Jurnal
Teknologi

Full Paper

FEASIBILTY OF KAOLIN AND MICA AS BLEACHING EARTHS FOR THE REMOVAL OF ORGANIC COMPOUNDS FROM CRUDE PALM OIL

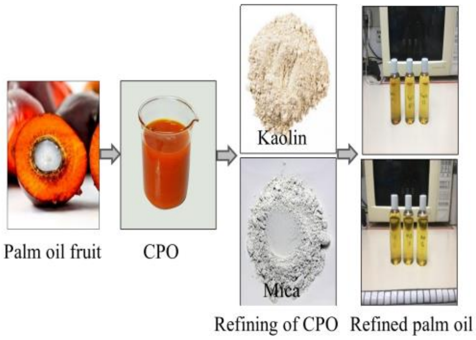
Article history
Received
15 March 2022
Received in revised form
22 June 2022
Accepted
4 July 2022
Published Online
21 August 2022

Mohd Hakimi Rosli[a], Ahmer Ali Siyal[a], Rashid M Shamsuddin[a]*, Aaron Low[b]

[a]HICoE, Centre for Biofuel and Biochemical Research (CBBR), Institute of Sustainable Living, Department of Chemical Engineering, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak Darul Ridzuan, Malaysia
[b]Ligar LP, Raukura Research Campus, Hamilton, 3214, New Zealand

*Corresponding author
mrashids@utp.edu.my

Graphical abstract



Abstract

This paper describes the feasibility of use of locally available kaolin and mica for refining crude palm oil (CPO) and compares their performance with commercially available bleaching earth (Attapulgite) which is commonly used in the palm oil industry. The materials were characterized for chemical composition, surface area, pore size and pore volume, functional groups, and microstructure. The performance of refining was determined by measuring the removal of color, phosphorous, free fatty acids (FFA), and peroxide from palm oil. Attapulgite, kaolin and mica mainly contained silica, alumina and ferrous oxide and they were mesoporous materials with surface area of 89.932, 4.889, and 8.195 m^2/g respectively. Functional group analysis showed decrease in the intensity of peaks due to adsorption of phosphorous which was in the order of attapulgite>mica>kaolin. Microstructural analysis showed heterogenous behavior of adsorbents with the presence of particles of different size. The refining of CPO results indicated that both kaolin and mica were able to adsorb impurities from the CPO. Attapulgite had the highest bleaching efficiency followed by mica and kaolin. Based on the obtained results, mica has the potential of refining of CPO and its performance could be further improved by activation using different agents.

Keywords: Palm oil, bleaching earth, kaolin, mica, attapulgite

Abstrak

Kertas kerja ini menerangkan kebolehsanaan penggunaan kaolin dan mika yang tersedia secara tempatan untuk penapisan CPO dan membandingkan prestasinya dengan tanah peluntur sedia ada secara komersial (Attapulgite) yang biasa digunakan dalam industri minyak kelapa sawit. Bahan-bahan tersebut dianalis untuk komposisi kimia, luas permukaan, saiz dan isipadu liang, kelompok berfungsi, dan struktur mikro. Prestasi penapisan ditentukan dengan mengukur penyingkiran warna, fosforus, asid lemak bebas (FFA), dan peroksida daripada minyak kelapa sawit. Kandungan utama attapulgite, kaolin dan mika adalah silika, alumina dan ferus oksida dan mereka adalah bahan mesopori dengan luas permukaan masing-masing 89.932, 4.889, dan 8.195 m^2/g. Analisis kelompak berfungsi menunjukkan penurunan dalam keamatan puncak disebabkan oleh penjerapan fosforus yang berada dalam urutan attapulgite> mika> kaolin. Analisis mikrostruktur menunjukkan tingkah laku heterogen penjerap dengan kehadiran zarah yang berbeza saiz dan liang. Penapisan keputusan CPO menunjukkan bahawa kedua-dua kaolin dan mika mampu menyerap kekotoran daripada minyak kelapa sawit mentah. Attapulgite mempunyai kecekapan peluncuran tertinggi diikuti oleh mika kemudiannya kaolin. Berdasarkan keputusan yang diperolehi, ia telah dicadangkan bahawa mika mempunyai potensi untuk menapis CPO dan prestasinya boleh dipertingkatkan lagi dengan pengaktifan menggunakan agen yang berbeza.

Kata kunci: Minyak sawit, pelunturan bumi, kaolin, mika, attapulgite

© 2022 Penerbit UTM Press. All rights reserved

1.0 INTRODUCTION

Edible oil products are primarily obtained from African oil palms known as Elaeis-guineensis which were first discovered near the Gulf of Guinea in West Africa. The fruit from this tree can produce two types of oils: palm oil from the mesocarp of the fruit and palm kernel oil from the kernel of the nut. The two types of oil contain different chemical and physical properties. Palm oil is one of the most highly consumed vegetable oil worldwide due to its high nutritional values, health benefits, competitive pricing, and other superior characteristics [1, 2]. Even though palm oil is indigenous to Africa, Malaysia and Indonesia are currently the two largest producers of palm oil in the world.

