

Characterisation of Bleaching Earth and its Performance in Palm Oil Processing

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Abstract – This paper study the characterisation of three different type of absorbent which is one of the major tool that will used to predict its performance for palm oil processing. Bleaching earth sample will be collected from Sime Darby research Sdn. Bhd. were characterized by using X-ray Fluorescence (XRF), Inductively Coupled Plasma (ICP-OES) and Fourier Transform Infrared Radiation (FTIR). From XRF result, the composition of each component that exist in the absorbent can be determined such as silica, alumina and magnesium. The composition analysis by using ICP-OES showed the ratio between $\text{Na}_2\text{O}:\text{CaO}$ of each absorbent where it need to be less than one. Other than that, it also can be used to determine the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio which need to be greater than one and it indicate the suitability for bleaching processing. Actual laboratory test also has been conducted to determine the performance evaluation and confirmed with the prediction from the characterisation. Few analysis have been conducted such as free fatty acid (FFA) value, Peroxide value (PV), colour and bleaching efficiency. Absorbent one show the best result out of all adsorbent by comparing the characteristic and performance. Based on the XRF absorbent contain highest amount of silica, SiO_2 and alumina, Al_2O_3 which 43.386 and 14.18 compared to the other adsorbent. It shown lowest amount of metal contain in it such as magnesium, ferum and sodium with value of 17.699, 18.984 and 0.244 respectively. Therefore, absorbent I shown the best result compared to the others.

Keywords— bleaching earth, crude palm oil, edible oi, palm oil, performance

I. INTRODUCTION

Palm tree or scientifically known as *Elaeia Guineensis* play one of the major role for Malaysia economy growth. Basically, the economic life for palm oil are within range of 20 to 25 years where each palm bears 8 to 12 bunch annually [9]. There are two type of palm oil that produced from the fleshy mesocarp and also from it seed that obtain from the palm oil fruit.

Crude palm oil is known as an edible oil that come from the ripe palm fruit. Palm oil extracted from the mesocarp of palm fruit contains approximately 50% fats and 40% unsaturated fats [8]. The oil palm consists of 16 carbon saturated fatty acid, palmitic acid, monounsaturated oleic acid and 10% linoleic acid, which is an unsaturated omega-6 fatty acid where linoleic acid is one of the two essential fatty acids that humans require [1]. Vitamin K and dietary magnesium are the main component in palm oil. It is rich in minor components which have nutritional attributes with about 500-700ppm of carotene consisting mainly of α and β carotenes that constitute 90% of the total carotene [10].

Carotenes found in palm oil play an important role in the prevention of cancer, cataracts and degenerative diseases such as heart diseases [2]. Other minor components of palm oil are phytosterols which are very useful in pharmaceutical industries, tocotrienols and tocopherols which serve as powerful radical antioxidant in scavenging free radicals and squalene [9]. Palm oil contribute to many uses of chemical industries such as margarines, waxes, toothpaste, cosmetic, detergent and biofuels. Other than that, it helps to reduce the risk of arterial thrombosis and atherosclerosis.

There are three main processing in producing oil refining that know as degumming, bleaching and deodorization. Degumming process will help to remove the peroxides and secondary oxidation products. Other than that, it helps to remove pigments and any trace of the gums during this refining step [6]. Bleaching process need to be conducted in vacuum condition where it help to prevent the water to contact with the water and the removal of moisture [11]. The formation of the oxidation product will lead to the degeneration and short life of the final products [7]. The desired condition for bleaching process to be carried out at contact temperature in the range of 80–120°C and within the contact time ranging from 20–40 minutes under vacuum condition. During the desired condition, absorption of colouring matter on activated clay can be equilibrated under sufficient activation [7]. The dosage of the beaching earth will vary based on the quality of the crude palm oil itself. Basically, 2–4% bleaching earth can be used to meet final colour requirements [4] and the dosage of activated clay should be the minimum amount to effect removal of impurities as measured by peroxide reduction [6]. Some oil have lost during bleaching process due to the filter cake. It is reported that for oil retention, a typical value is approximately 40% [5] and the oil loss can be reduced by undergo suitable procedure such as by using nitrogen gas at the end of the filtration processing. Therefore, efficient filtration, short filtration times and minimization of oil retention on filter cake are necessary [3]. The bleaching that have be used will be dried before the prior used to prevent the reduction of bleaching power due to decreases of the surface area. Due to that, moisture will drive off rapidly and causing collapse of the bleaching earth structure.

