

Effect of Fluoride Acid Activation of Natural Bentonite on Bleaching of Palm Oil

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Abstract—A natural bentonite from Indonesia was activated with 1 % of fluoride acid. In characterizing the activated and raw clay samples, XRD, BET and infrared spectroscopy were utilized. Bleached oil was analysed to find out peroxide value content, the percentage of colour reduction (%CR), acid value as well as the percentage of free fatty acid (%FFA) content before and after bleaching. Bleaching efficiency was calculated from measurement of absorbance of UV light by frying oil before and after treatment with activated clay. The BET results obtained exhibited the values of surface area and pore volumes were 26.893 m²/g as well as 0.067 cc/g each for natural bentonite, after the activation with 1 % of HF acid these values changed to 43.167m²/g and 0.108cc/g, respectively. The optimum bleaching condition of clay dosage and contact time of bleaching were 2 gram and 120 minutes resulted in %FFA was 0.27%, acid value was 0.537, peroxide value was 9.57meq/kg, oil retention was 54.48% and 80% of luminance of colour reduction. Our results show that activated bentonite can be used to reduce the concentration of peroxide value, the darkness colour of frying oil to reduce, and free fatty acid adsorption or reduction in acid value efficiencies increase with higher adsorbent dosages

Keywords—bleaching, palm oil, bentonite, acid activation, fluoride

I. INTRODUCTION

Clay is a layered material (smectite) that consists of one layer of octahedral and two tetrahedral layers or commonly known as composition of 2:1 layer clay mineral [1]. It is generally called bentonite. Natural clay such as fuller's earth and bentonite have commonly been utilized as bleaching clay to remove colour impurities from both edible and non-edible oil [2]. Besides the adversely charged of surface layer bentonite, electrostatic force occurs and van der Waals powers are frail to the point that other cations simply substitute the cation within bentonite interlayers. Because of the utilization of bentonite surface area and low thermal constancy, the application has restrictions. Generally, the bentonite dries out and harms the structure at the high temperature response. Therefore, altering structure of surface of clays becomes essential [3]. There have been several studies to find out several methods to modify clay minerals aiming at enhancing their adsorption capacities which include treatment with cationic surfactants, acid

activation, clay-rubber composite, polymer addition by inter particle polymerization, thermal activation, binding of inorganic and organic anions, and grafting of organic compounds. One of the most commonly employed modification techniques is acid activation due to its easy and economical process [4]. In the process of modification of the clay mineral structure with acid, the separation of the interchangeable cations from protons is done first. The next phase incorporates flushing of Al, Mg and Fe from octahedral and tetrahedral sheets. After that, the SiO₄ groups of tetrahedral sheets remain complete at lower acid concentration and the octahedral sheets were corroded by the acid [5-6]. The main aim of this work was to enhance the bleaching activity of natural bentonite after activation by fluoride acid. The study is also aims to discuss the variation of some of physicochemical properties of natural bentonite after acid treatment.

II. MATERIAL AND METHODS

II.1 Material

Gathered from Tasikmalaya, Indonesia, white bentonite clay was utilized as the main material. The chemicals used, analytical reagent grade was acquired from the Merck Company. In all tests, double-ionized water was used for creating the solutions and suspensions.

II.2. Methods

II.2.1. Acid activation. First, natural bentonite was grounded to pass through a 250 mesh sieve. Double ionized water was used to wash the bentonite to remove impurities, and the bentonite was dried at 60°C for 12 hours and then was grounded to pass through a 250 mesh sieve. Activation of acid samples were prepared by treating bentonite with 1% HF according to the procedure described by Toor et al. [4]. The bentonite (100 g) was handled with 400 mL of fluoride acid (analytical grade) at 25°C for 1 hour in a stirred glass reaction vessel with reflux. The sample was distilled as well as cleaned using double ionized water after the completion of acid treatment. The sample was

dried at 60°C for 12 hours and was grounded to pass through a 250 mesh sieve.