Palm oil is used in many food items such as chocolates, ice cream, snacks, and bakery products. It is also used in non-food products such as cosmetics, soaps, and candles. Minor components such as free fatty acids (FFA), phosphatides, sterols, partial acylglycerols, tocotrienols, tocopherols, pigments, hydrocarbons, vitamins and heavy metals are formed or extracted during sterilisation, threshing, stripping, oil extraction, clarification and purification of the fresh fruit bunch (FFB) extract crude palm oil (CPO) [3]. It is necessary to lower the amounts of FFA, phospholipids, trace metals, sterols, and oxidation products to below acceptable levels for the palm oil to meet the required regulations as an edible oil. FFA exist in palm oil as part of the triacylglycerol molecule [4]. Their presence in the oil indicates low oil quality [5]. FFA exists in two forms: trans-fatty acids and cis-fatty acids. Trans-fatty acids decrease good cholesterol levels and increase bad cholesterol levels in the body [6]. It is detrimental to heart and can cause cardiac death [7]. The presence of organic compounds such as carotenoids especially beta-carotene and its derivatives xanthophyls, chlorophyll, pheophytin, gossypol and their degradation products result in the undesirable colour of palm oil [8]. It is not essential to remove all components present in CPO as some components such as tocopherols and tocotrienols are essential as they protect oil from oxidation and possess vitamin E activity [9]. CPO is refined to produce a bland taste, a light colour and good oxidative stability [10, 11]. Chemical and physical methods are used to refine CPO. Physical methods are usually preferred due to their fast processing time, low operational cost, lower oil loss, and lower waste emissions [7, 10]. Physical treatment consist of two stages; pre-treatment of CPO (degumming and bleaching) and steam stripping or deodorization [12]. Initially degumming is carried out to remove phosphatides which disrupt the stability of oil at later stages. After the degumming process, the minor components in the oil such as colorants are removed by adsorption bleaching. The compounds which promote deterioration of oil quality mainly due to their pro-oxidative properties are also removed during the bleaching process [8]. Colour pigments such as carotenoids in palm oil physically adsorb on to the bleaching clay through van der walls forces while other components are chemically bonded through covalent or ionic bonds [10, 13]. The degumming and bleaching processes must be efficiently operated at optimum conditions to get high quality refined oils. The bleaching process is the most important step in the refining of CPO. During this process bleaching earth is mixed with the oil in a bleaching chamber between 20-30 minutes [10, 14]. Bleaching earth adsorb colouring pigments and other components such as soaps, phospholipids, oxidation products, trace metals and contaminants [15, 16]. The Malaysian Palm Oil Board (MPOB) standard for color index of a refined bleached and deodorized palm oil (RBDPO) is 3R [12]. The deodorization process is a vacuum stripping process at high temperatures (up to 300 °C). Free fatty acid (FFA) and other volatile components are removed during deodorization.

Bleaching using bleaching earth is the most expensive component of the CPO refining process and is responsible for 20% of the refining cost mainly due to the use of imported bleaching agents. Moreover, the bleaching earth also adsorbs around 20-40% of oil during bleaching process which is not removed and the used bleaching earth is disposed of in landfills without any pre-treatment [17, 18]. Therefore, it is desirable to use locally available and regeneratable materials to reduce the cost of bleaching of CPO and increase sustainability of the industry. A variety of materials such as natural clays, acid-activated clay, carbon-activated clay, activated carbon, and silicates have been used as bleaching earths in the refining of CPO [19, 20]. However, Malaysia has an abundant source of clays such as kaolin and mica which can be used as potential cheap alternative adsorbents to replace imported bleaching earths. Therefore, kaolin and mica are proposed for bleaching of CPO.

This paper describes the characterization of bleaching earth (attapulgite), kaolin and mica such as chemical composition, surface area and pore size analysis, functional group analysis, and microstructural analysis and the application of these three adsorbents in the refining of CPO, especially for the removal of colour, phosphorous, and free fatty acids (FFA). The performance of locally available kaolin and mica was also compared with the commercially available bleaching earth (attapulgite).

2.0 METHODOLOGY

2.1 Materials

Kaolin and Mica were obtained from Kaolin Sdn. Bhd, in Shah Alam, Selangor, Malaysia. Crude palm oil (CPO) imported bleaching earth (Attapulgite) and binder were obtained from Sime Darby Jomalina in Teluk Panglima Garang, Selangor, Malaysia. Analytical grade magnesium oxide (MgO), nitric acid (HNO_3), ammonium molybdate ($(NH_4)_2MoO_4$), and ammonium monovanadate (NH_4VO_3) were purchased from Sigma Aldrich.

2.2 Methods

2.2.1 Characterization of Adsorbents

Chemical Composition Analysis

Adsorbent samples of attapulgite, kaolin and mica were dried at 110 °C in an electric oven (UFF 110, Memmert, Germany) for 2 hours and ground to a uniform particle size using mortar and pestle. Samples were put on boric acid backed discs and analyzed for multi-elements using X-Ray Florescence (XRF, S8 Tiger, Bruker, Germany).

Surface Area and Pore Size Analysis

The surface area, pore size and pore volume of attapulgite, kaolin and mica were determined through N_2 gas adsorption-desorption isotherms using Micrometrics ASAP 2020. Brunauer–Emmett–Teller (BET) multi point, Barrett-Joyner-Halenda (BJH) and t-plot methods were used for determining the total surface area, mesopore size distribution and micropore volume and surface area.

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

15 mg of the dried attapulgite was mixed with 1 g of potassium bromide (KBr) powder. The mixture was ground in a mortar and pestle until the particle size was uniform. The powder mixture was pelletized using a steel die. About 0.25 g of the pellet was put on a sample holder for FTIR analysis at the range of 400 to 4000 cm^{-1} using a Perkin-Elmer Spectrum One FTIR. The same method was used for kaolin and mica.

Microstructural Analysis

A sample of attapulgite was coated with gold nanoparticles prior to microstructural analysis. The sample was tightly scattered on double-sided adhesive and conductive carbon. Air was blown on the sample to remove light particles. The same method was used to prepare kaolin and mica for microstructural analysis. The micrographs of adsorbents before and after refining of CPO were recorded in the magnification of 600X and 500X. The VPFESEM, Zeiss Supra 55 VP was used for microstructural characterization of attapulgite, kaolin, and mica.

2.2.2 Refining of Crude Palm Oil (CPO)

Degumming

The CPO was melted in a water bath and 1 litre was measured using a measuring cylinder. The sample was then poured into a flask. The head of the flask was sealed completely to avoid the air from entering the flask. The sample was agitated at 520 rpm and heated until it reached 85 °C. The volume of phosphoric acid was calculated using equation (1).

$$\begin{aligned}&\text{Volume of phosphoric acid} = \\ &\text{Volume of oil used} \times \\ &\text{\% of phosphoric acid}\end{aligned} \qquad [1]$$

The amount of phosphoric acid calculated was inserted into the sample. The temperature was maintained at 85 °C for 20 minutes. The same procedure was repeated for other samples of CPO.

