.

2.4 Bleaching of CNO using bentonite - biochar composite

The phosphatide element in CNO was removed by the degumming process. The degumming process was conducted by adding phosphoric acid solution (0.05 % of the oil weight) into CNO. Before the addition of phosphoric acid, the CNO was heated at 80°C and after the addition of phosphoric acid; the mixture was constantly

stirred at 400 rpm for 15 min. After the degumming process had completed, the gum was separated from the CNO by centrifugation. The color of the degumming oil was analyzed using Lovibond tintometer.

The bleaching process was carried out at several temperatures (80, 90, and 100°C). A known amount of composite (3.0 gram) was added to 100 mL of degumming CNO. Subsequently, the temperature of the system was increased until the desired temperature was reached, the system was kept at that temperature for 60 min and stirred at 400 rpm. After the bleaching process had completed, the oil and composite were separated using centrifugation. The color index of oil was determined using Lovibond tintometer.

3. RESULTS AND DISCUSSIONS

3.1 Characterization of the adsorbents

The adsorption and desorption isotherms of bentonite and bentonite - biochar composite (1:4) are given in Figure-1. Some microporous structure of both bentonite and composite are observed in Figure-1.

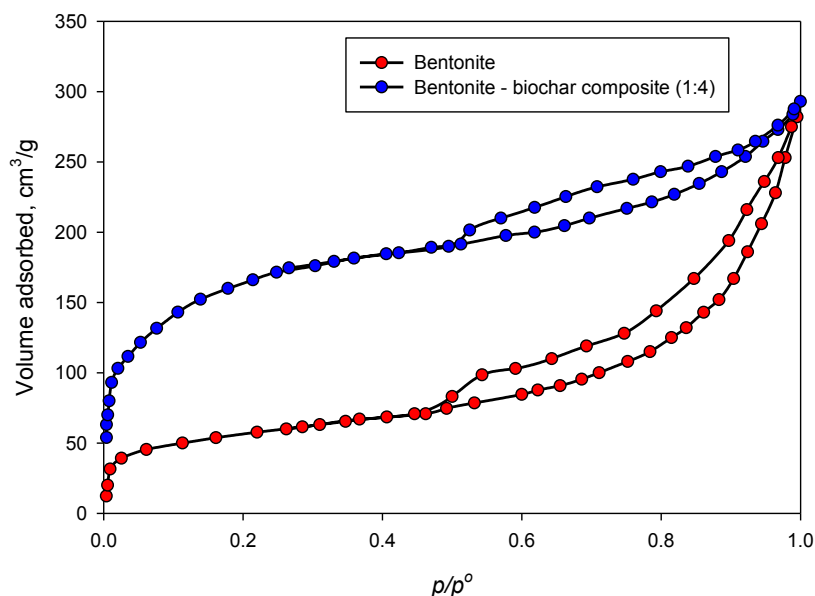


Figure-1. Nitrogen sorption isotherm of bentonite and bentonite - biochar composite.

The presences of microporous structure on both of samples indicate by rapid intake of nitrogen gas at a low relative pressure. The nitrogen adsorption and desorption isotherms of bentonite indicate that this adsorbent has type H_3 hysteresis. This type of hysteresis shows that bentonite

possesses a slit-shaped pore characteristic. A combination of microporous and mesoporous pore structure is observed for bentonite- biochar composite as seen in Figure. The BET surface area and pore volume of bentonite and composites are summarized in Table-1.

**Table-1.** The physical characteristic of bentonite and composites.

Adsorbent	BET, m ² /g	Pore volume, cm ³ /g
Bentonite	69.5	0.158
Bentonite - biochar (1:1)	148.3	0.188
Bentonite - biochar (1:2)	191.2	0.214
Bentonite - biochar (1:3)	267.3	0.274
Bentonite - biochar (1:4)	352.1	0.381

The SEM images of bentonite and bentonite - biochar composites are given in Figure-2. The surface morphology of all samples indicates that the bentonite and composites have the heterogeneous structure.

