

INFLUENCE OF CHEMICAL COMPOSITION OF ACTIVATED CALCIUM BENTONITES AND SODIUM BENTONITES ON PALM OIL BLEACHING CAPACITY AND OIL QUALITY

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ABSTRACT

The efficiency of clays in bleaching degummed palm oil depends on their unique characteristics. This study sheds new light on a novel characteristic which impacts on the quality and bleaching capacity of activated clay. Although bentonites may originate from different areas, their structural modifications can make them ideally suited for bleaching. Calcium (Ca)-bentonites and sodium (Na)-bentonites, including activated forms of both clays, were investigated in depth. Interestingly, X-ray fluorescence (XRF) spectrometry indicated that the high bleaching capacity of Na-bentonite was correlated with silica (SiO₂) and alumina (Al₂O₃) contents in the range of 68.90%-85.20% and 8.96%-16.60% by weight (wt), respectively. The results showed that Na-bentonite treated with 1.5 M sulphuric acid (H₂SO₄) at a clay:acid ratio of 10:50 (w v⁻¹) and refluxing time of 8 hr had a higher bleaching capacity (78.04%) than commercial clay (67.09%). These characteristics can provide a suitable reaction space at the interlayer for adsorption of pigments and impurities. Moreover, the specific surface area and total pore volume of this activated clay also increased. After bleaching by treated Na-bentonite with 1.5 M H₂SO₄, degummed palm oil appeared to be of good quality, leading to less deterioration and rancidity due to decreased free fatty acid (FFA), unsaturated fatty acid, iron (Fe) and phosphorus (P) contents.

Keywords: bleaching, calcium bentonite, colour, palm oil, sodium bentonite.

Received: 27 October 2020; **Accepted:** 25 August 2021; **Published online:** 29 October 2021.

INTRODUCTION

Crude palm oil (CPO) is found to contain pigments, such as carotenoids, especially β -carotene, and their derivatives xanthophylls, chlorophyll, pheophytin, tocopherols and gossypol, as well as oxidised fatty acids, trace soaps and trace metals [copper ions

(Cu²⁺), ferric ions (Fe³⁺)] (Rossi *et al.*, 2011), which negatively influence the taste, smell and colour of the oil. Thus, removal of these substances causes a light yellowish colour and improves the stability and sensory quality of the oil for greater acceptance by consumers.

Bleaching is one of the most important steps in vegetable oil refining; in this step, pigments and undesirable impurities are removed by a process involving van der Waals forces and covalent bonds (Nwabanne and Ekwu, 2013). The efficiency of palm oil bleaching has been reported in many types of adsorbents such as palm oil boiler ashes, activated coconut pod ash, perlite, smectite, activated kaolinite, pyrolysis waste material peanut hulls, press mud, rice husks and synthetic

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silica) (Ismail *et al.*, 2016; Lau *et al.*, 2019; Meesuk and Seammai, 2010; Rossi *et al.*, 2003; Warasith and Goodman, 2020; Tebandeke *et al.*, 2014). However, adsorption materials used nowadays throughout the world by vegetable oil refiners are mainly activated montmorillonite clays due to its structural unit consisting of an octahedral alumina sheet sandwiched between two sheets of tetrahedral silica. Bentonite consists mostly of montmorillonite and has been widely employed in refining edible oil because its swelling, adsorption capacity and surface acidity properties make it suitable for wide variety of applications (Ayari *et al.*, 2005). Numerous literature reports affirm that the activation of bentonites with acids such as sulphuric, hydrochloric and oxalic acids, as well as anionic and cationic surfactants, could increase their adsorbent properties (Gunawan *et al.*, 2010; Joy *et al.*, 2007; Salawudeen *et al.*, 2007; Warasith and Goodman, 2020). Activation is expected to improve certain features of clay, such as its specific surface area, porosity, functional groups and framework collapse and, thereby, its bleaching capacity (Aung *et al.*, 2014; Joy *et al.*, 2007; Kashani Motlagh *et al.*, 2011; Nde *et al.*, 2019; Nwabanne and Ekwu; 2013; Silva *et al.*, 2013; Usman *et al.*, 2013). As mentioned above, various research efforts on the best conditions for modified clays and then new bleaching clays were investigated in terms of their characteristics and mechanisms for bleaching oil. However, it is difficult to control the quality of clays after modification because they originate from various locales, which affects their properties (Afolabi *et al.*, 2017). Therefore, this study sheds new light on a novel characteristic of bentonites which impacts the quality and bleaching capacity of activated clay. Although bentonite clays are sourced from different areas, the preparation of clays should result in suitable amounts of the major constituents, especially silica (SiO_2) and alumina (Al_2O_3). There are no reports about the influence of the chemical composition of bentonites after activation on bleaching capacity. For instance, in the case of kaolin, which has a different clay structure from that of bentonite, suitable SiO_2 and Al_2O_3 contents of activated kaolin for rice bran oil bleaching were approximately 62.40%-65.10% and 31.20%-4.20%, respectively (Aung *et al.*, 2015).

Therefore, the aim of this research was to determine a suitable chemical composition in the structure of activated Ca-bentonites and Na-bentonites to predict clay quality in the bleaching process. The correlation between unique characteristics such as chemical composition (SiO_2 , Al_2O_3 , iron (III) oxide (Fe_2O_3) and magnesium oxide (MgO) contents) in clays and bleaching capacities were evaluated. Meanwhile, the crystal structure, surface area and pore volume were characterised to support the properties of the clays. In addition,

aspects of oil quality after bleaching, such as free fatty acids (FFA), moisture content, peroxide value, iodine value and iron (Fe) and phosphorus (P) contents, were investigated.