Bleaching

The sample was heated until it reached 95 °C. The bleaching earth was poured into the flask and the vacuum pump was turned on. The temperature of the sample was maintained at 95 °C for 30 minutes. Then the sample was filtered. The same procedure was used for both kaolin and mica, and the amount of phosphorus removed was determined. The mass of bleaching earth was calculated using equation (2).

$$\begin{aligned}&\text{Mass of bleaching earth} = \text{Specific gravity of oil} \\ &\times \text{volume of oil used} \times \text{dosage of bleaching earth}\end{aligned} \qquad [2]$$

Deodorization

The bleached sample was poured into the flask and the water was added. The vacuum pump was started. The heater for steam was turned on and set to 3 bar. The binder was turned on and the temperature was set according to the condition of each sample. The time taken for the deodorization process was recorded as the binder's temperature reached 260 °C. After 1 hour and 30 minutes, the sample was cooled.

2.2.3 Performance Analysis of Adsorbents

Color Analysis

The colour of refined palm oil was measured using the AOCS (American Oil Chemist's Society) Lovibond method. A glass cell with a bond length of 25.4 mm was filled with sample of the refined palm oil. The glass cell was then placed in a Tintometer and the sample colour was matched with red and yellow and expressed as 5R+Y [21].

Phosphorous Content

0.1 grams of magnesium oxide was put into a porcelain dish and the 6 grams of sample was added. The sample was burned into white ash by heating the furnace at 800 °C for 2 hours. The sample was cooled down and then 5 ml of aqueous nitric acid solution was added into the sample. 20 ml of aqueous ammonium molybdate solution and 10 ml of aqueous ammonium monovadate solution were mixed for 20 minutes. A blank test was conducted under the same conditions. The extinction at 400 nm was measured against the blank solution. The absorbance was measured using ultra-violet visible spectroscopy (UV 1800, Shimadzu, Japan) and the concentration of phosphorous was determined.

Free Fatty Acids (FFA)

50 mL of IPA was poured into a beaker containing 10 grams of the refined palm oil sample. 2-3 drops of phenolphthalein were added into the sample. The sample was agitated and heated to 120 °C. The samples of refined palm oil were titrated using potassium hydroxide (KOH) until it reached purplish colour. The amount of potassium hydroxide added was calculated by subtracting the final reading of the burette from the initial reading. The amount of free fatty acid was calculated by using the equation (3).

$$FFA = VNM/10W \qquad [3]$$

Where,
W: Weight of sample
V: Volume of potassium hydroxide (KOH) solution used

3.0 RESULTS AND DISCUSSION

3.1 Initial Crude Palm Oil (CPO) Composition

The initial composition of CPO (colour, phosphorous content, and free fatty acids (FFA)) is shown in Table 1. CPO has a red colour, contains 106 ppm of phosphorous after degumming (11 ppm before degumming), and 3.089% of FFA. The content of phosphorous increased after degumming due to the attachment of phosphorous with phosphatides. The peroxide value of CPO is 5.54%.

Table 1 Composition of crude palm oil

Property	Value
Colour (R)	30
Phosphorus (ppm)	11
Phosphorus after Degumming (ppm)	106
Free Fatty acid (%)	3.089
Peroxide value (%)	5.54

N: Normality of potassium hydroxide (KOH)
M: Molecular weight of sample

3.2 Characterization of Adsorbents

3.2.1 Chemical Composition of Adsorbents

The chemical composition of adsorbents is shown in Table 2. Attapulgite, kaolin and mica mainly contain SiO_2, Al_2O_3 and Fe_2O_3 in higher amounts while other compounds such as magnesium oxide (MgO), calcium oxide (CaO), potassium oxide (K_2O), titanium oxide (TiO_2), phosphorous pentoxide (P_2O_5), and zirconium dioxide (ZrO_2) are present in lower amounts. The content of SiO_2 is higher in kaolin as compared to attapulgite and mica while the content of Al_2O_3 is higher in mica as compared to attapulgite and kaolin. The contents of F_2O_3, MgO, CaO, TiO_2, and P_2O_5 are higher in attapulgite when compared to kaolin and mica. The chemical composition of attapulgite, kaolin and mica is comparable to oil palm boiler ash (OPBA) used for the refining of palm oil [12]. The compounds present in attapulgite bleaching earth are also present in kaolin and mica which shows that the kaolin and mica can also be used as potential adsorbents for the refining of CPO.

Table 2 Chemical compositions of attapulgite, kaolin, and mica

Components	Composition (wt. %)		
	Attapulgite	Kaolin	Mica
SiO_2	51.7	63.7	53.9
Al_2O_3	7.12	23.9	25.0
Fe_2O_3	13.4	1.99	4.03

Components	Composition (wt. %)		
	Attapulgite	Kaolin	Mica
MgO	4.82	0.953	1.50
CaO	16.3	0.304	0.291
K_2O	2.74	6.50	12.0
TiO2	2.03	1.28	1.79
P2O5	1.18	1.05	1.02
ZrO_2	0.0175	0.159	0.0753

3.2.2 *Surface Area and Pore Size Analysis of Adsorbents*

The nitrogen gas adsorption-desorption isotherms of attapulgite, kaolin and mica are shown in Figure 1. The adsorption-desorption isotherm of attapulgite, kaolin and mica at lower pressure resemble to the type I of the isotherm classification of International Union of Pure and Applied Chemistry (IUPAC) [22]. Type I describes adsorbents as microporous while isotherms of attapulgite, kaolin and mica follow type IV at higher pressure which describes adsorbents as porous materials. The surface area, pore size and pore volume results of attapulgite, kaolin and mica are shown in Table 3. The surface area of attapulgite, kaolin and mica are 89.932, 4.889 and 8.195 m^2/g respectively. This shows that the surface area of attapulgite is 18.395 and 10.974 times higher than kaolin and mica. The pore size analysis of adsorbents shows that the attapulgite, kaolin and mica are mesoporous materials possessing pore sizes in the range of 8.533 to 11.970 nm while the pore volume of attapulgite is higher than kaolin and mica. The surface area and pore volume of attapulgite is higher than kaolin and mica. Mica has higher surface area and pore volume as compared to kaolin. The surface area of kaolin and mica is comparable to chitosan flake used for the adsorption of residue oil from mill effluent which shows that kaolin and mica can be used adsorbents for the refining of CPO [23].