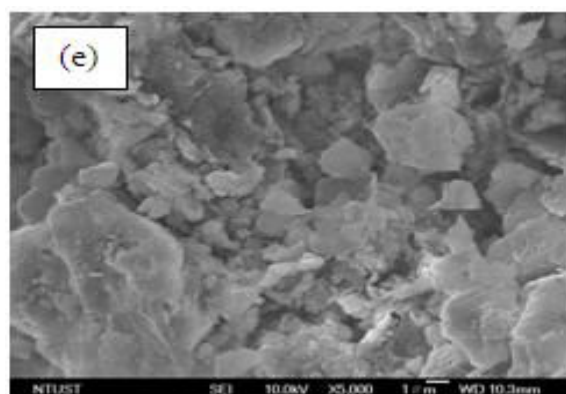
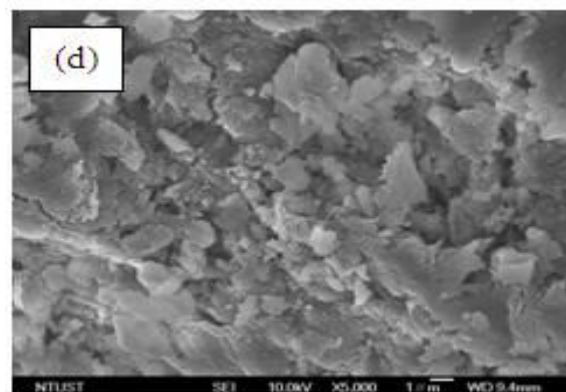
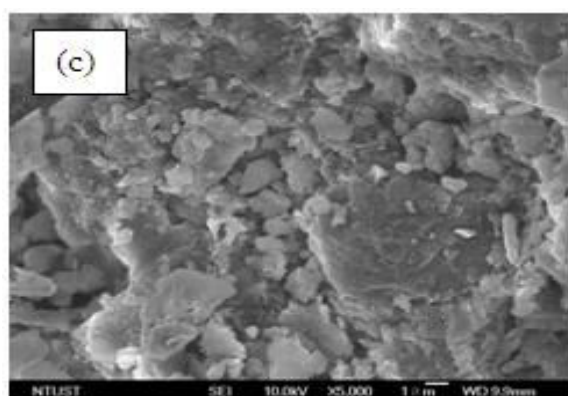
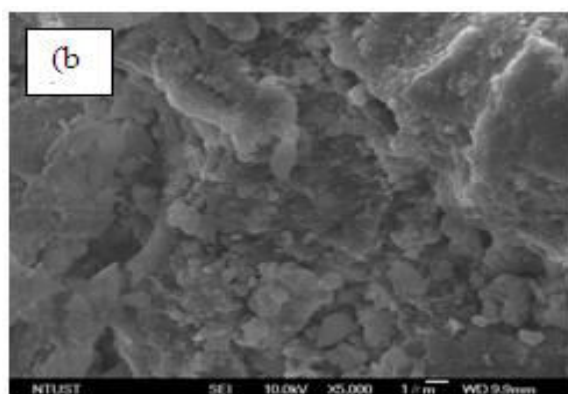
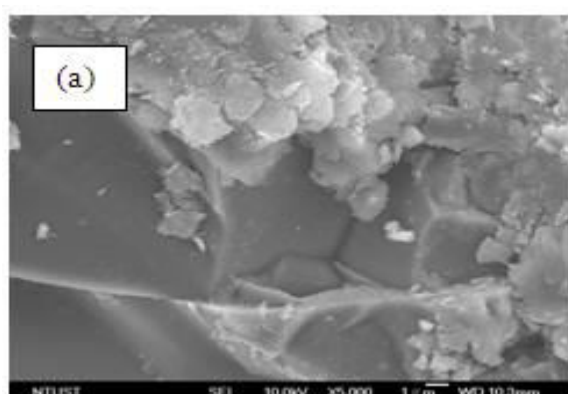


Figure-2. SEM micrographs of (a) bentonite, (b) bentonite - biochar composite (1:1), (c) bentonite-biochar composite (1:2), (d) bentonite-biochar composite (1:3), (e) bentonite - biochar composite (1:4).