MATERIALS AND METHODS

Materials

Samples of Ca-bentonite and Na-bentonite were obtained from Thep Agricultural Industry Co., Ltd., Thailand. The clay samples were dried at 70°C for 24 hr and sieved through 200 mesh to obtain particles (75 μm). Commercial bleaching clay (montmorillonite) obtained from Taiko Clay Marketing, Malaysia was used as the reference clay for the bleaching tests. Degummed palm oil was obtained from Olen Co., Ltd., Thailand. This oil had an orange-red appearance and contained 49.9 red and 5.9 yellow Lovibond units (Lovibond Tintometer Model F, Tintometer Ltd., United Kingdom).

Refluxing Process

Ten-gram bentonite samples were introduced into a round-bottom flask, 500 ml of sulphuric acid (H_2SO_4) in concentrations of 0.2-5.0 M was added to give a 1:50 (w v^{-1}) clay:acid ratio, and the mixture was then heated at 90°C for 4 hr under agitation. In the case of pre-heated materials, bentonites were prepared by heating in a muffle furnace at 300°C-700°C for 1 hr. Then, 10 g of each heated sample was refluxed with 500 ml of 2.0 M H_2SO_4 in a round-bottom flask under agitation at 90°C for 4 hr. Sodium bentonite samples were treated with various H_2SO_4 concentrations (0.6-3.0 M) at clay:acid ratios of 1:50, 5:50 and 10:50 (w v^{-1}), followed by refluxing at 90°C under agitation. The refluxing time was varied between 4, 6, 8 and 10 hr.

Next, the samples were washed several times with distilled water until the solution reached pH 3, corresponding to the optimum pH for bleaching of vegetable oil (Girgis, 2005). Subsequently, the samples were oven-dried at 80°C for 24 hr to reduce the moisture content, crushed into a powder form and sieved through 400 mesh. All samples were stored at room temperature for further experiments.

Bleaching Experiments

One-hundred-milligram clay samples were added into 10 ml of CPO, and then the mixtures were heated at 90°C in an oil bath for 30 min under constant agitation. After that, the oil samples were centrifuged at 4500 rpm for 15 min and then filtered through Whatman No. 5 filter paper. The bleaching process was performed in triplicate. Finally, the

colours of the palm oil samples were measured in a spectrophotometer at 450 nm (Thermo Scientific™, type Evolution 201, Waltham, MA, USA). The bleaching capacities were calculated according to Equation (1):

$$\text{Bleaching capacity (\%)} = [(A_0 - A) / A_0] \times 100 \quad (1)$$

where A_0 and A are the absorbances of the unbleached and bleached oil at 450 nm, respectively.

Characterisation of Clays by X-ray Diffraction (XRD), X-ray Fluorescence (XRF) and Measurement of Pore Structure

The XRD patterns of samples were recorded using a D8 Advance powder diffractometer (Bruker AXS, Germany) with Cu-K α radiation at $\lambda = 1.54056 \text{ \AA}$, operated at 40 kV and 40 mA in the range of 10°-100°. A wavelength-dispersive X-ray fluorescence (WD-XRF) spectrometer (model S4 Pioneer, Bruker AXS, Germany) was used to determine the elements present in clay samples. The XRF spectrometer was equipped with a 4-W Rh anode X-ray tube, 60-kV generators, and eight diffracting crystals of various diffraction spacings. The porous properties of clay samples were measured by the adsorption-desorption isotherms of nitrogen gas with a surface area analyser (Autosorb-1, Quantachrome Instruments, USA). The Brunauer-Emmett-Teller (BET) equation was applied to estimate the specific surface area, total pore volume, micropore volume and average pore size of samples.

Physicochemical Characterisation of Palm Oil

Initial crude oils and bleached oils were characterised by assessment of moisture content (method Ca 2c-25), FFA (method Ca 5a-40), iodine value (method Cd 1c-85), peroxide value (method 965.32) and fatty acid composition (method Ce 1e-91) (Cunniff, 1997; Firestone, 1997). The colour of oil samples was estimated using a 5 ¼" path length and a Lovibond Tintometer Model F, according to method Cc 13b-45 (Firestone, 1997). In addition, the oil samples were ashed according to the AOAC 999.11 method for Fe and P analysis (Jorhem, 2000). Fe content was determined using inductively coupled plasma optical emission spectrometry (ICP OES; Horiba, JY2000, Japan), while the P content was determined by the colorimetric method.

Statistical Analysis

The data were statistically analysed by one-way analysis of variance (ANOVA) using the Statistical Package for Social Sciences (SPSS). Significantly different means were assessed by Duncan's multiple range test ($p < 0.05$).

RESULTS AND DISCUSSION

Bentonite is aluminium phyllosilicate clay that consists mostly of montmorillonite but also contains impurities and is classified into Na or Ca types, depending on the dominant exchangeable cations (Hassan and Abdel-Khalek, 1998). Based on this classification procedure, Ca-bentonite and Na-bentonite were categorised as calcium (Ca-bentonite) and sodium Na-bentonite) types, respectively. In this study, however, the XRD pattern indicated that montmorillonite was a major component of bentonites (Figure 1).

Commercial clay (montmorillonite) has a bleaching potential for degummed palm oil of approximately 67.09%, while original of Ca-bentonite and Na-bentonite can bleach this oil approximately 9.02% and 0.89%, respectively. This may be due to the unique characteristics of these clays. Commercial clay, Ca-bentonite, and Na-bentonite are mainly composed of SiO₂, Al₂O₃ and Fe₂O₃. The SiO₂ and Al₂O₃ contents in commercial clay used for bleaching degummed palm oil are 80.70% and 10.20%, respectively. The XRF results of commercial clay showed a higher SiO₂ content (80.70%) than was found in Ca-bentonite (66.40%) and Na-bentonite (48.40%), while Al₂O₃ (10.20%) showed a lower content than was found in Ca-bentonite and Na-bentonite (20.30% and 19.40%, respectively) (Figures 2 and 3).