In previous studies kaolin and mica have been used for the adsorption of heavy metals [24, 25] and it can be expected that they will perform better than other materials for adsorbing impurities from crude palm oil.

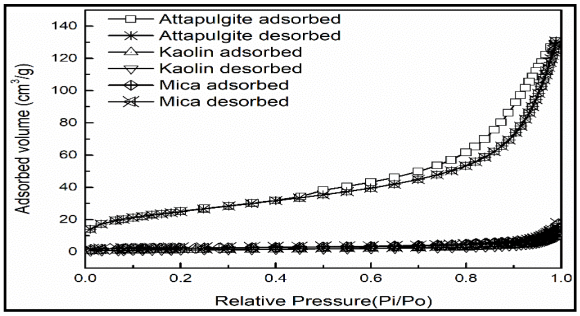


Figure 1 N_2 adsorption-desorption isotherm of attapulgite, kaolin and mica

Table 3 Surface area and pore size analysis of adsorbents

Surface Property	Attapulgite	Kaolin	Mica
Surface area (m^2/g)	89.932	4.889	8.195
Pore size (nm)	8.533	11.970	10.030
Pore volume (cm^3/g)	0.191	0.014	0.020

3.2.3 *Fourier Transform Infrared Spectroscopy (FTIR) Analysis*

FTIR spectra of attapulgite, kaolin and mica before and after bleaching process is shown in Figure 2 (a-c).

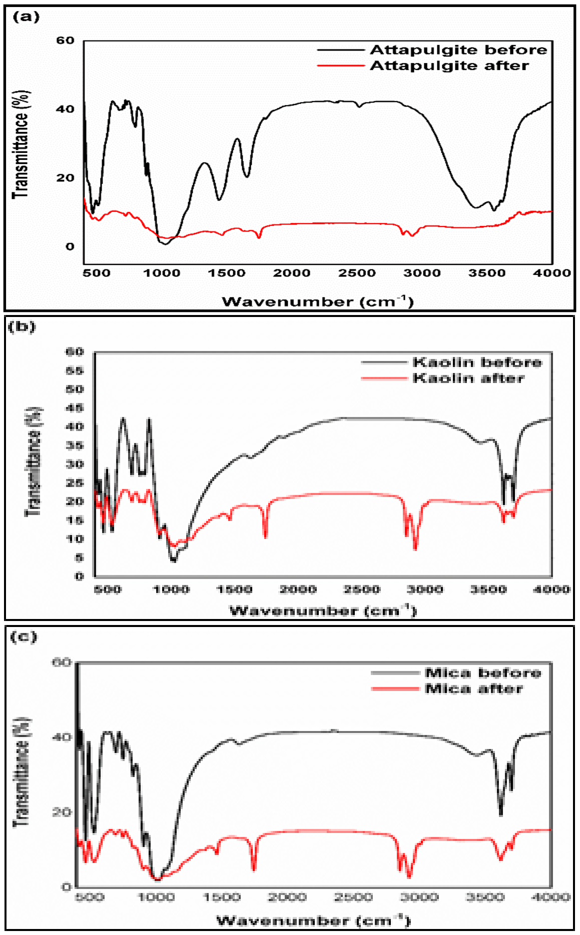


Figure 2 FTIR spectra of attapulgite, kaolin, and mica before and after bleaching

The peaks at 3551 cm^{-1} and 3412 cm^{-1} are due to stretching vibration of N-H in attapulgite. The peak at 1656 cm^{-1} is due to stretching vibration of C=C and the peak at 1439 cm^{-1} is due to bending vibration of C-H bonds. The peaks at 3696 cm^{-1}, 3651 cm^{-1}, and 3620 cm^{-1} in the kaolin were due to stretching vibration of -OH bonds [26]. The peak at 3435 cm^{-1} was due to O-H stretching (Al-OH or Si-OH) while the peak at 1031 cm^{-1} was due to Si-O-Si symmetric stretching [27, 28]. Mica showed peaks at 3698 cm^{-1}

and 3620 cm^{-1} due to stretching vibration of Si-OH bonds. The peak at 3436 cm^{-1} was due to stretching vibration of O-H bonds. The peak at 1083 cm^{-1} was due to stretching vibration of Si-O-Si and the peak at 830 cm^{-1} was due to vibration of silicate layer [29, 30].

After bleaching, the peaks at 1161 cm^{-1} (attapulgite), 1159 cm^{-1}, 1116 cm^{-1}(kaolin), and 1088 cm^{-1} (mica) were due to P=O bonds. The peaks at 1040 cm^{-1} (attapulgite), 1031 cm^{-1} (kaolin), and 1080 cm^{-1} (mica) were due to P-O-C bonds. The peaks at 1745 cm^{-1} (attapulgite), 1745 cm^{-1} (kaolin), and 1745 cm^{-1} (mica) are due to C=O bonds of phosphorous. The amount of phosphorus adsorbed by three adsorbents was in the order of attapulgite > mica > kaolin. These results indicated that the locally available adsorbents kaolin and mica were able to adsorb phospholipids. The performance of the locally available adsorbents was comparable to the industrially used attapulgite adsorbent.

3.2.3 *Microstructural Analysis*

Microstructural images of attapulgite, kaolin, and mica before and after refining of CPO are shown in Figure 3 (a-f).