II.2.2. Bleaching of frying oil. Frying oil (50 mL) was weighed into a round bottom flask and heated to a temperature of around 70°C. A known weight of acid activation bentonite was added to the preheated oil under steady stirring for an hour in a rotary evaporator. Mixture of oil-clay was slowly heated to a bleaching temperature of 95°C for certain period. The sludge was then sieved off on a centrifuge after the bleaching process.

II.3. Determination of physicochemical properties of bleaching of frying oil

II.3.1. Acid value and free fatty acid (FFA). The acid value is the quantity of mg of potassium hydroxide needed to neutralize the free acid in 1 g of the substance. Titrimetric technique was employed to determine acid value and FFA content of the oil.

II.3.2. Peroxide value (PV) Determination. In determining oil oxidation, it was carried out by estimating the measure of peroxides. Peroxide value is regularly expressed as mille equivalent of oxygen per kilogram of fat. The production of iodine is from potassium iodide solution by the peroxides presented in oil and titrated towards 0.01 M sodium thiosulphate.

II.3.3. Percentage of colour reduction. Spectrophotometry UV-Vis was utilized to figure out the percentage of color decrease of the oil after bleaching. Complete adsorption spectrum was created throughout the wave lengths, between 435.5 nm and 645.9 nm. The determination of absorbance of the samples was at the maximum wavelength (570-580) nm by diluting 5 ml of bleached oil in 15 ml acetone. Changing the absorbance units to β -carotene concentration was carried out to calculate the adsorbed amount of the coloring agent.

II.4. Samples Characterization

The acquisition of x-ray diffractograms (XRD) of samples was done using a Bruker D8 Advance diffractometer (with Cu-K α radiation, powered at 40 kV and 30 mA). Atomic force microscopy (Agilent Technologies 5500 equipment) was used to analyze the morphology of samples. Utilizing a Shimadzu 8400 S spectrometer, with samples arranged by the conventional KBr disc method, FT-IR spectra were attained. The measurement of the particular surface area was done at 77.30K utilizing BET method with a Micromeritics Gemini 2360 instrument utilizing the gas of N₂. The pore-size distribution of the samples was measured from desorption isotherms, and the BJH method was employed for the measurement.

III. RESULTS AND DISCUSSION

III.1. Physicochemical characterization of acid activation bentonite

It can be seen in Fig. 1 about the XRD patterns of the natural and acid-activated samples. Natural bentonite has sodium rich montmorillonite with the $d_{(001)}$ value of 1.55 nm as the foremost clay mineral. Montmorillonite appears to be very much solidified. Cristobalite, quartz, gypsum, feldspar as well as calcite were also identified. As seen from XRD patterns, important mineralogical changes were produced from leaching of the sample with fluoride acid. The most articulated alteration happens in the montmorillonite $d_{(001)}$ top (the primary peak showing up in 2 theta angle approximately 5°) demonstrating the decrease in power because of acid attack. The XRD results reveal that structural changes in the treated smectites occur because of the enactment of acid. The decrease in intensity as well as growth in width of the 001 peak (1.64 nm) show that the acid activation has greatly influenced crystallinity of the natural bentonite. This demonstrates the process supports the production of amorphous phase by decaying the structure of montmorillonite. Conversely, the presence of montmorillonite peak after acid treatment might mean that the structure has been partially damaged [7].

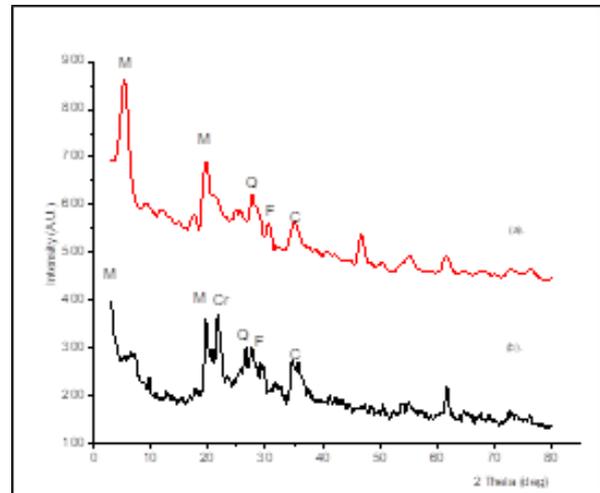


Figure 1. X-ray diffraction patterns of the acid activation (a) and natural bentonite (b) samples (M = montmorillonite; Cr = cristobalite; Q = quartz; F = feldspar; C = calcite).