FTIR spectra of bentonite - biochar composites are given in Figure-3. Several characteristic bands of montmorillonite are still observed in this Figure such as Al(Mg)-O-H stretching (3623 cm⁻¹), Si-O-Si stretching vibration (1058 cm⁻¹), Al-OH (904 and 625 cm⁻¹), and (Al, Mg)-O (842 and 795 cm⁻¹) (Koswojo *et al.*, 2010; Unlu *et al.*, 2012). The presence of the carboxylic group on the surface of the composite was observed at wavenumber 1708 cm⁻¹ (stretching vibration of C=O) (Prahaz *et al.*, 2008). A relatively low-intensity peak at wave number around 3111 cm⁻¹ represents O-H stretching vibration in phenol was also observed in all composite. The presence of methyl group in the composite was observed at wave number 2906 cm⁻¹.

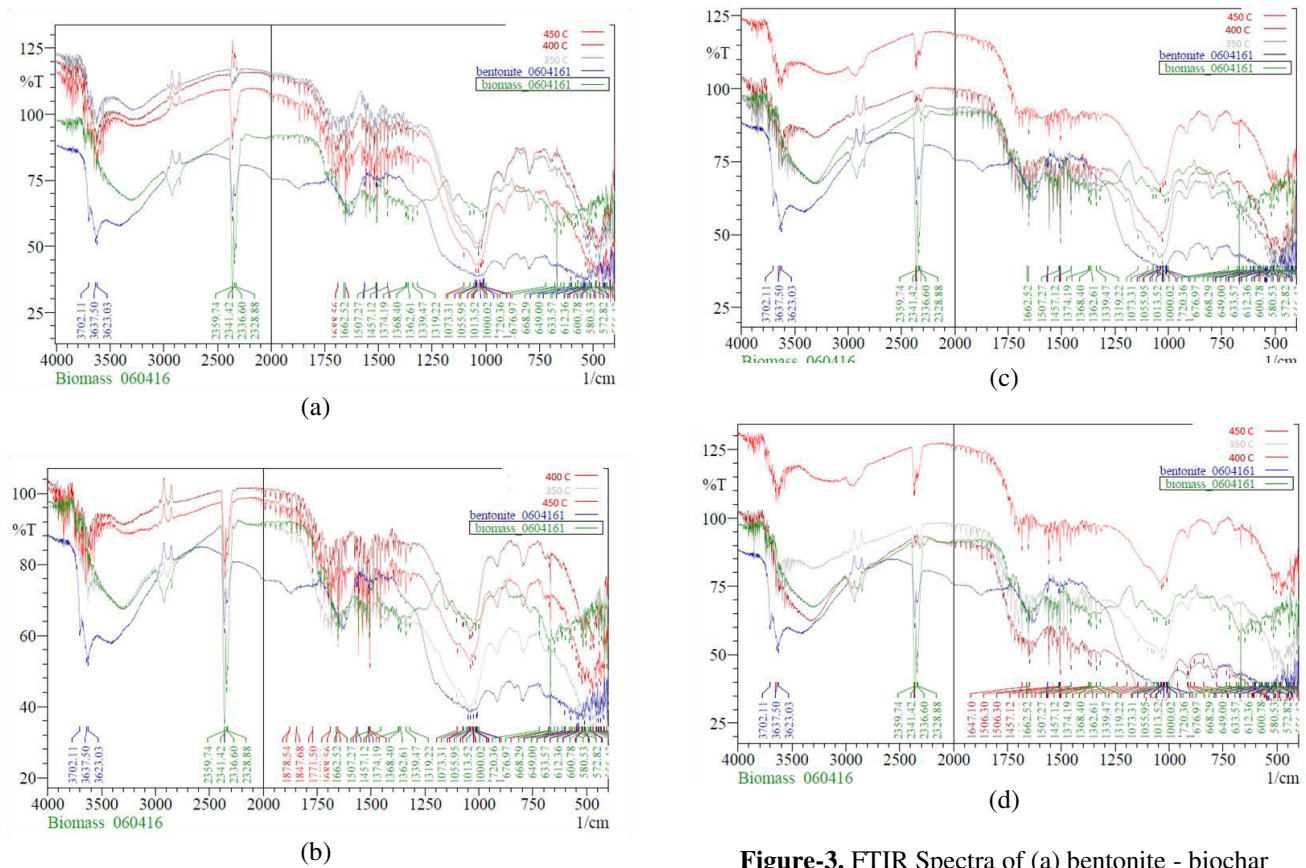


Figure-3. FTIR Spectra of (a) bentonite - biochar composite (1:1), (b) bentonite - biochar composite (1:2), (c) bentonite - biochar composite (1:3), (d) bentonite - biochar composite (1:4)

3.2 Bleaching of CNO

The bleaching experiments of CNO using bentonite-biochar composites were conducted at 80, 90, and 100°C, and the results are given in Figure-4.