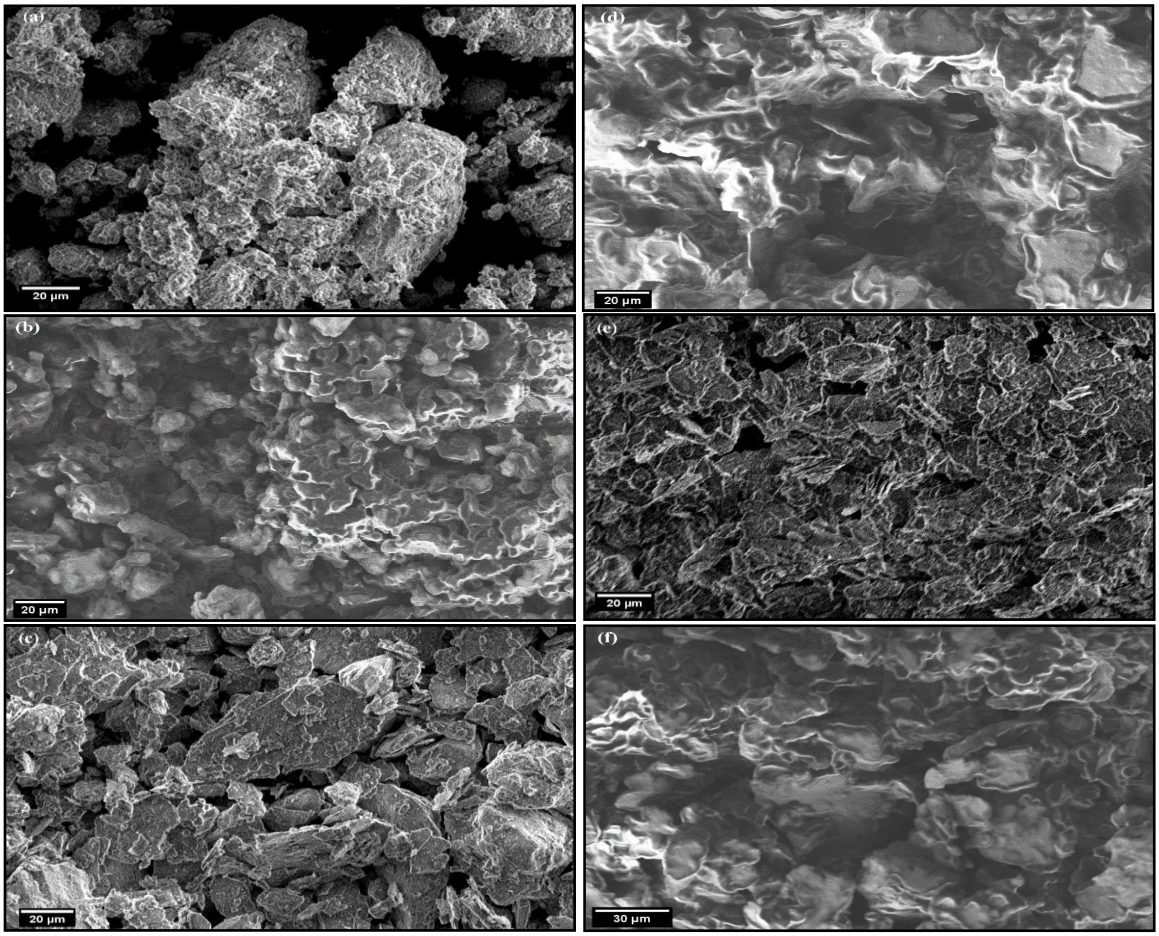


Figure 3 Microstructural images of a)attapulgite-before, b)attapulgite-after, c)kaolin before, d)kaolin-after, e) mica-before, and f) mica-after

All three adsorbents had an irregular shape consisting of small and large particles. Attapulgite contained flakes on its surface and some pores can also be seen as shown in Figure 3 (a). Kaolin contained a higher quantity of small particles as compared to large particles. Mica contained a mixed composition of small and large particles. Attapulgite, kaolin, and mica contains carbon, oxygen, aluminium (Al), and silicon (Si) as shown in Table 4. The microstructure of attapulgite, kaolin and mica were covered with oil particles after refining of CPO which was due to adsorption of oil particles on the surface of adsorbents as shown in Figure 3 (b, d, and f).

The microstructures of kaolin and mica was similar. Kaolin and mica have been used in the adsorption of heavy metals and dyes [30-33] and the covering of their surface after bleaching with oil shows that these have adsorbed impurities from oil.

Table 4 EDX composition of adsorbents

Element	Weight%		
	Attapulgite	Kaolin	Mica
C	22.92	9.26	9.75
O	42.24	57.14	48.10
Mg	2.72	-	-
Al	17.19	7.01	14.30
Si	14.92	26.60	27.85

3.3 Refining of Crude Palm Oil Using Locally Available Adsorbents

3.3.1 Effect of Adsorbent Dosage on Color Removal

The results of colour removal using dosages of 1, 3 and 5% of attapulgite, kaolin and mica are shown in Figure 4(a). Increasing the adsorbent dosage reduced the colour index and changed the colour of palm oil from red orange to light yellow. Increasing the adsorbent dosage increased the number of active adsorption sites which resulted in the higher removal of colour pigments. The highest colour removal was achieved at adsorbent dosage of 5%. The colour index of 1.0 R, 4 R, and 3 R were obtained for attapulgite, kaolin and mica respectively. The highest colour removal was achieved by attapulgite due its higher surface area. The colour removal by the three adsorbents was in the following order: attapulgite>mica>kaolin.

The Malaysian Palm Oil Board (MPOB) standard for colour index of a refined bleached and deodorized palm oil (RBDPO) is 3 R [12]. The experimental results may not produce similar results as compared to palm oil refinery due to pressure and vacuum conditions which cannot be achieved in lab scale experiments [10]. As can be seen from the results, the locally available bleaching earth mica has achieved a colour index of 3 R. The colour removal by kaolin and mica was higher when compared to results obtained in other studies using press mud, rice husk, and peanut hulls [34]. This suggests that mica can be used as a potential substitute for conventional bleaching earth.

3.3.2 Effect of Adsorbent Dosage on Phosphorous Removal

During the degumming process, phosphorous in the form of phosphatides are formed which must be removed during the bleaching process [35]. Phosphorous in the CPO exists in the forms of phospholipids, gums, and inorganic phosphates [36]. The results of the phosphorous removal are shown in Figure 4(b). Increasing the dosages of attapulgite, kaolin, and mica decreased the phosphorous content due to increased number of active adsorption sites. Increased phosphorous removal with increasing adsorbent dosage is consistent with literature studies [36]. The lowest phosphorous content of 3 ppm was achieved at 5% of adsorbent dosage. Attapulgite removed 98% of the phosphorous whereas kaolin and mica removed 46% and 48% respectively. Attapulgite had the highest removal of phosphorous from CPO. Mica performed better then kaolin from the locally available adsorbents.