This research aimed to study the characteristic of each bleaching earth to provide useful insight into its potential and particularly its performance which to assess how well this prediction correlates with the actual laboratory result.

II. METHODOLOGY

A. Materials

Three bleaching earth that known as Absorbent I, II and III and crude palm oil are obtaining from the Sime Darby Research Sdn. Bhd. which located at Teluk Panglima Garang. The crude palm oil will act as reference to determine the performance of the bleaching earth while bleaching will act as absorbent in crude palm oil processing the crude palm oil. All chemicals are using base of the analytical grade and provided by Faculty of Chemical Engineering, University of Technology Mara, Shah Alam and Sime Darby Research Sdn. Bhd., Teluk Panglima Garang.

B. Characterisation of samples

The characterisation of each bleaching earth sample will be perform by using few instruments that available in Faculty of Chemical Engineering, University of Technology Mara, Shah Alam. X-ray Fluorescence will analyse component composition that contain in each bleaching earth. The percentage of each component of each result were compared with each adsorbent. The quantities of SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , Na_2O , K_2O , and MgO in the clay wee determined by using Inductively Coupled Plasma (ICP-OES). Another equipment were used is FTIR which help to determine the intensity of the existing component and make the comparison for each bleaching earth.

C. Performance of bleaching earth

Crude palm oil undergo degumming, bleaching and deodorisation process. In degumming process, 0.1% of concentrated phosphoric acid added into the oil at 85 °C and continuously stir. For bleaching process it is carried out at temperature 95 °C for 30 minutes and addition of bleaching earth is based on the 1 % of crude palm oil use. While, in deodorisation process, the palm oil were heated up until reach 260 °C and under vacuum condition of 7 – 10 mBar.

By using Lovibond instrument, the colour of degumming, bleaching and deodorisation oil were determined and compared with the crude palm oil. Value of free fatty acid in the oil can be determine by undergoing titration Then mixed the solution well the mixture and lastly, it were titrate by using sodium hydroxide until the mixture change the colour to permanent pink. While for peroxide value, the mixture of oil mixed with peroxide solution and stirred for a minute. Then, potassium iodide solution mixed with the mixture and stir for a minute. Lastly, the mixture wee added few drop of starch and titrate by using sodium thiosulphate until the black solution turn to clear solution.

D. Comparison of the oil performance

Based on the result, the comparison were made and distinguish which bleaching earth shown the best result based on the analysis value that have been obtained. Other than that, the comparison also can be obtained from the reading of UV-Vis spectrophotometer and other analysis. Based on the result, conclusion of which bleaching earth show better result in characterisation and good performance of bleaching earth were made.

III. RESULTS AND DISCUSSION

Few analysis have been conducted to determine the characteristic of the bleaching earth which by using XRF, ICP-OES and FTIR. While for the performance of the bleaching earth, crude palm oil has been used and undergo refining process which involved degumming, bleaching and deodorisation process. The result then be compared and decided which bleaching earth show the best result by compared their characteristic and performances.