The element composition and content of clay structure can change the clay's unique characteristics. Interestingly, this study proposes that the bleaching capacity of degummed palm oil is related to suitable SiO₂ and Al₂O₃ contents. After acid activation, the crystallinity of Ca-bentonite and Na-bentonite was not changed (Figure 1) but the structure of Ca-bentonite and Na-bentonite was modified, as indicated by the change in the chemical composition, especially the SiO₂ and Al₂O₃ contents (Figures 2 and 3). This might be because the exchangeable cations and impurity elements in the interlayer cations were replaced by hydrogen ions (H⁺) ions, after which dissolution of elements in the octahedral sheet occurred. With increasing acid concentration, the SiO₂ content increased while the Al₂O₃, Fe₂O₃, MgO, calcium oxide (CaO), sodium oxide (Na₂O), and potassium oxide (K₂O) contents decreased, possibly because leaching was likely to occur in octahedral and exchangeable cations. On treatment of Na-bentonite with various H₂SO₄ concentrations, Na minerals were increasingly eluted from the interlayer of the clay, demonstrating that calcium ions (Ca²⁺) and magnesium ions (Mg²⁺) were the main exchangeable cations rather than Na. Meanwhile, Ca²⁺, potassium ions (K⁺), Mg²⁺ and sodium ions (Na⁺) still appeared in H₂SO₄-treated bentonite samples as exchangeable cations in the interlayer. The best activation condition was

Na-bentonite refluxed with 1.5-3.0 M H_2SO_4 solution, which correlated positively with SiO_2 and Al_2O_3 contents in the range of 74.80%-85.20% and 8.96%-13.30% by weight (wt), respectively, which was close to the composition of commercial clay.

It has been well documented that the orange-red pigmentation of degummed palm oil is mainly due to the presence of carotenoid compounds. Decolourisation of palm oil from orange-red to pale yellow improves the oil's appearance. In this study, XRF characterisation of Ca-bentonite, Na-bentonite and both activated clays revealed an association between the bleaching capacity and the SiO_2 and Al_2O_3 contents. By increasing the H_2SO_4 concentration from 0.2-5.0 M in the activation of Ca-bentonites, the SiO_2 content was increased from 71.00% to 80.00%. This clay could remove less than 30.00% of the colour, and the palm oil remained orange-red (Figure 2). After activation of bentonite with 5.0 M H_2SO_4 , the bleaching capacity tended to increase up to 38.95%, likely due to the high acid concentration used, which induced leaching of aluminium (Al) and the elements from the interlayer cations, and the SiO_2 content increased by up to 87.30%. In addition, when the Ca-bentonites

were preheated to 300°C and 500°C for 1 hr in a muffle furnace prior to refluxing with 2.0 M H_2SO_4 (F300 CBR 2.0 and F500 CBR 2.0), there was also an increase in SiO_2 content from 88.70% to 89.70%, and the Al_2O_3 content tended to decrease slightly from 7.10% to 6.55%, leading to a slightly increased bleaching capacity of 40.70%-53.33% (Figure 2). Clays preheated at a high temperature before activation display a higher specific surface area and total pore volume than non-preheated samples, as the clay is fully converted to an amorphous phase, which can easily leach aluminium ions (Al^{3+}) and exchangeable cations (Fernandez *et al.*, 2011; Foo *et al.*, 2011). Preheating of the Ca-bentonites at 700°C for 1 hr in a muffle furnace prior to refluxing with 2.0 M H_2SO_4 (F700 CBR 2.0), which showed a high SiO_2 content (92.30% by wt) and a low Al_2O_3 content (left only 4.28% by wt), was not favourable for the sorption of organic pigment and was ineffective for the decolourisation of palm oil (18.47% bleaching only) (Figure 2). This was possibly due to extensive leaching of the Al_2O_3 content, resulting in disruption or destruction of the clay sheets, which negatively affected the bleaching capacity.