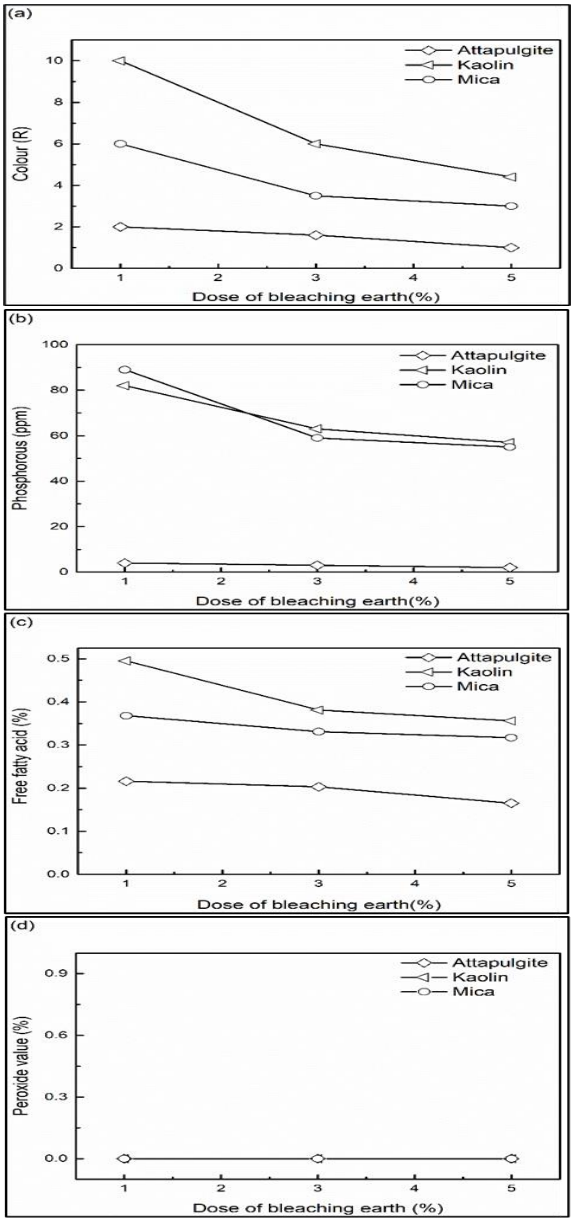


Figure 4 Effects of bleaching dosages on a) colour, b) phosphorous, and c) FFA removal, and d) peroxide value using attapulgite, kaolin, and mica

3.3.3 Effect of Adsorbent Dosage on FFA Removal

The results of the free fatty acids (FFA) removal are shown in Figure 4(c). Increasing the dosages of attapulgite, kaolin and mica decreased the FFA content of the palm oil. The adsorbent dosage of 1%

was optimum. The decrease of FFA with the increase of adsorbent dosage was due to increase of number of active adsorption sites. All adsorbents used in this study kept FFA content below 5%. The maximum allowable level of FFA in the CPO is 5% (expressed as palmitic acid) [37]. The results show that the content of FFA in CPO is below 0.5% using attapulgite, kaolin and mica. Attapulgite had the best performance for removing FFA from palm oil. The performance of mica was better than kaolin. Mica has good potential for the removal of FFA from CPO and it can be used as an alternative adsorbent for the refining of CPO. The results obtained in this study are consistent with the literature findings [38].

3.3.4 Effect of Adsorbent Dosage on Peroxide Value (POV)

The results of peroxide value are shown in Figure 4(d). The results show that the peroxide value decreased to zero after refining of CPO at an adsorbent dosage of 1% and further increase in adsorbent dosage did not show any effect on the removal of peroxide. Attapulgite, kaolin and mica are equally effective in removing peroxide from CPO. It shows that the kaolin and mica also possess same capability to remove peroxide from the CPO. The results show that the refined palm oil is free from peroxide value and it will take long time to deteriorate [39].

3.3.5 Bleaching Efficiency

The results of the bleaching efficiency are shown in Figure 5. The increase of dosages of adsorbents increased the efficiencies of bleaching earths from 97-98%,17-44% and 18-46% for attapulgite, kaolin and mica respectively. Attapulgite showed highest bleaching efficiency at a dose of 3%. After attapulgite mica showed good bleaching efficiency as compared to kaolin. The results showed that the bleaching performance of attapulgite was the best, but mica can also be used as an alternative material as it showed promising performance. The bleaching efficiency of attapulgite is higher than oil palm ash (OPA) based adsorbent but it has higher efficiency than kaolin and mica [16].

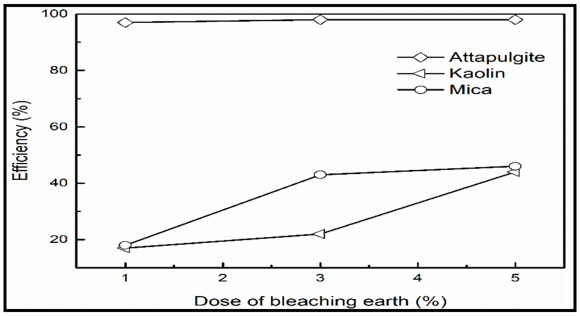


Figure 5 Graph of Bleaching Efficiency against Dosage of Bleaching Earth

3.4 Economic Analysis

To make the refined bleached palm oil (RBDPO) marketable, the main characteristic is the color of RBDPO. The benchmark for the color of a normal RBDPO is 3.0 Red and below. The dosage of bleaching earth needed to obtain the desired result can be predicted by MATLAB software. The calculation of cost and dosage needed can be calculated using MATLAB results and Equation (4).