Based on the Table 1, the data show the percentage of the component that exist in each of absorbent. The ratio between Na_2O and CaO need to be less than 1 which indicates the absence of swelling bleaching earth. While for SiO_2 and Al_2O_3 ratio in the absorbent need to be greater than 1. If the bleaching earth fall in the range of both ratio, the bleaching earth is suitable to be used in the refining process of the edible oil. By calculating the both ratio, all the absorbents show that they fall in range they required and three of them are suitable to be used in the refining process. Absorbent I show highest ratio between SiO_2 and Al_2O_3 with value of 2.732. While the lowest ratio between SiO_2 and Al_2O_3 is Absorbent II with value of 2.4557 and Absorbent III ratio is 2.463. By comparing the amount of SiO_2 and Al_2O_3 , Absorbent I show highest composition with value of 38.75% and 14.18% respectively. While for Absorbent II and III show slightly lower than Absorbent I and effect the value of the ratio. For ratio between Na_2O and CaO , Absorbent II show the lowest value which is 0.0298 compared to the others. This is due to the value of Na_2O of Absorbent II show the smaller value compared to Absorbent I. While for Absorbent I and III ratio value between Na_2O and CaO are 0.0363 and 0.0352 respectively.

Table 1. Comparison of the adsorbent by using XRF

Compound	Absorbent I	Absorbent II	Absorbent III
Silica, SiO_2	38.75	33.012	31.730
Alumina, Al_2O_3	14.180	13.443	12.882
Ferric oxide, Fe_2O_3	18.984	22.270	23.806
Titanium Oxide, TiO_2	1.005	1.079	0.970
Lime, CaO	6.718	5.847	4.947
Magnesia, MgO	17.699	22.938	24.336
Phosphoric pentoxide, P_2O_5	0.079	0.098	0.143
Sulphuric anhydride, SO_3	1.577	0.448	0.027
Potassium oxide, K_2O	0.687	0.620	0.813
Sodium oxide, Na_2O	0.244	0.174	0.174
Copper oxide, CuO	0.074	0.071	0.066

Another element that need to be reduce in the bleaching earth are heavy metals such as Ferum, Magnesium, Copper and Potassium. The smallest amount of metal contains in the absorbent by using the XRF is Absorbent I. Absorbent show smallest value of in Magnesium, Copper, Ferric and Sodium content with value

of 17.699, 0.074, 18,984 and 0.244 respectively. While the highest contains of heavy metal is Absorbent III with amount of Magnesium, Copper, Ferric and Sodium were 24.336, 0.066, 23.806 and 0.174 respectively. The heavy metal content in bleaching earth were affected the heavy metal content in the edible oil since the heavy metal from the bleaching earth would be trapped in the oil during bleaching process.

Components that exist in the absorbent determined by using ICP-OES instrument where the result shown the concentration of the element in the bleaching earth. basically, the bleaching earth must undergo acid digestion first before the sample were analyzed. From the result in Table 2, Absorbent I showed highest amount of aluminum element compared to Absorbent II and III with value of 43.386 ppm. While amount of aluminum in Absorbent II and III were 38.871 ppm and 37.889 ppm respectively. Aluminum and silica is the most important element that need to be exist in the bleaching earth since it helped to absorb the impurities in the crude palm oil. Other than that, the remaining metal element that tabulated in Table 2 show that Absorbent I have the lowest amount compared to the others. The presence of the heavy metal in the bleaching earth may increase the reading of the heavy metal content in the refining oil which undesired. Absorbent III show the highest amount of heavy metal compared to the Absorbent II and I. Absorbent III shows the huge amount of ferum, calcium and also magnesium where the values were 1.661, 9.915 and 5.561 respectively. While for absorbent I the amount of ferum, calcium and magnesium are 4.612, 7.859 and 2.620 respectively. The heavy metal lead to the increased amount of heavy metal in the edible oil. Therefore, less amount of heavy metal in the bleaching showing the quality of the bleaching earth itself. Other than that, the huge amount of silica and aluminum is needed to remove impurities in the oil sample.