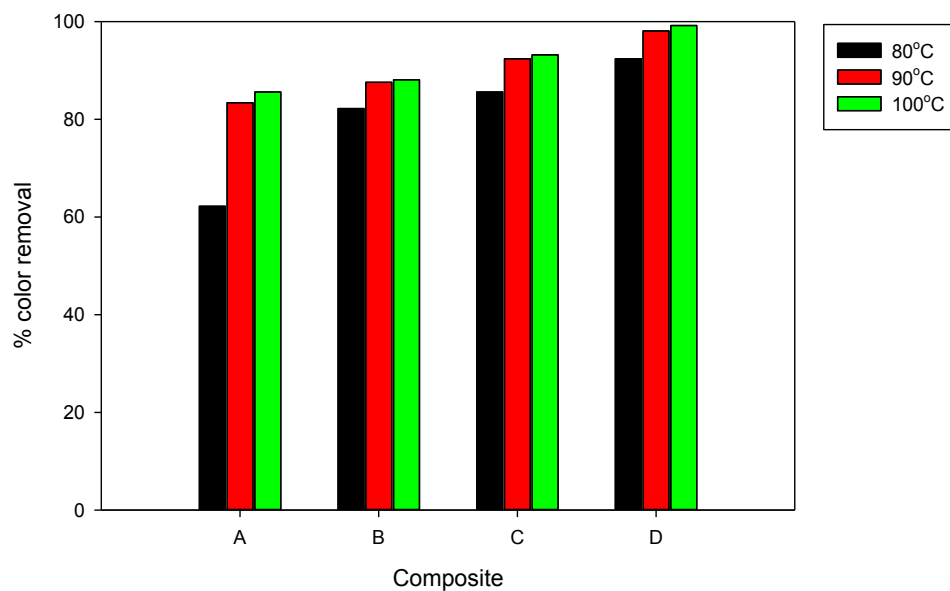


Figure-4. Bleaching of CNO using A. composite 1:1, B. composite 1:2, C. composite 1:3, D. composite 1:4.



From Figure-4 it can be seen that the ratio of bentonite and cassava peel powder gave significant influence on the removal of color from CNO. During heat treatment at high temperature, the cassava peel will decompose into char, condensable gasses, and gases. The condensable gases and gases leave the system while the solid (biochar) remains in the system with bentonite to form bentonite-biochar composite. During the activation with CO_2 , some of the carbons in the biochar structure were oxidized to form CO or other simple gases and create some micropores in the composite. With the increase of the amount of cassava peel, the amount of biochar also increase, and the amount of micropore in the composite also increase. With the increase of micropores in the system, the adsorption active sites also increase as indicated by the increase of BET surface area in Table-1. The increases of adsorption active sites in the composite enhanced the uptake of color, and increase the removal efficiency.

The maximum uptake or maximum removal of the color from CNO was achieved at 100 °C. The adsorption mechanism of the color uptake from CNO by the composites is chemisorption. For chemisorption, the temperature has a positive influence on the amount uptake, the increase of temperature increase the adsorption of color as indicated in Figure-4.

4. CONCLUSIONS

Cassava peel was used as the precursor for the preparation of bentonite-biochar composites. The composites were prepared with a different ratio of bentonite and cassava peel. The bentonite - biochar composites were characterized using nitrogen sorption, Scanning Electron Microscopy (SEM), and Fourier Transform Infra-Red (FTIR) methods. The adsorption capability of composites was tested for bleaching CNO. The bleaching capabilities of composite increase with the increase of the amount of cassava peel powder. The increase of temperature enhanced the removal efficiency of the composite.

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