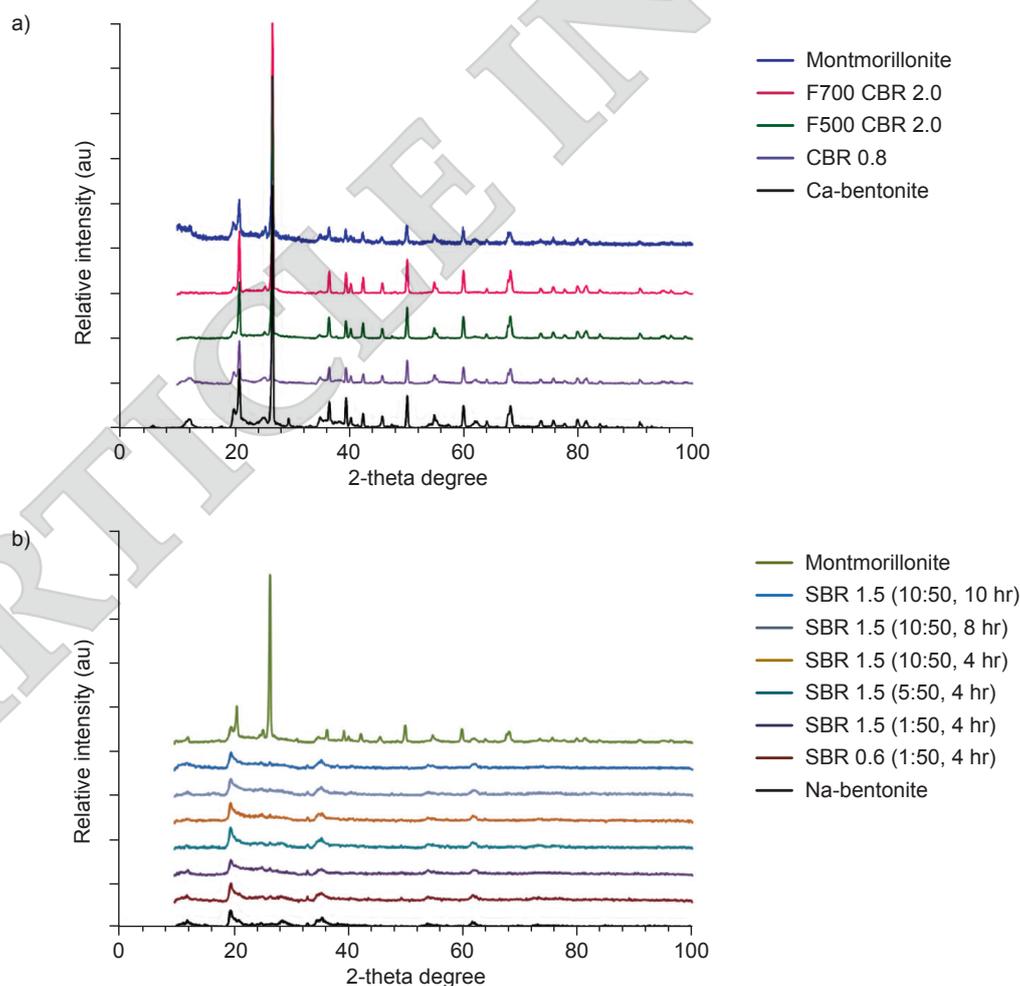
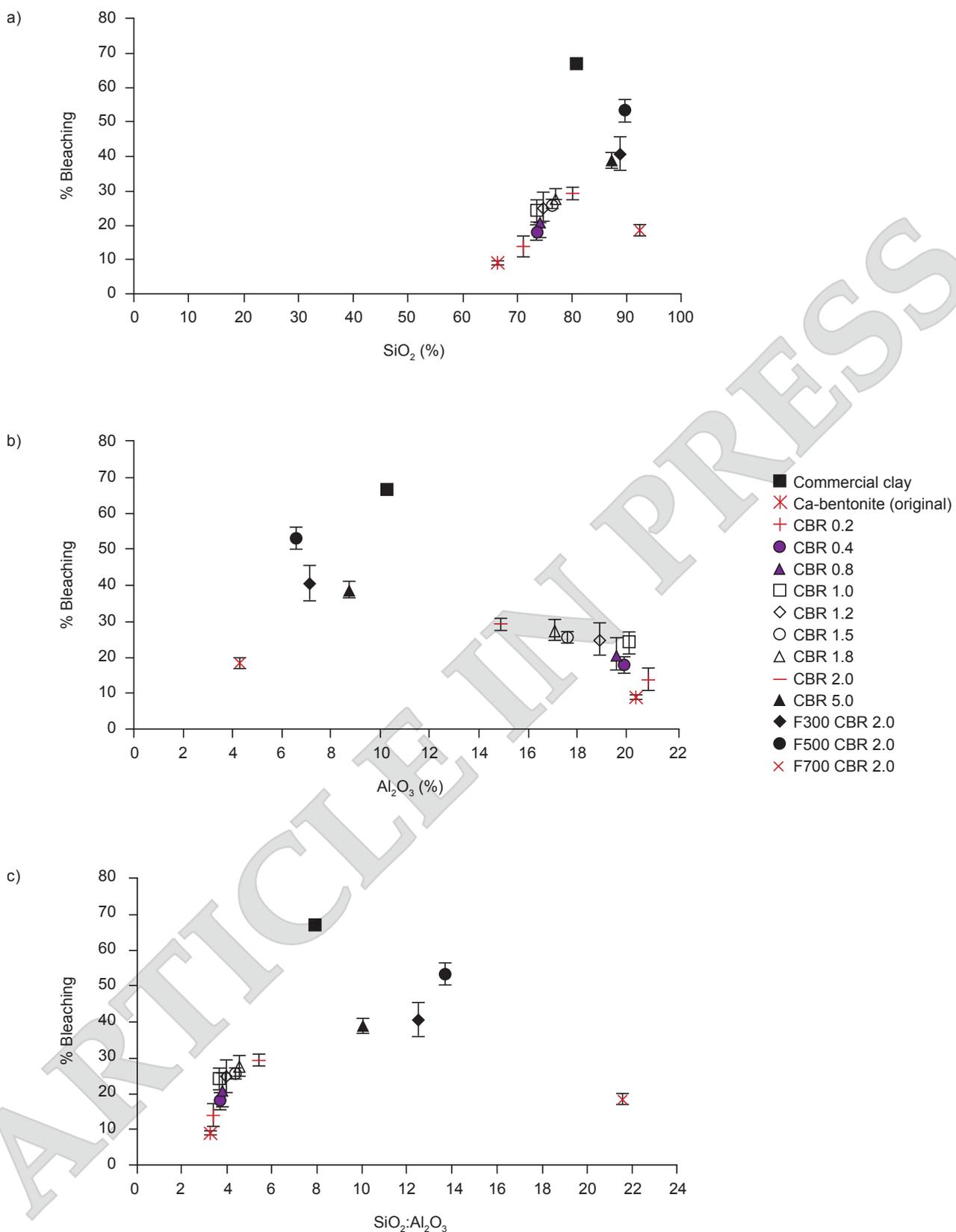
