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An Assessment of Refining of Crude Palm Oil Using Local Clay

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Abstract: Cosmetic industries, bioenergy industries, agro and oleo chemical industries among few are in great demand for palm oil as raw material. For the palm oil to be used, it has to be refined to remove impurities that have altered the chemical state of the oil. Thus, as a result of this adsorbents have to be used to remove these organic pigments, metallic traces, etc. This research effort made an investigation into the use of local clay within Nigeria (particularly Iseyin clay) in the refining process of crude palm oil, by acid activation of the clay and corroborated it to be a close substitute to be considered over expensive imported adsorbents, e.g. fuller's earth, etc. The results show that the bleaching rate varies directly with the contact time, temperature as well as the dosage of the clay. The project results also gave reasonable correlations of R^2 = 0.9035 and R^2 = 0.8954 when the experimental results were, respectively subjected to both Langmuir and Freundlich adsorption isotherms. The adsorption process was found to be exothermic ΔH = with 0.259 kJ mol^{-1}.

Key words: Palm oil, adsorption, degumming, bleaching, clay, saponification

INTRODUCTION

Oil palm, a tree crop is the main source of palm oil which is a water insoluble substance consisting predominantly of glycerol esters of fatty acids or triglycerides (Achife and Ibemesi, 1989). Demand for this refined palm oil has increased the world over in the past few years due to increase in world population, rising standard of living and consumer preference.

The domestic and industrial use of edible palm oil includes cooking, frying, soap making among others. Food and cosmetic industries make use of the edible palm oil as a major raw material in the production of margarine, cheese, cosmetics, detergent, etc. Also, oleo chemical and energy industries make use of the refined, bleached and deodorized palm oil in the manufacture of a range of fatty acids, rosins and rosin-derivatives as well as biofuel. Before this crude palm oil can be used, it has to be converted to a purer product called the edible oil through the refining process to remove impurities such as organic pigments, oxidation metals, trace metals and traces of soaps which have negative influence on the taste and smell of the oil as well as its appearance and shelf life stability thus, reducing consumer acceptance and marketability. Thus, the refining of these oils, especially palm oil, through adsorptive bleaching, remains inevitable in the oil refining industry. Crude palm oil is a vegetable oil rich in minor components which have nutritional attributes (Wei *et al*., 2004). An ideal crude palm oil contains about 600-1000 mg kg^{-1} of tocopherols and 500-700 mg kg^{-1} carotenoids, mainly α- and β-carotene (Goh *et al*., 1985). These compounds help in health maintenance, since carotenes play an important role in the prevention of cancer, cataracts and health diseases. Despite, the health benefits derived from palm oil, it must be refined to improve the purity and characteristics desirable in edible oil.

The removal of pigment and other trace constituents by adsorption process (bleaching) is one of the most important steps in vegetable oil refining and this process removes the carotenes, chlorophyll and other pigments as impurities. The process makes the oil more appealing and convenient for use. Activated clay has been widely employed as adsorbent. Nigeria clays have been found competent in the adsorption bleaching of vegetable oil. In recent years, a number of attempts have been made in the refining of palm oil using locally sourced raw materials as adsorbents (Salawudeen *et al*., 2007; Nwabanne and Ekwu, 2013; Usman *et al*., 2013). Local clay is a combination of phyliosilicate minerals, organic matter and traces of metallic oxides which is typically formed over years by gradual chemical weathering of rocks or hydrothermal activity. These silicate-bearing parent rocks are acted upon by low concentrated carbonic acid and other diluted solvents which migrate through the rock after leaching through the upper weathered layers.

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The primary clay also known as kaolins are usually located at the site of formation while the secondary clay deposits have been removed by erosion and water from their primary location.

The four main groups of clay include kaolinite, montmorillonite-smectitie, illite and chlorite. When, the clay is treated with acid or alkali, it becomes activated. The aim of this study was to develop good local substitutes for the commercially imported adsorbent (fuller's earth). Studying the isotherms and refining activities of our local clay with such oil as palm oil is very critical and necessary step for developing a pathway for the refining process.

Langmuir isotherm follows the adsorption that the process happens at uniform surface. Christidis and Kosiari (2003) reported that the removal of β-carotene from crude maize oil with activated low grade bentonite from Cyprus conformed to the Freundlich isotherm.

MATERIALS AND METHODS

The clay sample was obtained from Iseyin in Oyo State while the crude palm oil was obtained from Mushin market, Lagos State both in Nigeria.