$$\text{Mass of bleaching earth} = SG \times V \times D \qquad [4]$$

Price of 1 Metric Tonne of attapulgite= RM 630/tonne
The dosage needed to achieve a color of 3.0 = 1.533% (software results)
Assuming 1 tonne of oil used to refine,
Specific gravity (SG) of oil: 0.9
= 1 tonne x(1.533/100) x 0.9
= 0.013797 tonne Price of Attapulgite
= 0.013797 tonne x RM 630/tonne= RM 8.69211

Price of 1 tonne of Kaolin (Kaolin SDN BHD): RM 700
Interpolating dosage to get the desired color, 3.0: 6.834%
Assuming 1 tonne of oil used to refine,
Specific gravity (SG) of oil: 0.9
= 1 tonne x (6.834/100) x 0.9
= 0.061506 tonne Price of Kaolin
= 0.061506 tonne x RM 700/tonne
= RM 43.05

Price of 1 tonne of Mica (Kaolin SDN BHD): RM 600
Interpolating Dosage to get the desire colour, 3.0: 4.1832% Assuming 1 tonne of oil used to refine,
Specific Gravity (SG) of oil: 0.9
= 1 tonne x (4.1832/100) x 0.9
= 0.0376488 tonne Price of Mica
= 0.0376488 tonne x RM 600/Tonne

= RM 22.60

Based on the cost analysis of each bleaching earth, mica has the lowest cost compared to kaolin and attapulgite, but attapulgite has the lowest cost as compared to kaolin and mica based on the dosage required to follow market specification of under 3.0 Red.

4.0 CONCLUSIONS

The crude palm oil (CPO) was successfully refined using locally available adsorbents kaolin and mica. Both adsorbents removed colour pigments, phosphorous, and free fatty acids (FFA) from CPO. The bleaching efficiencies of 97.17%, 48.11%, and 40.56% for attapulgite, mica, and kaolin. Due to higher dose of kaolin and mica required as compared to attapulgite to obtain the desired colour of oil, attapulgite is cheap adsorbent to refine CPO. The performance of mica was comparable to the industrially used bleaching earth attapulgite. Mica possesses capability to be used as a bleaching earth for refining of CPO. The performance of mica can be further improved by activation using different activation agents.

Acknowledgement

Authors are thankful to the Universiti Teknologi PETRONAS for the research facilities and Department of Chemical Engineering, Universiti Teknologi PETRONAS, Malaysia for funding this work.

References

[1] M. H. Mat Yasin, R. Mamat, G. Najafi, O. M. Ali, A. F. Yusop, and M. H. Ali. 2017. Potentials of Palm Oil as New Feedstock Oil for a Global Alternative Fuel: A Review. *Renewable and Sustainable Energy Reviews*. 79: 1034-1049.

[2] O. R. Stone and U. F. Chigozie. 2014. Experimental Process Design for Sorption Capacity of KOGI and IBUSA Clay-activated with HNO_3 and H_2SO_4 Acids in Palm Oil Bleaching. *Journal of Emerging Trends in Engineering and Applied Sciences*. 5(8): 174-182.

[3] B. Nagendran, U. R. Unnithan, Y. M. Choo, and K. Sundram. 2000. Characteristics of Red Palm Oil, a Carotene- and Vitamin E–rich Refined Oil for Food Uses. *Food and Nutrition Bulletin*. 21(2): 189-194.

[4] N. E. G. Frank, M. M. E. Albert, D. Ekwe, E. Laverdure, and K. Paul. 2011. Assessment of the Quality of Crude Palm Oil from Smallholders in Cameroon. *Journal of Stored Products and Postharvest Research*. 2(3): 52-58.

[5] U. N. Ekwenye. 2006. Chemical Characteristics of Palm Oil Biodeterioration. *Biokemistri*. 18(2).

[6] Y. Chen *et al.* 2014. The Analysis of Trans Fatty Acid Profiles in Deep Frying Palm Oil and Chicken Fillets with an Improved Gas Chromatography Method. *Food Control*. 44: 191-197.

[7] M. Rossi, M. Gianazza, C. Alamprese, and F. Stanga. 2001. The Effect of Bleaching and Physical Refining on Color and Minor Components of Palm Oil. *Journal of the American Oil Chemists' Society*. 78(10): 1051-1055.

[8] E. M. Ejikeme, S. O. Egbuna, and P. C. N. Ejikeme. 2013. Optimal Bleaching Performance of Acid Activated 'Ngwulangwu' Clay. *Int J Eng Innov Technol*. 3: 13-19.

[9] R. A. Azmi *et al.* 2015. Deacidification of Crude Palm Oil using PVA-crosslinked PVDF Membrane. *Journal of Food Engineering*. 166: 165-173.

[10] V. Gibon, W. De Greyt, and M. Kellens. 2007. Palm Oil Refining. *European Journal of Lipid Science and Technology*. 109(4): 315-335.

[11] K. A. Sampaio, R. Ceriani, S. M. Silva, T. Taham, and A. J. A. Meirelles. 2011. Steam Deacidification of Palm Oil. *Food and Bioproducts Processing*. 89(4): 383-390.

[12] S. Y. Lau, S. L. Phuan, M. K. Danquah, and C. Acquah. 2019. Sustainable Palm Oil Refining using Pelletized and Surface-modified Oil Palm Boiler Ash (OPBA) Biosorbent. *Journal of Cleaner Production*. 230: 527-535.

[13] D. R. Taylor, D. B. Jenkins, and C. B. Ungermann. 1989. Bleaching with Alternative Layered Minerals: A Comparison with Acid-activated Montmorillonite for Bleaching Soybean Oil. *Journal of the American Oil Chemists' Society*. 66(3): 334-341.

[14] W. Hamm, R. J. Hamilton, and G. Calliauw. 2013. *Edible Oil Processing*. Wiley Online Library.

[15] W. F. J. De Greyt. 2013. Edible Oil Refining: Current and Future Technologies. *Edible Oil Processing*. 127-151.

[16] C. Acquah, L. Sie Yon, Z. Tuah, N. Ling Ngee, and M. K. Danquah. 2016. Synthesis and Performance Analysis of Oil Palm Ash (OPA) based Adsorbent as a Palm Oil Bleaching Material. *Journal of Cleaner Production*. 139: 1098-1104.

