



## Note

## Bentonites modified with anionic and cationic surfactants for bleaching of crude palm oil

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## ABSTRACT

Bentonite Pacitan was modified with cetyl trimethylammonium bromide (CTAB) and LAS for bleaching crude palm oil. The organo-bentonites were prepared by normal heating and microwave irradiation. The advantage of using microwave irradiation is time efficiency. The bentonites were characterized by FTIR and XRD analysis. LAS modified bentonite was more effective as bleaching agent than CTA-bentonite.

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### 1. Introduction

The chemical nature and pore structure of bentonites generally determine their adsorption ability (Juang et al., 2002; Koyuncu, 2008). Because of hydrophilicity bentonites are usually not effective in adsorbing organic compounds. The adsorption capacity can be improved by surface-modification (Bergaya et al., 2006; Komadel and Madejova, 2006; Lagaly et al., 2006; Churchman et al., 2006; Khenifi et al., 2007; Ma and Zhu, 2007; Akimbaeva and Ergozhin, 2007; Koyuncu, 2008; Zhu et al., 2008). Bentonites are usually modified by alkaline, acid, and organic activation.

Bentonite is found in various regions in Indonesia in huge and abundant quantity, from the west to the east part of Indonesia. Currently, the major use of this material is for purification of crude palm oil and as drilling mud. The bentonite (then known as bleaching agent) used for discolouring crude palm oil usually is obtained by reacting bentonite with hot inorganic acids. The available acid-activated bentonite in Indonesian local market usually has very low pH value (due to excess use of acid) and is unstable in terms of quality. The use of these kinds of acid-activated bentonite for the purification of palm oil often creates many problems to oil companies such as corrosion of the process vessels, increasing of FFA (free fatty acid) and PV (peroxide

value) in oil products, etc. Furthermore, the excessive use of acid during activation can cause environmental problems.

In our study bentonite was modified with cationic and anionic surfactants and used for colour removal of low quality crude palm oil.

### 2. Materials and methods

The bentonite was obtained from a bentonite mining site located in Pacitan, East Java, Indonesia. The raw material was dried at 105 °C for 24 h and ground to obtain the particles <60/80 mesh. The cation exchange capacity of bentonite was determined to be 0.47 meq/g on the basis of the ASTM C837-99 procedure. Brief descriptions of the procedure are as follows: 300 mL of distilled water was added to 2 g of dried bentonite, the mixture stirred until the bentonites were uniformly dispersed. The pH of the slurry was measured; then sufficient amount of sulfuric acid was added to the slurry to bring the pH within the range from 2.5 to 3.8. The stirring was continued while the pH was being adjusted. With the slurry still under the mixer, the buret was filled with methylene blue solution, and 5 mL of methylene blue was added to the slurry, and stirred for 2 min. One drop of the slurry was placed on the edge of the filter paper. The end point was indicated by the formation of a light blue halo around the drop. Surfactants used in this experiment were cetyl trimethylammonium bromide (CTAB) and linear alkylbenzene sulfonate (LAS), purchased from Sigma Aldrich in analytical grade and used without any further treatment.

The organo-bentonite was prepared by normal heating and microwave irradiation. The amount of the surfactants added was 1.5 times of cation exchange capacity (CEC). In the conventional method, 25 g bentonite was mixed with 250 mL surfactant solutions and shaken for

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24h using a thermostatic shaker bath at 30 °C. The bentonite was separated by centrifugation at 5000 rpm for 15 min, washed several times with 500 mL deionised water, dried at 105 °C for 2 h and ground to pass 200 mesh. Microwave irradiation was conducted using 700 W microwaves power for 2 min.