Preparation and characterization of clay: Clay characterization was done using Atomic Absorption Spectrophotometer and X-ray Fluorescence (PW 4030 X-ray spectrophotometer). The properties of the unbleached palm oil were determined according to the method adopted by Afnor (1981).

Acid activation was done according to the method described by James *et al.* (2008) and Vincente-Rodriguez *et al.* (1996). The clay sample was air-dried (aeration) and then milled into fine powder using a hammer mill and a mini-sized ball. The milled sample was passed through a 150 μm sieve so as to remove impurities. Total 50 g of the clay sample was introduced into a 500 mL beaker and 200 mL of 1 M sulphuric acid was added.

The mixture was homogenized in a thermostatically controlled water bath at temperature of 95°C for 3. After stirring for 3 the resulting mixture was filtered. The filtered clay was thoroughly washed with distilled water to adjust the pH to neutral as determined by the indicator. The activated clay sample was dried in an electric oven at a temperature of 105°C until the weight of the clay remain constant.

The dried activated clay sample was milled again, passed through 150 μm sieve, labeled and stored in an air tight container.

Refining of crude palm oil: The refining process of the crude palm oil exists in four stages namely; degumming, neutralization of degummed oil, drying of the neutralized oil and bleaching of the dried oil.

Degumming: The crude palm oil was degummed using the method of (Hymore and Iyayi, 1989) by the addition of hot water and stirring the mixture in a flask, then removing the aqueous layer. This process was repeated to ensure removal of most gums.

Neutralization: Neutralization of the Free Fatty Acid (FFA) of the degummed palm oil was done using solution of NaOH at a temperature of 80°C with agitation. Sodium Chloride of 10% the weight of the oil was added to help settle out the soap formed. The natural oil was then washed with hot distilled water to remove soap remaining in solution. Three different solutions of NaOH 1.0, 1.5 and 2.0M were used during the neutralization.

Drying: The neutralized palm oil was then dried by heating the oil at 60°C under vacuum until no more bubbling of gas was observed. The FFA of the neutralized and dried palm oil samples were measured.

Bleaching process: Bleaching of palm oil was carried out according to the procedure described by Binwie Joy *et al.* (2007). Initially, the activated clay was ground to fines and then sieved with a 150 μm mesh. 0.6, 0.9, 1.2 g, 1.5, 1.8, 2.1 and 2.4 g, respectively or 2-8 of the weight of crude palm oil, respectively were used.

About 30 g of the prepared crude palm oil was poured into a 100 mL beaker and then heated up to 100°C on a magnetic hot plate. About 0.6 g the activated clay sample was added to the hot oil. The temperature was maintained at 100°C for 30 m. After 30 min, the mixture was filtered through Whatman No. 1 filter paper. This process was repeated with dosages of 0.9, 1.2, 1.5, 1.8, 2.1 and 2.4. The effect of temperature was studied at 40, 60, 80 and 100°C. The effect of time was done by varying the time (5, 10, 15, 20, 30, 45, 60 and 75 min).

The absorbance of palm oil was measured using a UV spectrophotometer (UV-1850). Total 0.1 g of bleached palm oil was measured and poured into a breaker containing 7.5 mL of petroleum ether. The mixture was poured in the cuvette and the value of the absorbance was read at 445 nm wavelength using petroleum ether as reference (Binwie Joy *et al.*, 2007). The percentage was calculated using Eq. 1:

$$\text{Balanced}(\%) = \frac{\text{Ao} - \text{At}}{\text{Ao}} \times 100 \quad (1)$$

Where:

A_0 = Absorbance of crude palm oil
A_t = Absorbance of bleached palm oil at time (t)

The mathematical analysis was developed using the Microsoft Excel application as well as the graphical plot through MATLAB (Ajemba and Onukwuli, 2013).

RESULTS AND DISCUSSION

The results of the assessment of refining of crude palm oil using local clay are presented in Table 1-3 and Fig. 1-5. Table 1-3 also show the results of chemical analysis AAS characterization: physico-chemical property of local clay.