Table 2. Component analysis by using ICP-OES

Component, ppm	Absorbent I	Absorbent II	Absorbent III
Aluminum, Al	43.386	39.871	37.889
Calcium, Ca	7.859	9.766	9.915
Copper, Cu	0.033	0.446	1.536
Ferum, Fe	4.612	8.181	11.120
Phosphorus, K	1.161	1.393	1.661
Magnesium, Mg	2.620	4.237	5.561
Manganese, Mn	0.021	0.087	0.118
Sodium, Na	0.139	0.141	0.241
Lead, Pb	0.023	0.041	0.115
Zinc, Zn	0.455	0.432	0.443

Figure 1 shows FTIR spectra of samples Absorbent I, II and III and Table 3 show summarizes the major vibrations observed. By comparing the graph and also the table, each absorbent shows different intensity for each band

assignments. For Absorbent I, it showed highest intensity of SiO stretching with value of 1740.44 cm^{-1} while for Absorbent II and III value for SiO stretching in average are 1544.23 cm^{-1} and 1543.23 cm^{-1} respectively. It show that Absorbent I have the highest amount of silica in the bleaching earth. While Absorbent II showed the second highest amount in intensity which similar with the comparison in the Table 1. Other than that, Absorbent I show highest intensity of OH deformation that linked to 2 Al^{3+} with the value of 1014.61 cm^{-1} which can be relate with the composition that have been obtain by using XRF in Table 1. For Absorbent II and III, the intensity value for OH deformation that linked to 2 Al^{3+} are 982.91 cm^{-1} and 977.19 cm^{-1} respectively.

Based on the FTIR spectra in Figure 1, Absorbent I doesn't show the intensity for OH deformation that linked to Al^{3+} and Mg^{2+} and only Absorbent II and III show the intensity value. OH deformation that linked to Al^{3+} and Mg^{2+} for absorbent II and III were 879.19 cm^{-1} and 875.02 cm^{-1} respectively. By comparig with the XRF and ICP-OES data in Table 1 and 2, it shows that Absorbent I have the lowest value compared to the Absorbent II and III. Therefore, the result is tally by comparing the result from each data. Other than that, for OH stretching in Absorbent III have the lowest value of 3360.37 cm^{-1} compared to the others. OH stretching for Absorbent I and II are 3365.63 cm^{-1} and 3380.97 cm^{-1} respectively. The OH stretching may contribute to the characterisic of the dioctahidral clay that present in the bleaching earth

Table 3. Characteristic FTIR bands for bleaching earth

Wave number	Band assignment
3624 – 3239	OH stretching
3416	Hydration, OH stretching
1638 – 1618	Hydration, HOH deformation
1089 – 1042	SiO stretching
915	OH deformation, linked to 2 Al^{3+}
845	OH deformation, linked to Al^{3+} and Mg^{2+}
793	Silica phase
626 – 467	SiO deformation and AlO stretching

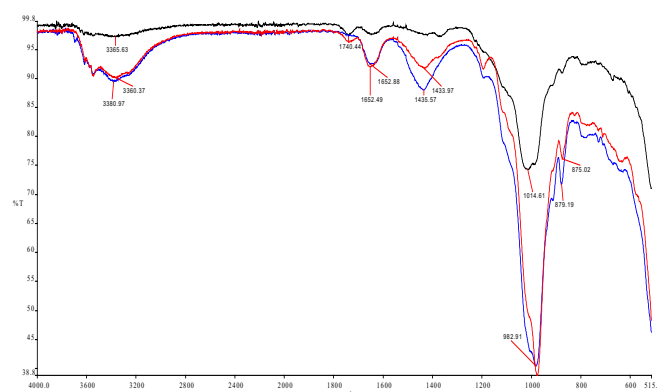


Figure 1. FTIR intensity graph of adsorbents

The formation of fatty acid formed in hydrolysis process of triglycerides which happen due to the presence of moisture in the palm oil. Lower amount of free fatty acid was suggested to produce good quality of edible oil. By referring on the past studies, the allowable value of free fatty acid in cooking oil need to be lower than 0.05. The reduction of free fatty acid can be achieved by undergo

bleaching process and reduction in value showed us the freshness of the palm oil that we used. Based on Table 4, amount of free fatty acid from the crude palm oil was decreased by using the absorbent. Free fatty acid value of crude palm oil was 3.867 and when the crude palm oil undergoes refining process the value would be decrease. Absorbent I able to reduce the highest free fatty acid value and it shown the best result compare to other absorbent which was 0.0214. While Absorbent III show the highest and unfavorable free fatty acid value compare to the other absorbent which 0.0435. Absorbent II still in the range since the free fatty acid value was 0.0326.