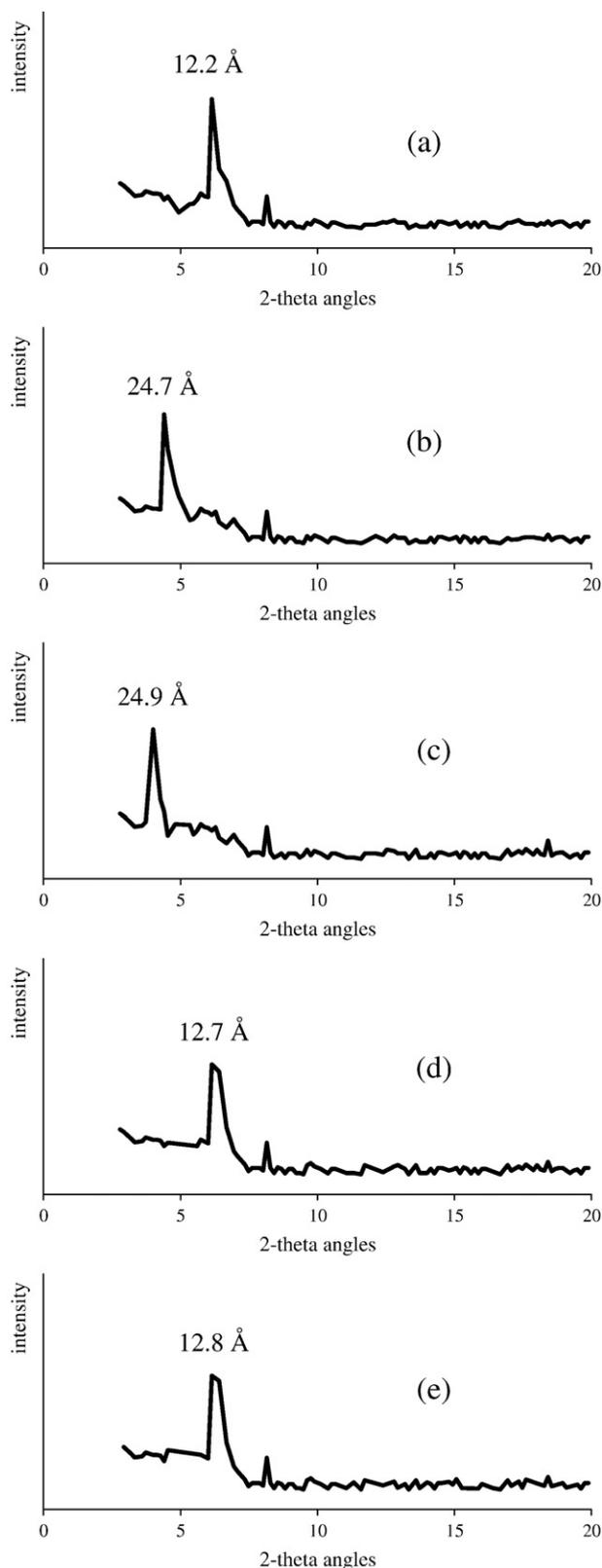


Fig. 1. XRD patterns of (a) B, (b) COC, (c) COM, (d) LOC, and (e) LOM.

Table 1

R (colour removal), FFA (decrease of free fatty acid content), PV (peroxide value) on degummed and bleached palm oil.

Oil	R (%)	FFA (%)	PV
Degummed	–	6.7813	1.4
Bleached B	49.35%	6.7457	0.4
Bleached COC	30.00%	6.4661	0.3
Bleached COM	31.05%	6.0600	0.3
Bleached LOC	65.26%	6.4279	0.3
Bleached LOM	65.44%	6.0622	0.3

Bleaching of crude palm oil process was performed using five different adsorbents: bentonite (B), CTA-bentonite prepared by conventional heating (COC) and microwave irradiation (COM), and LA-bentonites LOC and LOM. The amount of adsorbent used in the bleaching process was 3% (m/v) of degummed palm oil.

Total colour, free fatty acid content (FFA) and peroxide value (PV) of degummed palm oil and bleached palm oil were analyzed by several methods. The colour of palm oil was determined in a lovibond tintometer and the colour removal was calculated using Khrisnan equation (Srasra et al., 1989) as follows:

$$R = \frac{\text{total colour of (degummed palm oil - bleached palm oil)}}{\text{total colour of degummed palm oil}} \times 100\%$$

FFA and PV analyses were conducted according to the AOAC Official Method 940.28 and 965.33.

### 3. Results and discussions

The XRD patterns are shown in Fig. 1 together with the  $d_{001}$ -value (basal spacing). The basal spacing of COC and COM was increased to 24.7 Å and 24.9 Å, due to the intercalation of CTAB present in the bentonite (Li et al., 2006). As expected, LAS was not intercalated and the basal spacing of LOC and LOM remained at 12.7 Å and 12.8 Å.