Table 1: Chemical Properties of raw Clay

Oxide	Composition (%)
Al_2O_3	15.9
S_iO_2	53.8
C_aO	1.98
T_iO_3	2.35
F_eO_5	21.7
V_2O_5	0.14
Cr_2O_3	0.17
MnO	0.34
N_iO	1.51
C_uO	0.11
Z_nO	0.16

Table 2: AAS characterization of Iseyin clay

Element	Concentration (PPM)
Fe	24.9210
Al	34.7732
Na	10.9240
Cu	0.0198
K	0.0175
Zn	0.0166
Ca	0.1321
Mg	0.1182
Mn	0.2197
Ni	0.1108

Table 3: Physico-chemical properties of crude palm oil

Property	Values
Absorbance	2.251
Moisture content	0.220
Specific gravity	0.975
Density	975 kg m^{-3}
Acid Value	14.867 mg KOH^{-1}
FFA (%)	7.473
Refractive index	1.462
Iodine value	55
Saponification value	201.55 mg KOH

Chemical analysis of local clay: The result suggests the existence of calcium montmorillonite, since the silica content is high within the range of 50-70%. From Table 1, the clay is shown to have a high silica content which suggests its high potential in adsorption studies (Vincente-Rodriguez *et al*., 1996).

AAS characterization: From AAS analysis, the characteristics of Iseyin clay are presented in Fig. 2. The results show that iron followed by alluminium are predominant in the clay. This confirms the results of the chemical analysis which proves the clay to be rich in silica.

Properties of crude palm oil: The physico-chemical properties of the crude palm oil as used in this research work are shown in Table. The low value of the Free Fatty Acid (FFA) shows that the palm oil used is fresh.

According to Rohani as the life of the palm oil prolongs, its percentage free fatty acid increases owing to hydrolysis which occurred in the presence of water and heat. The free fatty acid is among the undesirable constituent to be removed and thus its low percentage enhances the efficiency of the refining process. From Table 3, the low value of the moisture content reveals the reason why the free fatty acid is low which is in support of the view of Hymore and Iyayi (1989). The iodine value shows that palm oil is non-drying oil as non-drying oil have iodine value >125 and the higher the iodine value, the higher the level of unsaturated fatty acids present. Thus, palm oil finds its use in applications where oxidation is undesirable. Also, the high saponification value suggests that the palm oil can be used for soap production.

Time effect on bleaching rate: The bleaching rate of the activated clay samples (adsorbent) at varied weights per time was monitored and measured. The results are shown in Fig. 1. At various temperature of 40, 60, 80 and 100°C the bleaching rate of the neutralized.

Oil after degumming was as shown in Fig. 2. From Fig. 1, it can be noticed that the percentage of bleached oil increases with bleaching allowable period. Also, as the dosage of the activated clay is increased, the bleached oil quantity increases as well.

From Fig. 2, the amount of bleached oil increases with temperature. Also, as the dosage of the activated clay is directly related to the bleached oil quantity, i.e., increased in the mass of the activated clay increases the amount of oil bleached.

Freundlich langmuir isotherm: As an adsorption principle, Fig. 3 illustrates the Freundlich type curve for