However, since mainly, impurities, feldspar containing calcium, sodium and potassium are available, a significant quantity of elements is still found in the enacted clays and is resistant to acid attack. Otherwise, they might generate as a new amorphous segment from the leachate. The second group consists of Fe²⁺, Mg²⁺ and Al³⁺ and are included within the octahedral sheet [8]. The acid activation does not dissolve the Si⁴⁺ cations at tetrahedral sites of smectite.

Fig. 2 shows the FT-IR spectra of the natural and acid activation samples in the wave number range

of 4000–500 cm^{-1} . The spectrum of the natural bentonite exhibits absorption bands at 3448 and 1635 cm^{-1} assigned to the stretching and bending vibrations of the OH groups for the water molecules adsorbed on the clay surface. The Si–O bands are really distinct in the silicate structure of the natural bentonite and can be easily identified in the infrared spectrum by very strong absorption bands in the 1100–1000 cm^{-1} area. The most intensive band at 1041 cm^{-1} is attributed to Si–O in-plane stretching and the shoulder at 1090 cm^{-1} is due to Si–O out-of-plane stretching vibration. Natural bentonite spectrum also contains a band at 794 cm^{-1} which is attributed to cristobalite [9]. After fluorination of bentonite, the νOH band around 3433 cm^{-1} usually assigned to adsorbed water widens and increases in intensity. However, the 1635 cm^{-1} band, corresponding to the δOH vibration of water, remained unchanged. The band intensity at 1041 cm^{-1} rises after acid leaching because three dimensional networks of amorphous Si–O–Si units are formed. However, persistence of a weak band at 1041 cm^{-1} means layer structure of the authentic clay is not entirely damaged, in line with the XRD results. The band at 794 cm^{-1} related to cristobalite not only survives the acid leaching but also increases the intensity throughout the process [10-11].

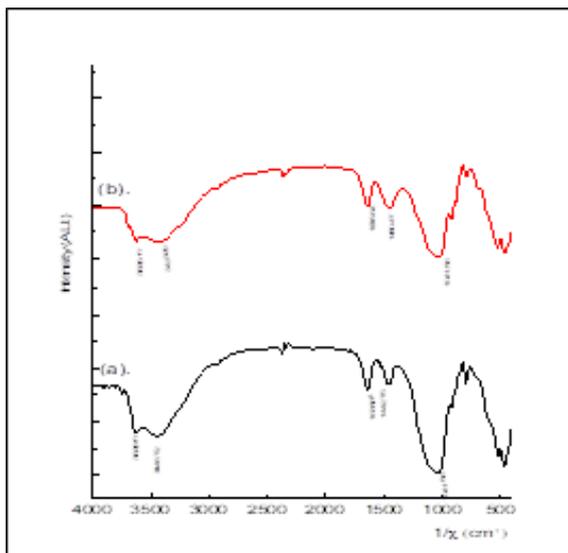


Figure 2. Infrared spectroscopy of bentonite: (a) natural bentonite and (b) acid activation (HF1%).