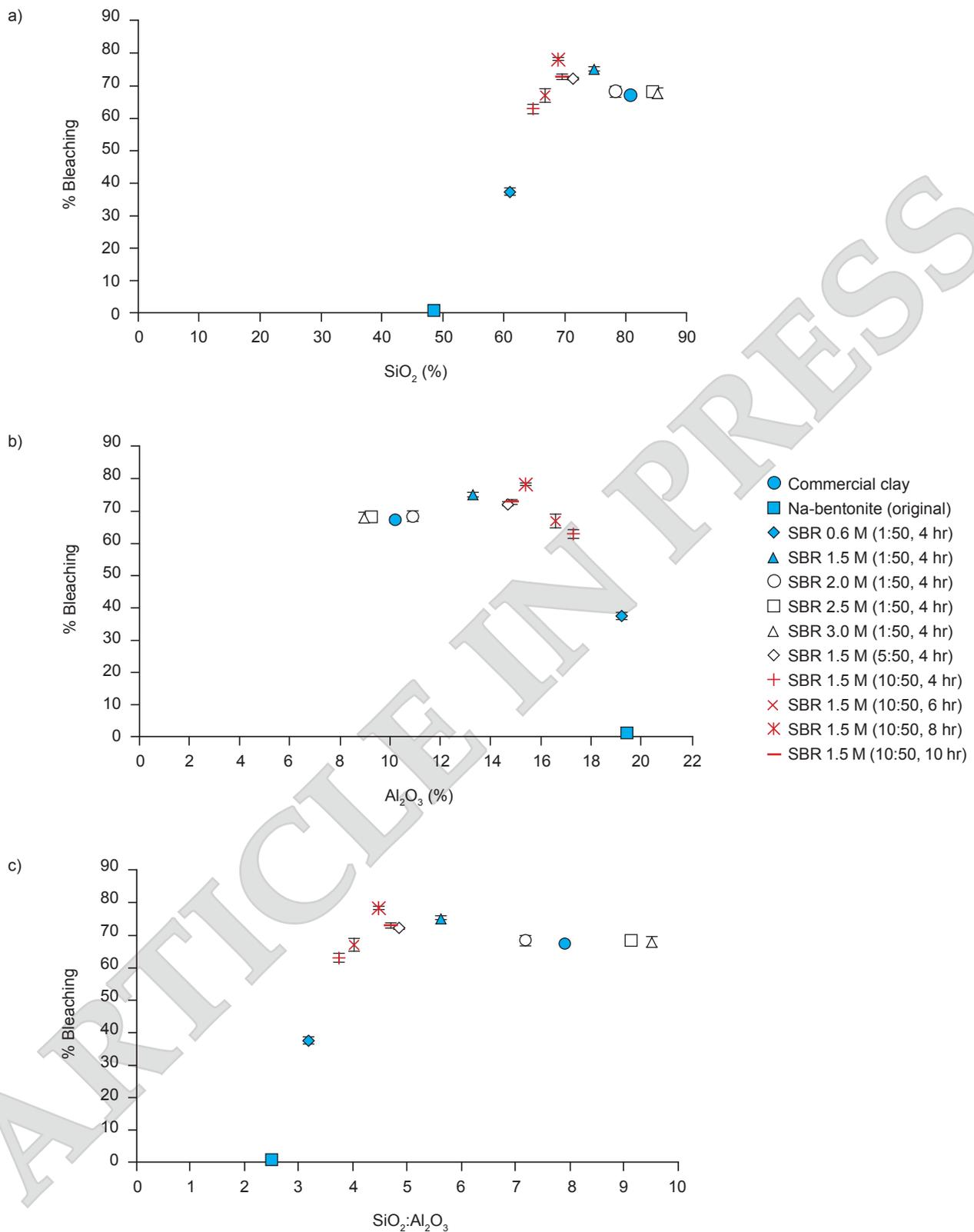