[17] S. K. Loh, S. James, M. Ngatiman, K. Y. Cheong, Y. M. Choo, and W. S. Lim. 2013. Enhancement of Palm Oil Refinery Waste – Spent Bleaching Earth (SBE) into Bio Organic Fertilizer and Their Effects on Crop Biomass Growth. *Industrial Crops and Products*. 49: 775-781.

[18] N. F. Zainudin, K. T. Lee, A. H. Kamaruddin, S. Bhatia, and A. R. Mohamed. 2005. Study of Adsorbent Prepared from Oil Palm Ash (OPA) for Flue Gas Desulfurization. *Separation and Purification Technology*. 45(1): 50-60.

[19] T. A. Kurniawan, G. Y. S. Chan, W.-h. Lo, and S. Babel. 2006. Comparisons of Low-cost Adsorbents for Treating Wastewaters Laden with Heavy Metals. *Science of the Total Environment*. 366(2-3): 409-426.

[20] T.-L. Lin and C.-I. Lin. 2009. Performances of Peanut Hull Ashes in Bleaching Water-degummed and Alkali-refined Soy Oil. *Journal of the Taiwan Institute of Chemical Engineers*. 40(2):168-173.

[21] O. AOCS. 1998. Methods and Recommended Practices of the American Oil Chemists' Society. American Oil Chemists' Society, Champaign, IL, USA.

[22] M. D. Donohue and G. L. Aranovich. 1998. Classification of Gibbs Adsorption Isotherms. *Advances in Colloid and Interface Science*. 76-77: 137-152.

[23] A. L. Ahmad, S. Sumathi, and B. H. Hameed. 2005. Adsorption of Residue Oil from Palm Oil Mill Effluent using Powder and Flake Chitosan: Equilibrium and Kinetic Studies. *Water Research*. 39(12): 2483-2494.

[24] S. Gier and W. D. Johns. 2000. Heavy Metal-adsorption on Micas and Clay Minerals Studied by X-ray Photoelectron Spectroscopy. *Applied Clay Science*. 16(5): 289-299.

[25] P. Srivastava, B. Singh, and M. Angove. 2005. Competitive Adsorption Behavior of Heavy Metals on Kaolinite. *Journal of Colloid and Interface Science*. 290(1): 28-38.

[26] H. Zhang *et al.* 2015. Equilibrium, Kinetic and Thermodynamic Studies of Adsorption of Th(IV) from Aqueous Solution Onto Kaolin. *Journal of Radioanalytical and Nuclear Chemistry*. 303(1): 87-97.

[27] B. Lorentz, N. Shanahan, Y. P. Stetsko, and A. Zayed. 2018. Characterization of Florida Kaolin Clays using Multiple-technique Approach. *Applied Clay Science*. 161: 326-333.

[28] B. Davarcioglu. 2010. Investigation of Central Anatolian region Nigde-Dikilitas (Turkey) Clays by FTIR Spectroscopy. *Epitoanyag-Journal of Silicate Based & Composite Materials*. 2010(2).

[29] W. Liu, X. Qiao, S. Liu, S. Shi, K. Liang, and L. Tang. 2019. A New Process for Pre-treatment of Electroless Copper Plating on the Surface of Mica Powders with Ultrasonic and Nano-nickel. *Journal of Alloys and Compounds*. 791: 613-620.

[30] A. C. Ribeiro *et al.* 2021. Physico-chemical and Electrostatic Surface Characterisation of Mica Mineral and its Applicability on the Adsorption of Safranin Orange and Reactive Black 5 Dyes. *Environmental Technology*. 1-14.

[31] V. Chantawong, N. W. Harvey, and V. N. Bashkin. 2003. Comparison of Heavy Metal Adsorptions by Thai Kaolin and Ballclay. *Water, Air, and Soil Pollution*. 148(1): 111-125. Doi: 10.1023/A:1025401927023.

[32] L. Mouni *et al.* 2018. Removal of Methylene Blue from Aqueous Solutions by Adsorption on Kaolin: Kinetic and Equilibrium Studies. *Applied Clay Science*. 153: 38-45.

[33] B. Dash, S. K. Jena, and S. S. Rath. 2022. Adsorption of Cr (III) and Cr (VI) Ions on Muscovite Mica: Experimental and Molecular Modeling Studies. *Journal of Molecular Liquids*. 357: 119116.

[34] M. I. Ismail, M. H. Hamidon, M. Zulhilmie, and M. Sofi. 2018. Renewable Bleaching Alternatives (RBA) for Palm Oil Refining from Waste Materials. *Journal Appl Environ Biol Sci*. 6(7S): 52-57.

[35] A. W. Nur Sulihatimarsyila, H. L. N. Lau, K. M. Nabilah, and I. Nur Azreena. 2019. Refining Process for Production of Refined Palm-pressed Fibre Oil. *Industrial Crops and Products*. 129: 488-494.

[36] P. C. Wei, C. Y. May, M. A. Ngan, and C. C. Hock. 2004. Degumming and Bleaching: Effect on Selected Constituents of Palm Oil. *Journal of Oil Palm Research*. 16(2): 57-63.

[37] N. E. G. Frank, M. M. E. Albert, D. E. E. Laverdure, and K. Paul. 2011. Assessment of the Quality of Crude Palm Oil from Smallholders in Cameroon. *Journal of Stored Products and Postharvest Research*. 2(3): 52-58.

[38] L. Ifa, L. Wiyani, N. Nurdjannah, A. M. T. Ghalib, S. Ramadhaniar, and H. S. Kusuma. 2021. Analysis of Bentonite Performance on the Quality of Refined Crude Palm Oil's Color, Free Fatty Acid and Carotene: The Effect of Bentonite Concentration and Contact Time. *Heliyon*. 7(6): e07230.

[39] M. E. Ojewumi, A. B. Ehinmowo, O. R. Obanla, B. M. Durodola, and R. C. Ezeocha. 2021. Comparative Analysis on the Bleaching of Crude Palm Oil Using Activated Groundnut Hull, Snail Shell and Rice Husk. *Heliyon*. 7(8): e07747.