The particular BET areas of the examined samples can be seen in Table 1. The acid activation bentonite surface area was 43,167 m^2/g , and 26.893 m^2/g for the measured natural bentonite surface area. The findings reveal that the particular surface area goes up with enactment of natural bentonite, that sample experiences quick deterioration followed by separating the layer of

montmorillonite. Firstly, the increase in particular surface area is a consequence of vacant octahedron and tetrahedron spaces staying from Mg^{2+} , Fe^{3+} and Al^{3+} ions that have left the layers of montmorillonite. As the initiation advances, the vacant spaces develop bigger and micro pores are changed into mesopores. At last, due to the disintegration of crystal structure at certain areas, a portion of the mesopores vanishes, prompting a drop in certain surface zone [12]. The particular pore increases quickly. As a result of the walls of those pores, there is a rapid increase in the particular surface area.

Table 1. Adsorbent characterization, specific surface area, pore radius, pore volume for natural bentonite and acid activation bentonite.

Samples	Adsorption			Desorption		
	face Area (m^2/g)	Pore Volume (cc/g)	Pore Radius (Å)	Surface Area (m^2/g)	Pore Volume (cc/g)	Pore Radius (Å)
Natural Bentonite	26.893	0.067	15.339	40.283	0.069	19.554
Acid activation Bentonite	43.167	0.108	15.300	60.391	0.109	19.598

In figure 3, it can be seen the adsorption-desorption isotherms given as a portion of the adsorbed nitrogen in the capacity of the relative weight (at - 196°C). The particular surface zone of P bentonite increases with the rise of concentration of the HF acid while for bentonite to some degree various changes take place. Based on the characterization of the IUPAC, isotherms possess a form which is included in type IV. Clear hysteresis loops can be recognized on the isotherms demonstrating that the adsorption and desorption processes do not happen in a similar way. Adsorption at little estimations of relative pressures shows the existence of micropores. In light of the introduced adsorption isotherms, the BET equation was utilized to calculate the particular surface area of natural and acid enactment bentonites. The distribution demonstrates that the greatest pore percentage is in the area 1.5–10 nm, that affirms the summary that bentonites are mesoporous and microporous [5].

It can be seen in figure 3 the N_2 adsorption-desorption isotherms of the bentonite. From Figure 3, we can see that N_2 adsorption qualities of the bentonite are notably influenced by the acid activation. After the bentonite is treated by acid, the nitrogen uptake is enormously expanded, particularly in the low pressure area ($p/p_0 < 0.1$), that demonstrates that acid enactment causes the creation of a large amount of micro mesoporous material. In addition, as can be seen from the pore structure parameters concluded in Table 1, the BET particular surface region and pore volume of the acid-bentonite are measurably expanded and the pore size is diminished compared with natural bentonite. This can be translated as the basic changes of acid-bentonite; numerous smaller scale pores are produced during the acid activation.

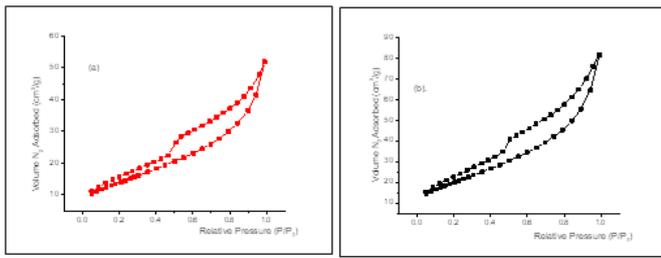


Figure 3. Nitrogen adsorption-desorption isotherms of (a) bentonite and (b) acid activation bentonite.

III.2. Frying oil bleaching

Frying oil is oil that is not suitable for consumption, in addition to dark-coloured and itchy throat. Frying oil quality is very low due to the content of peroxide, high free fatty acid, and acid value.

Table 2. The percentage decrease in acid number and peroxide value

Sample	FFA (%)	Acid Value	Peroxide Value (meq/kg)
Frying Oil	0.05	0.010	7.77
Used Frying Oil	0.41	0.815	13.81
Standard SNI	Max. 0.3		Max. 2

The data in Table 2 shows that the quality of frying oil has been under the SNI standard. This indicates that the frying oil is already unfit for consumption. Table 2 shows that the peroxide value of used frying oil was 13.81 meq / kg, its acid value and FFA were 0.815 and 0.41%, respectively already well above the maximum of ISO standard is 2 meq / kg and a maximum of 0.3%. Quality of frying oil can be increased further by integrating it with the adsorbent.