Figure 1. XRD patterns of (a) commercial clay, Ca-bentonite, and activated Ca-bentonites, and (b) Na-bentonite and activated Na-bentonites.



Note: CBR 0.2, CBR 0.4, CBR 0.8, CBR 1.0, CBR 1.2, CBR 1.5, CBR 1.8, CBR 2.0, CBR 5.0 = refluxing bentonite with H₂SO₄ solution with 0.2-5.0 M at 90°C for 4 hr and the ratio of clays to acid was 1:50 (w v⁻¹); F300 CBR 2.0, F500 CBR 2.0 and F700 CBR 2.0 = Ca-bentonites preheated at 300°C, 500°C and 700°C for 1 hr in a muffle furnace prior to refluxing with 2.0 M H₂SO₄ at 90°C for 4 hr and the ratio of clays to acid was 1:50 (w v⁻¹).

Figure 2. The relationship between % bleaching of palm oil and SiO₂ contents (a), Al₂O₃ contents (b), and the ratio of SiO₂ to Al₂O₃ contents (c) of commercial clay, Ca-bentonite, and activated Ca-bentonite under various conditions.

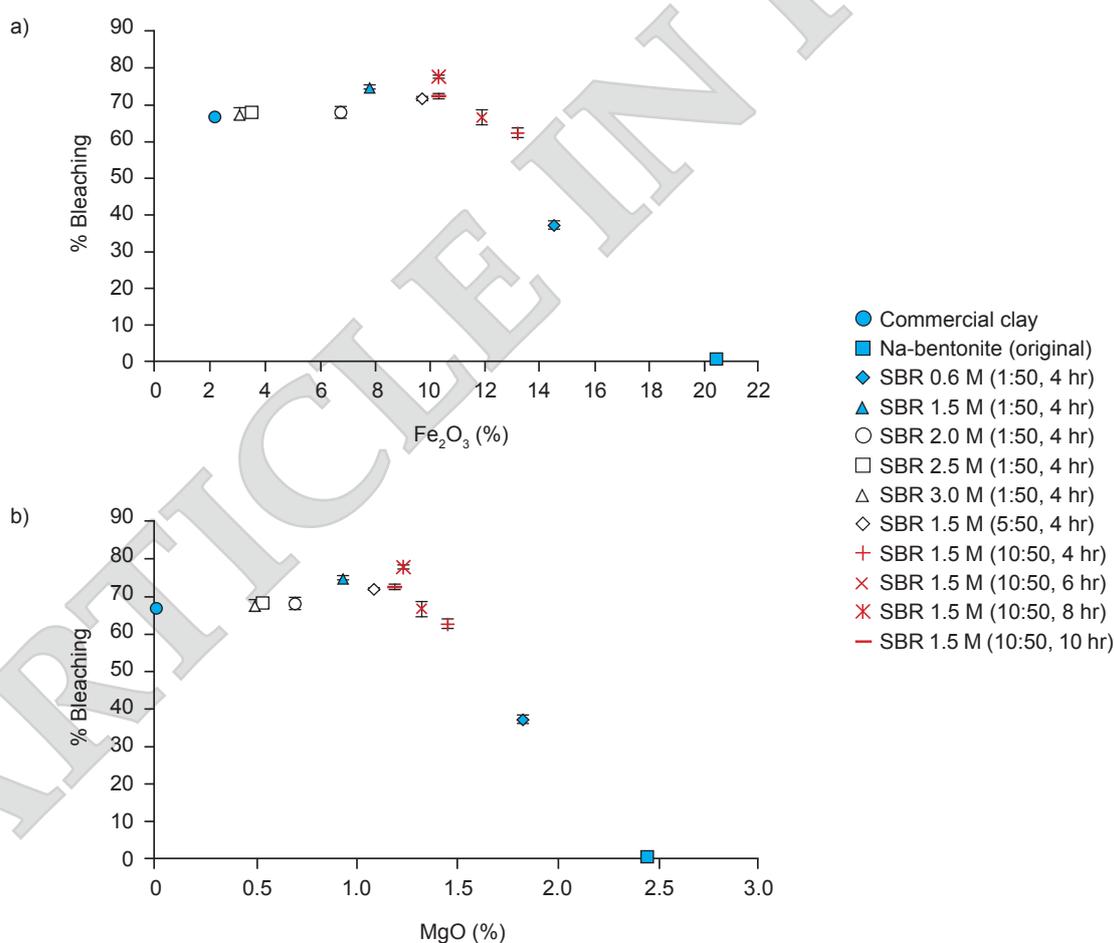


Note: SBR 0.6 (1:50, 4 hr), SBR 1.5 (1:50, 4 hr), SBR 2.0 (1:50, 4 hr), SBR 2.5 (1:50, 4 hr), SBR 3.0 (1:50, 4 hr) = refluxing Na-bentonite with H₂SO₄ solution with 0.6-3.0 M at 90°C for 4 hr and the ratio of clays to acid was 1:50 (w v⁻¹). SBR 1.5 (5:50, 4 hr), SBR 1.5 (10:50, 4 hr), SBR 1.5 (10:50, 6 hr), SBR 1.5 (10:50, 8 hr), and SBR 1.5 (10:50, 10 hr) = refluxing Na-bentonite with 1.5 M H₂SO₄ concentration at 90°C for 4-10 hr and the ratio of clays to acid was 5:50 (w v⁻¹) and 10:50 (w v⁻¹), respectively.

Figure 3. The relationship between % bleaching of palm oil and SiO₂ contents (a), Al₂O₃ contents (b), and the ratio of SiO₂ to Al₂O₃ contents (c) of commercial clay, Na-bentonite, and activated Na-bentonite under various conditions.

Although other studies mentioned that activated bentonite clay had a high efficiency for pigment removal (Christidis and Kosiari, 2003; Nde *et al.*, 2019; Silva *et al.*, 2013), our results illustrated that acid-activated bentonites had a low bleaching efficiency. This might be because the properties of bentonite and activated bentonites were not suitable for decolourisation of palm oil. Interestingly, the highest bleaching capability was observed for Na-bentonite activated by 1.5 M H_2SO_4 [clay:acid ratio of 1:50 ($w v^{-1}$), 4 hr] containing 74.80% SiO_2 and 13.30% Al_2O_3 ; it could remove more colour from palm oil (75.09%) than commercial clay (67.09%). Meanwhile, the bleaching capacities of Na-bentonite activated with a high concentration of H_2SO_4 were not significantly different from those of commercial clay (68.21%, 68.32% and 67.86% for 2.0, 2.5 and 3.0 M H_2SO_4 Na-bentonite, respectively), and its SiO_2 and Al_2O_3 contents were 78.30%-85.20% and 10.90%-8.96%, respectively (Figure 3). Moreover, no relationship was observed between these clays and

the amount of Ca, titanium (Ti), and K^+ , while the Fe_2O_3 and MgO contents of activated Na-bentonites (1.5-3.0 M H_2SO_4) also influenced the bleaching efficiency of palm oil (Figures 4a and 4b). On the other hand, a decline in the bleaching ability of clays was observed when a lower H_2SO_4 concentration (0.6 M) was used, which led to a different range of SiO_2 and Al_2O_3 contents (60.90% and 19.20%, respectively) (Figures 3a and 3b). These results suggested that the highest bleaching of degummed palm oil was correlated with SiO_2 and Al_2O_3 contents in the range of 74.80%-85.20% and 8.96%-13.30% by wt, respectively, with a $SiO_2:Al_2O_3$ ratio of 5.62-9.51 (Figure 3). This result suggested that the amount of H^+ ions increased when the acid concentration was increased, which caused remobilisation of the tetrahedral layers of silicon ions and delamination or depletion of cations such as Al^{3+} , Mg^{2+} and Fe^{3+} from octahedral layers (Rossi *et al.*, 2011; Temujin *et al.*, 2006) and then caused structural changes and partially decomposed the clay.



Note: SBR 0.6 (1:50, 4 hr), SBR 1.5 (1:50, 4 hr), SBR 2.0 (1:50, 4 hr), SBR 2.5 (1:50, 4 hr), SBR 3.0 (1:50, 4 hr) = refluxing Na-bentonite with H_2SO_4 solution with 0.6-3.0 M at 90°C for 4 hr and the ratio of clays to acid was 1:50 ($w v^{-1}$). SBR 1.5 (5:50, 4 hr), SBR 1.5 (10:50, 4 hr), SBR 1.5 (10:50, 6 hr), SBR 1.5 (10:50, 8 hr), and SBR 1.5 (10:50, 10 hr) = refluxing Na-bentonite with 1.5 M H_2SO_4 concentration at 90°C for 4-10 hr and the ratio of clays to acid was 5:50 ($w v^{-1}$) and 10:50 ($w v^{-1}$), respectively.