Peroxide value were used to indicates the quality and the stability of edible oil (Ekwu and Nwagu, 2004). Other than that, it helps to show the extent of the oil rancidity and the desired amount of peroxide value must be below than 10 meq/kg. The crude palm oil itself was below than the desired amount which is 3.867 and showed the freshness of the palm oil. After crude palm oil undergo refining processes, normally peroxide value was absence since the cooking oil was not undergo any oxidation process. Therefore, based on Table 4, all three absorbents shown the absence of peroxide value in the oil sample. But peroxide value can be obtaining if the oil undergo stability in the oven since oxidation were happen during the duration.

The colour value of the sample was another indicator of the edible oil quality. The standard range for the oil sample for palm oil are 2.5 – 3 red(R) and 26 – 28 yellow(Y) based on SON (2000). In Table 4, the colour of crude palm oil is 30R 30Y and the value of the crude palm oil will be reduced by undergo refining process. Compare to the three type of absorbent used, Absorbent I show the lowest value of colour which is 2.3R 23Y where the value is between the standard range. The other absorbent that fall between the standard range is Absorbent II with value of 2.7R 27Y. While for Absorbent III, the colour value show unfavorable result since it falls out of range with value of 2.9R and 29Y.

The colour absorbance value of the crude palm oil and refined oils was conducted by using UV-Vis spectrophotometer and measured at 450 nm. Based on the observation the absorbance value for the refined oil was lower than the absorbance value of the crude palm oil. In Table 4, the absorbance value of crude palm oil is 0.5336 and the lowest absorbance value for refined is Absorbent II with value of 0.367 with percentage of reduction colour 23.11%. There was small difference for Absorbent II and III where the value of percentage of colour reduction of Absorbent II is 23.11%. While the highest value of percentage of colour reduction is 27.98% where the value obtains from the Absorbent I. The result obtains based on the removal of colouring pigment during the refining process. Other than that, it also states that the type of absorbent used in the bleaching process may affect the reduction of colour in palm oil.

Table 4. Performances of palm oil after refining

	Crude Palm Oil	Absorbent I	Absorbent II	Absorbent III
Free Fatty Acid	3.687	0.0214	0.0326	0.0435
Peroxide Value	3.1398	NIL	NIL	NIL

Colour	30R 30Y	2.3R 23Y	2.7R 27Y	2.9R 29Y
Percentage of Colour Reduction, %	-	27.98	23.11	25.54

Where R = red and Y = yellow

Other than that, the performance of the absorbents were been shown by comparing the colour, free fatty acid value, peroxide value and percentage of colour reduction. Since Absorbent I showed the lowest value in FFA, PV and colour value and highest value in percentage of colour reduction compared to the other absorbent. It was relatable by comparing the characteristic of the bleaching earth and its performance since good characteristic of the bleaching earth will give good performance in refining process of crude palm oil.

IV. CONCLUSION

Conclusion that can be made on this research that the characteristic of the bleaching earth may affect the performance on the palm oil processing. Absorbent I show higher amount of silica, SiO and Alumina, Al₂O₃ and low amount of metal such as ferum and magnesium compare to the others. Performance of palm oil is highly affected by the characteristic of the bleaching earth and the palm oil quality. Good quality of the bleaching earth may adsorb all the impurities in the crude palm oil and remove it through the refining process. Therefore, refining process must at the optimum condition to ensure good quality of the end product which it will remove all the impurities in the palm oil. Based on the result, it shows that the end product of palm oil that show better result is Absorbent I. Performance of Absorbent I show lowest amount of free fatty acid, peroxide value, colour and highest in percentage of colour reduction.