All adsorbents (Table 1) reduced the colour of degummed crude palm oil. The highest colour removal was observed with LOM. The reason of the enhanced carotene adsorption is probably the interaction between the nuclei of LAS and carotene as shown in Fig. 2b, bentonite with its hydrophilic surface was not very effective in bleaching of palm oil. Molecular simulation using MM2 in Chem3D (Cambridge Soft) shows that steric hindrance of adsorption of  $\beta$ -carotene on CTA-bentonite was higher than on LA-bentonite. Thus, adsorption of  $\beta$ -carotene onto LA-bentonite is more favored than on CTA-bentonite, improving colour removal.

In general, the modification of Pacitan bentonite gave no significant effect on FFA removal during the bleaching process (Table 1). However, a significant decrease in PV value was observed. The decrease of the PV value during the bleaching process was due to the adsorption of peroxide compounds and transformation of peroxide into secondary oxidation products and followed by the adsorption of secondary oxidation products on the organo-bentonite particles (Rossi et al., 2003).

### 4. Conclusion

All bentonites used in this study reduced the colour of degummed crude palm oil. The highest effect was reached by bentonite modified with LAS during microwave heating.

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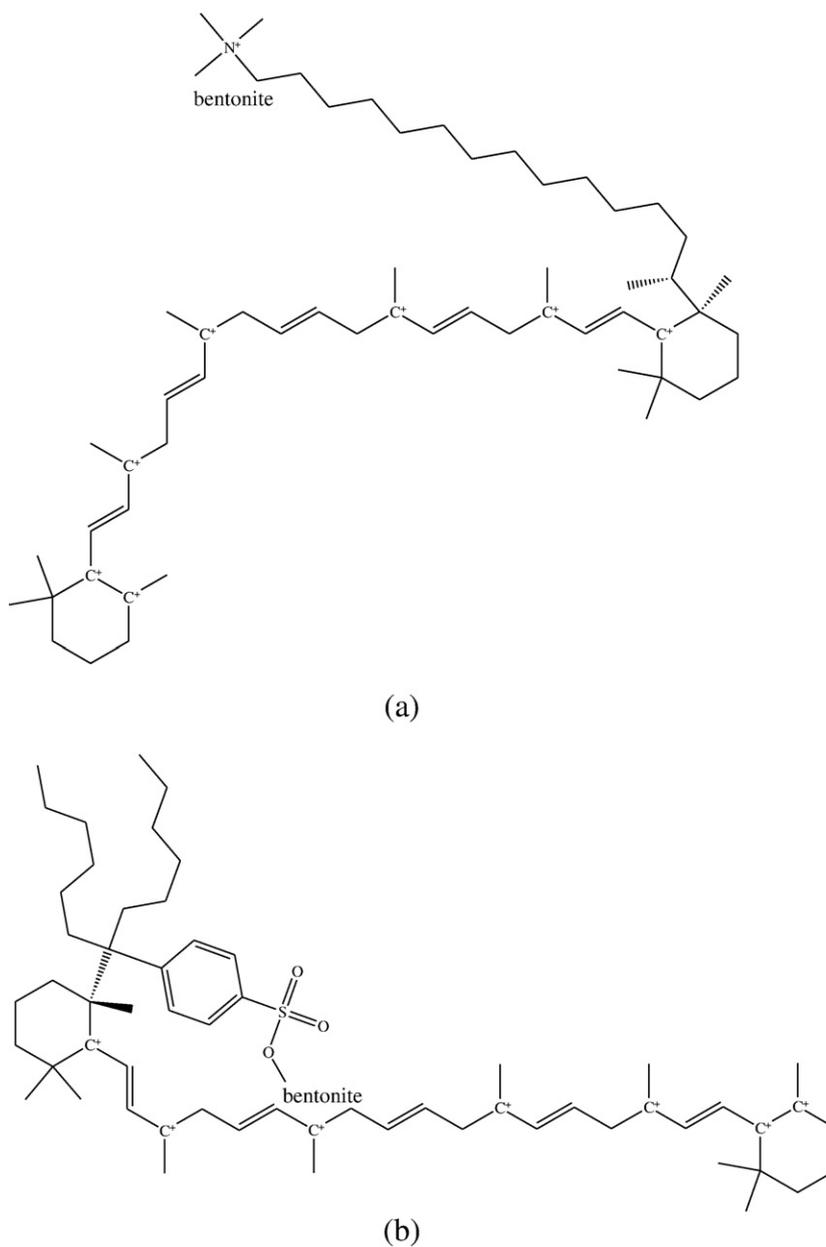


Fig. 2. Adsorption  $\beta$ -carotene on (a) CTA-bentonite and (b) LA-bentonite.

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