Figure 4 shows that the spectra of the three of patterns seen that the Fig.4(a) exhibits sharp absorption peaks at 1743 is due to conjugated of unsaturated fatty acid from fatty triglycerides. Fig.4(c) shows that the band at 3471 cm^{-1} absorption band from the group O-H phenol and bands at 725 cm^{-1} from the group benzene substituted tocopherol. The band at 2923.9 cm^{-1} and its overtone at 1458 cm^{-1} of a methylene group, the most intensive at 2854 cm^{-1} of C-H stretching alkanes or alkyl, however at 1651 cm^{-1} band corresponding to C-C stretching, the band at 1373 cm^{-1} arise from the bending modes of a methyl group in which the absorption bands from the carbon chains of carotene or acid. Based on the analysis of these spectra, it can be assumed that the intensity of peaks in Fig.4 (c) increases compared to the Fig. 4(b), so we can conclude that the adsorbent used can absorb β -carotene, lycopene or ψ -carotene, fatty acid, and tocopherols.

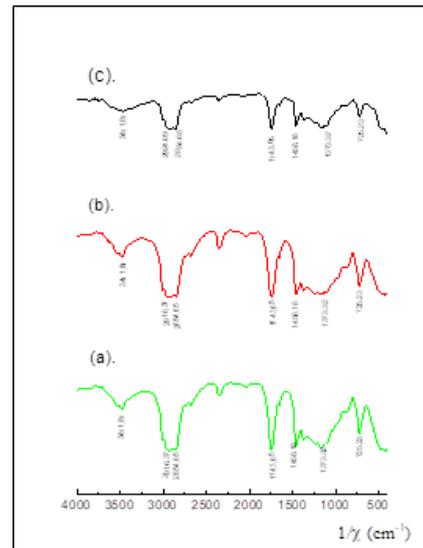


Figure 4. FT-IR spectra of (a).New cooking oil, (b).Cooking oil before bleaching and (c).Cooking after bleaching.

III.3. Acid value and FFA

Free fatty acid was a reaction product of triglyceride hydrolysis. FFA oxidation will produce odour and taste awful. Therefore, the acid value in the oil is often used as one of the parameters frying oil damage. At the time of the oil used, at the beginning of the process of FFA produced by the process of oxidation breakdown. However, in the later stages of FFA, it results from the hydrolysis process caused by the presence of water. Based on the results, the acid rate reduction by the adsorption using activated bentonite, that the acid value and FFA decreases with the longer the operating time, so the longer process of adsorption to occur the longer the contact time between the acid-activated bentonite with frying oil. The contact time in the adsorption process was so long, so the amount of acid activation bentonite adsorbed was more [13]. This proves that the increasing amount of added adsorbent, the active surface area particles were also getting bigger by acid activation bentonite. The functional group from an organic compound is a factor affecting the adsorption affinity. The organic compounds with acid functional group will adsorb well on polar surfaces. Chemically activated bentonite is expected to have a polar nature so that it can adsorb FFA, in this case the carboxylic acid. Figure 5 (a) shows that the optimum adsorbent dosage for residual and adsorbed on the adsorbent past 2 grams with % FFA ranges from 0.14% (67.74%) and 0.05% (32.26%), respectively. The data in Figure 5 (b) can be concluded that the optimum contact time on 120 minutes for residual and adsorbed are 0.27% (48.15%) and 0.14% (51.85%), respectively.

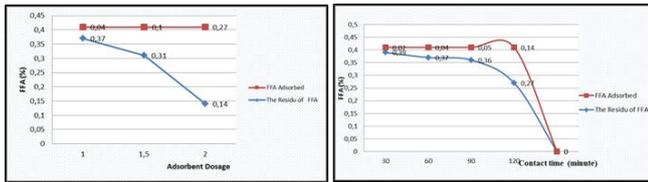


Figure 5. Effect of variation of adsorbent dosages (a) and contact time bleaching (b) in %FFA of frying oil bleaching performance.