Other parameter can be considered to ensure the quality of final product rather than the characterisation of the bleaching earth itself. Temperature, pressure and quality of the crude palm oil are the parameter that may affect the final result. Different temperature and pressure would give different result since it would affect the impurities removal. At low temperature or pressure, less amount of free fatty acid will be remove since it required more than 180 °C and under vacuum condition. While at high temperature and pressure, peroxide value will be increased if the temperature is exceeding the optimum condition. Other than that, other analysis can be done to determine the performance of the bleaching earth such as moisture, viscosity, density and 3-chloropopane-1,2-diol (3-MCPD) value. This analysis also may help to determine and give more accurate result. another research can be done in this research is to determine the desired condition to reduce the 3-chloropopane-1,2-diol (3-MCPD). This component is not a good component to be exist in the palm oil. the amount need to be reduce as low as it can. This trial is still under research and once the condition has been determined, it is very useful for palm oil processing industry since it is one of the requirement in Europe country for this edible oil to be imported to their market.

ACKNOWLEDGMENT

Thank you to my supervisor, Dr Sherif Abdulbari Ali and University Teknologi Mara (UiTM) for supporting me to finish this research. And not to forget, Sime Darby Research, En. Mohammad Saiful Nidzam B Ismail who support this research by allowing to use the facility in Sime Darby to carry out this research.

References

- [1]Analava, M. and Sutapa, M. (2009). Health Effects of Palm Oil. *Journal of Human Ecology*, 26(3):197-203 (2009)
- [2]Choo, Y. M. (2000). Specialty Products: Carotenoids. *Advances in Oil Palm Research* (Basiron, Alani, BS and Chan, K. eds). Vol. II. MPOB, Bangi P., 1036 – 1060.
- [3]D.A.Morgan,D.B.Shaw,M.J.Sidebottom,T.C.Soon,andR. S. Taylor, “The function of bleaching earths in the processing of palm, palm kernel and coconut oils,”*Journal of the American Oil Chemists’ Society*, vol. 62, no. 2, pp. 292–299, 1985
- [4]D. F. Valenzuela and S. P. De Souza, “Studies on the acid activation of Brazilian smectitic clays,” *Quimica Nova*, vol. 24, no. 3, pp. 345–353, 2001.
- [5]K. Baranowsky, W. Beyer, G. Billek et al., “Technologies for industrial processing of fats and oils,” *European Journal of Lipid Science and Technology*, vol. 103, pp. 505–551, 2001.
- [6]L. H. Wiedermann, “Degumming, refining and bleaching soybeanoil,”*JournaloftheAmericanOilChemists’ Society*,vol. 58, no. 3, pp. 159–166, 1981.
- [7]M. A. Usman, V. I. Ekwueme, T. O. Alaje and A. O. Mohammed (2011). Characterisation, acid activation and blacing performance of Ibshe clay, Lagos, Nigeria, *Journal of Chemical Engineering*. Available from: Department of Chemical Engineering of University of Lagos
- [8]Ogwu, F.M., Odo M, and Osborne O. (2012). The quality of locally processed palm oil from Ebonyi and Enugu states. *Proceedings of the 26th Annual NIFST conference*, 4th - 8th Nov. 2012: 47-48.
- [9]Okolo J. C., Adejubo D. A. (2014). Effect of bleaching on some quality attributes of crude palm oil. *Journal of engineering*. Available from: Department of Agricultural and Bioresources Engineering, Federal University of Technology, Minna, Nigeria.
- [10]Puah, C. W., Choo Y. M., Ma, A. N. and Chuah, C. (2004). Degumming and Bleaching: Effect on selected Constituents of palm oil. *Journal of Oil Palm Research* 16 (2) 57 – 63.
- [11]“Young’s Corporation, User’s Guide of Activated Clay,” <http://www.youngscorp.com/>.