Figure 4. The relationship between % bleaching of palm oil and Fe_2O_3 contents, (a) MgO contents, (b) of commercial clay, Na-bentonite, and activated Na-bentonite under various conditions.

In addition, Lovibond analysis showed that the colour of the degummed palm oil was 49.9 red and 5.9 yellow Lovibond units, whereas that bleached with 1.5 M H₂SO₄ Na-bentonite had a colour of 16.9 red and 79.9 yellow units and was a lighter yellow than commercial clay (23.4 red and 41.8 yellow units). Therefore, although Na-bentonite clays come from different areas, the preparation of clays should give suitable SiO₂ and Al₂O₃ contents.

FFA is one of the factors that can affect oil quality. Oil bleached by commercial clay and 1.5 M H₂SO₄ Na-bentonite showed FFA (as palmitic acid) concentrations of 8.99% and 8.94%, respectively, whereas the degummed palm oil had a fatty acid content of 13.65% (Table 1). Presented results here on the adsorption of FFA were in agreement with those reported in a previous work (Joy *et al.*, 2007), although normally FFA adsorption was found during discolouration. The adsorption of FFA of oil is described by the diffusion of FFA from oil to the active site of the clay followed by the interaction between adsorbate and the active site (Baptiste *et al.*, 2020). The analysis of adsorptive properties reveals that activated Na-bentonites had a large specific surface, total pore volume and microporous, which gives them great adsorption properties (Table 2). Although activation of Na-bentonites could decrease their FFA content, the FFA content of activated Na-bentonites remained higher than standard specifications. For trading purposes, the maximum FFA content set by the Palm Oil Refiners Association of Malaysia in CPO is 5%, indicating that the use of low-quality CPO with a relatively high FFA content as the input of the bleaching process might result in a low smoke point and, consequently, high impairment of oil quality (Khor *et al.*, 2019). The lengthy storage period of the CPO used in the study might have affected FFA production, thus, affecting the quality of the palm oil as a result of enzymatic lipase degradation of triglycerides. In addition, the proportion of FFA is related to the moisture content and can accelerate to rancidity levels by increasing the penetration of oxygen into the oil molecule (Hammond and White, 2011; Tan *et al.*, 2017). In the presence of a high moisture content, more FFA could be generated by lipase oxidation or autocatalytic hydrolysis, resulting in rapid development of rancidity (Frank *et al.*, 2011). After bleaching oil with commercial clay and 1.5 M H₂SO₄ Na-bentonite, the moisture content was below 0.10%, which could prevent an increase in FFA content (Pal *et al.*, 2015).

The peroxide value is an indicator of oxidative rancidity and deterioration due to lipid peroxidation or oxidative degradation and is, consequently, an important parameter used to assess the quality of palm oil. Moreover, a high peroxide value affects the generation of free radicals, which may have adverse health impacts, such as carcinogenesis (Rossel, 1999). The peroxide value of degummed

palm oil was 6.81 meq kg⁻¹, which is lower than the maximum peroxide value recommended by the Codex Alimentarius/FAO/WHO norm (10 meq kg⁻¹) (Codex Alimentarius Commission, 2011). After oil was bleached with commercial clay and 1.5 M H₂SO₄ Na-bentonite, peroxide values decreased to approximately 2.25 and 2.31 meq kg⁻¹, respectively, indicating good-quality palm oils. In addition, unsaturated fatty acids are recommended for good health over oils with highly saturated fatty acids. However, the iodine value of CPO (57.36 Wijs) is higher than the standard specification (50-55 Wijs), which indicates the ease of oxidation of the oil. Interestingly, 1.5 M H₂SO₄ Na-bentonite resulted in bleached oil having a lower iodine value (53.52 Wijs) than that obtained from commercial clay application (54.05 Wijs). Because of its anion exchange properties, activated clay often displays a high affinity for anion contaminants, including short- and long-chain alkyl carboxylates, and allows the intercalation of contaminants in the interlayer space (Celis *et al.*, 2014). Moreover, modified clay can provide suitable reaction space for the dimerisation of unsaturated fatty acids and act as a catalyst, which improves dispersibility for the unsaturated fatty acid molecules to enter the interlayer (Huang *et al.*, 2018). A decrease in the iodine value shows a decrease in unsaturated fatty acids, and it indicates oxidation of palm oil, representing a good quality edible oil which has a positive effect on human health (Table 1).

The current results showed that activation of Na-bentonites by 1.5 M H₂SO₄ could also reduce the levels of elements such as Fe, which is known to increase the rate of secondary oxidation products (Gibon *et al.*, 2007). Moreover, the presence of high levels of Fe and P can contribute to changes in the flavour, colour and odour of oil. The reduction in the iron content of 1.5 M H₂SO₄ Na-bentonite was 0.78 ± 0.02 mg kg⁻¹, which is less than the maximum acceptable level stipulated in the CODEX standard (1.5 mg kg⁻¹) (Codex Alimentarius Commission, 2011), while commercial clay could reduce the iron content by approximately 1.67 ± 0.05 mg kg⁻¹ (Table 1). The decrease in content of Fe in the bleached oils was greatest from 1.5 M H₂SO₄ Na-bentonite, possibly because it had the optimum Si and Al contents. The acid-activated clay shows availability of more adsorption sites in the matrix that are occupied by exchangeable ions in the interlayers. Furthermore, P adsorbed onto bleaching clays was removed effectively by the adsorbent 1.5 M H₂SO₄ Na-bentonite (1.94 ± 0.07 mg kg⁻¹) and commercial clay (3.13 ± 0.08 mg kg⁻¹). This information indicated that 1.5 M H₂SO₄ Na-bentonite could improve the hydrolytic stability of bleaching oil.