III.4. Peroxide value

The results of the analysis of peroxide frying oil after undergoing a process of adsorption using acid activation bentonite at different dosages of adsorbent and adsorption time are presented in Table 3. Peroxide value frying oil before the bleaching obtained 13.81 meq / kg. The high number is due to the peroxide oxidation processes during the cooking process or storage, the reaction is the formation of peroxides in the oil caused by oxidation by oxygen with a number of unsaturated fatty acids, in this case is oleic acid contained as much as 39-45% in the frying oil. Figure 6 (a) illustrates that the optimum adsorbent dosage during the adsorbent 2 grams with peroxide number 9.57 meq / kg (16.72%) residual and 7.97 meq / kg (83.28%) was adsorbed. According to Figure 6(b) describes that the optimum contact time of frying oil bleaching was 120 minutes.

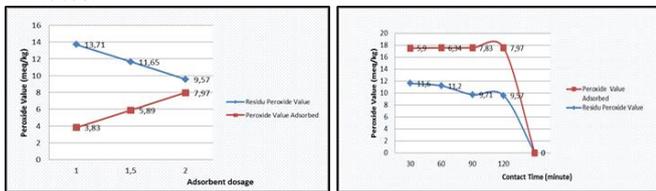


Figure 6. Effect of variation of adsorbent dosage (a) and contact time bleaching (b) in peroxide value of frying oil bleaching performance.

Absorptive capability of peroxide component in frying oil by active bentonite was caused by the silanol group formed from SiO₂ in the bentonite compound upon activation of the acid. Interaction between the active site of acid activation bentonite in this study made it possible for physical adsorption due to the particles close to the surface of adsorbate and adsorbent through vander walls interaction or hydrogen bonds, which is due to the potential energy difference between the adsorbent with the adsorbate [14-15]. Based on the SNI 3741-2013 about standard frying oil for peroxide value (up to 2 meq / kg), it appears that the initial frying oil has been broken and it does not fit to be consumed due to high levels of peroxide (13.81 meq / kg). According to our results show that the purification process with an adsorbent acid activation on all the conditions of the dosage of adsorbent and contact time bleaching can lower peroxide frying oil ranges from > 35%), although it has not been able to pass the maximum limit of SNI standard frying oil.

III.5. Percentage colour reduction

Colour of oil is one determinant of the frying process. Oil should not be used again if the colour has changed

permanently compared to the original colour. Colour absorption process consists of the physical and chemical absorption. The use of adsorbent with adsorption process is a way of processing of physics. Oil discoloration can be caused by a Maillard reaction product and triggers. According to the results, it can be concluded that the highest colour intensity is treated by bentonite dosage (2 grams) and adsorption contact time (120 minutes) is 80% of luminance. This is because the amount of bentonite affect the colour of the oil, where more and more bentonite is used, the colour of the oil will be even brighter.

IV. CONCLUSION

Acid activation of bentonite clay containing sodium montmorillonite as the major clay mineral caused important structural modifications. XRD results demonstrated partial damage of the smectite and removal of gypsum and calcite. The existence of Kaolinite in all the samples means that the activation process did not damage the clay structure but rather improved the kaolinite grade by decreasing the composition of the minerals. Partial destruction of montmorillonite increased the particular surface area starting 26.893m²/g until 43.167m²/g. The process conditions studied were time (minutes) and clay dosage (gram). The bentonite clay was activated using 1% HF for 1 hour. The numerical optimization selected the optimum conditions based on their desirability's which were as follows: time of 120 minutes and adsorbent dosage of 2 gram with the best predicted results were 0.27 of %FFA, 0.537 of acid value, 9.57 of meq/kg peroxide value, 54.8% of oil retention, and colour reduction was 80% of luminance, yellow.

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