In addition, the most effective adsorbent for palm oil colour removal was activated Na-bentonite. The optimum activation condition was investigated

TABLE 1. PHYSICOCHEMICAL PROPERTIES OF DEGUMMED PALM OIL BEFORE AND AFTER BLEACHING WITH COMMERCIAL CLAY AND ACTIVATED Na-BENTONITES

Physicochemical property	Degummed palm oil	Commercial clay	SBR 1.5 (1:50, 4 hr)
Free fatty acid (%)	13.65 ± 0.45 ^b	8.99 ± 0.65 ^a	8.94 ± 0.31 ^a
Moisture content (g 100 g ⁻¹)	0.23 ± 0.10 ^b	0.04 ± 0.01 ^a	0.04 ± 0.01 ^a
Peroxide value (meq kg ⁻¹)	6.81 ± 0.20 ^b	2.25 ± 0.10 ^a	2.31 ± 0.10 ^a
Iodine value (Wijs)	57.36 ± 0.21 ^b	54.05 ± 0.42 ^a	53.52 ± 0.15 ^a
Iron content (mg kg ⁻¹)	4.13 ± 0.51 ^c	1.67 ± 0.05 ^b	0.78 ± 0.02 ^a
Phosphorus content (mg kg ⁻¹)	12.56 ± 0.72 ^c	3.13 ± 0.08 ^b	1.94 ± 0.07 ^a

Note: SBR 1.5 (1:50, 4 hr) = refluxing Na-bentonite with 1.5 M H₂SO₄ concentration at 90°C for 4 hr and the ratio of clays to acid was 1:50 (w v⁻¹). Data are mean ± SE (n=3); different letters in the same row indicate statistically significant differences (Anova test, Duncan, p<0.05).

TABLE 2. SPECIFIC SURFACE AREA, TOTAL PORE VOLUME, MICRO PORE VOLUME AND AVERAGE PORE SIZE OF COMMERCIAL CLAY AND ACTIVATED Na-BENTONITES

Sample names	Specific surface area (m ² g ⁻¹)	Total pore volume (cc g ⁻¹)	Micro pore volume (cc g ⁻¹)	Average pore size (Å)
Commercial clay	160.90	0.3200	0.0900	80.47
Ca-bentonite	42.30	0.1010	0.0341	37.74
Na-bentonite	67.47	0.1256	0.0052	30.22
SBR 1.5 (1:50, 4 hr)	340.50	0.4465	0.2642	48.08
SBR 1.5 (5:50, 4 hr)	303.90	0.3780	0.2184	46.80
SBR 1.5 (10:50, 4 hr)	270.40	0.3164	0.1849	43.41
SBR 1.5 (10:50, 8 hr)	373.20	0.4672	0.2862	52.06
SBR 1.5 (10:50, 10 hr)	308.40	0.4150	0.2247	46.91

Note: SBR 1.5 (1:50, 4 hr), SBR 1.5 (5:50, 4 hr) and SBR 1.5 (10:50, 4 hr) = refluxing Na-bentonite with 1.5 M H₂SO₄ concentration at 90°C for 4 hr and the ratio of clays to acid was 1:50 (w v⁻¹), 5:50 (w v⁻¹) and 10:50 (w v⁻¹), respectively.

at a clay:acid ratio of 1:50 with 1.5 M H₂SO₄. In this experiment, a comparison of the bleaching capacity of Na-bentonite treated with 1.5 M H₂SO₄ at 90°C for 4 hr at clay:acid ratios of 1:50, 5:50 and 10:50 (w v⁻¹) was performed. The result showed that increasing the clay:acid ratio caused a decrease in the bleaching capacity (Figure 3). When the clay:acid ratio was increased from 1:50 to 10:50 (w v⁻¹), the structure of the clay slowly collapsed, lowering the specific surface area and total pore volume (Table 2). Therefore, a longer refluxing time was needed in the leaching process to investigate the most suitable conditions and SiO₂ and Al₂O₃ contents. The result showed that increasing the refluxing time from 4 hr (minimum) to 6-8 hr increased the bleaching capacity of activated Na-bentonite, but at the clay:acid ratio equal to 10:50 (w v⁻¹), the optimum time was 8 hr (78.04%). The longer time of 10 hr might have destroyed the clay structure and thus, giving a lower bleaching capacity (72.70%) than 8 hr. Therefore, the best activation condition of Na-bentonite was at H₂SO₄ concentration of 1.5 M at 90°C for 8 hr at a clay:acid ratio of 10:50 (w v⁻¹), which resulted in the clay with the highest bleaching capacity (approximately 78.04%). Alternatively, the ratio of 5:50 (w v⁻¹) and a time of 4 hr could also be applied in industry because the bleaching efficiency

was only a little lower than that given by a ratio of 1:50 (w v⁻¹) (1.5 M H₂SO₄, 4 hr), but the amount of clay used in the refluxing process increased by up to five times.

CONCLUSION

The bleaching capacities were correlated with SiO₂ and Al₂O₃ contents in bleaching clay. The most suitable clay for bleaching contained SiO₂ and Al₂O₃ in the range of 68.90%-85.20% and 8.96%-16.60% by wt, respectively. This knowledge can be applied to modify other Na-bentonites from other sources to bleach palm oil efficiently. In this study, 1.5 M H₂SO₄-treated Na-bentonite was a suitable clay for bleaching palm oil. The best activation condition was Na-bentonite refluxed with 1.5 M H₂SO₄ solution at 90°C for 8 hr at a clay:acid ratio of 10:50 (w v⁻¹). Activated Na-bentonites could decolourise palm oil better than activated Ca-bentonite and commercial clay. Moreover, 1.5 M H₂SO₄ Na-bentonite was also giving the good results for the adsorption of FFA and in the elimination of peroxide, iodine, Fe, P and moisture contents. It appeared clear that activated Na-bentonite could give an attractive colour to palm oil, and also produce a stable oil of good quality.

ACKNOWLEDGEMENT

This research was supported by King Mongkut's University of Technology Thonburi, Thailand.

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