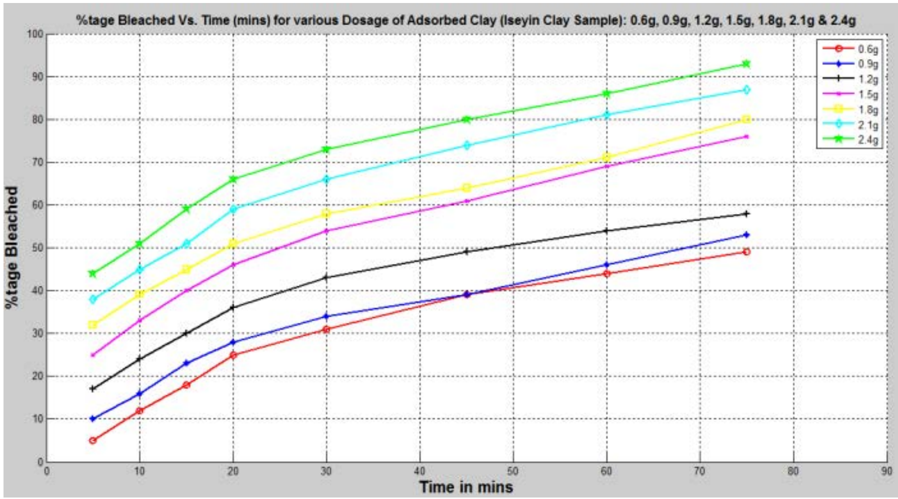

Fig. 1: Time effect of activated clay samples on bleaching rate of palm oil

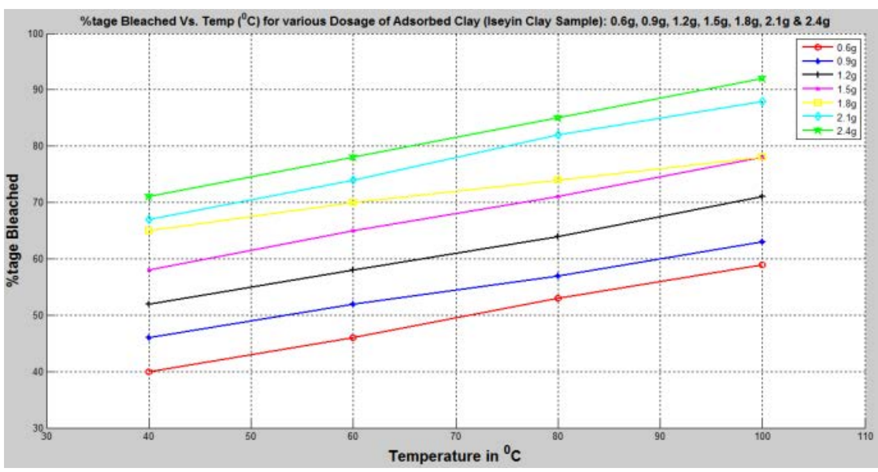

Fig. 2: Temperature effect of activated clay samples on bleaching rate of palm oil

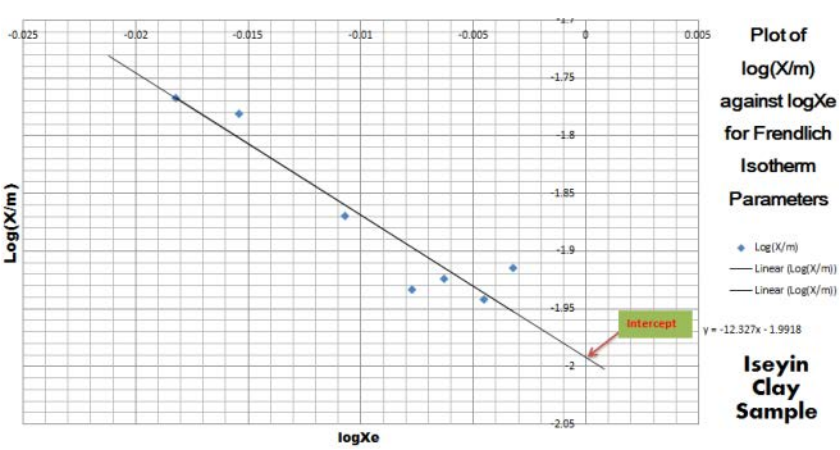

Fig. 3: Clay adsorption isotherm

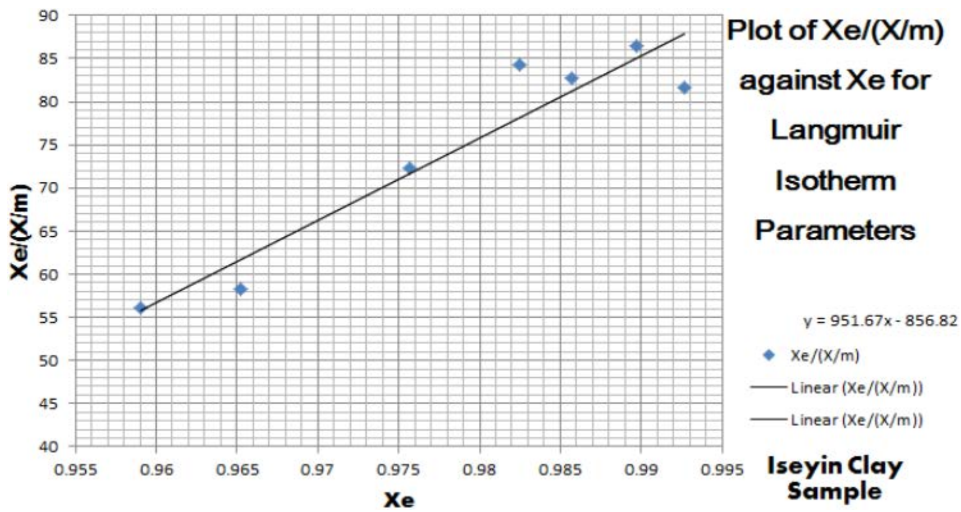

Fig. 4: Heat of adsorption plot

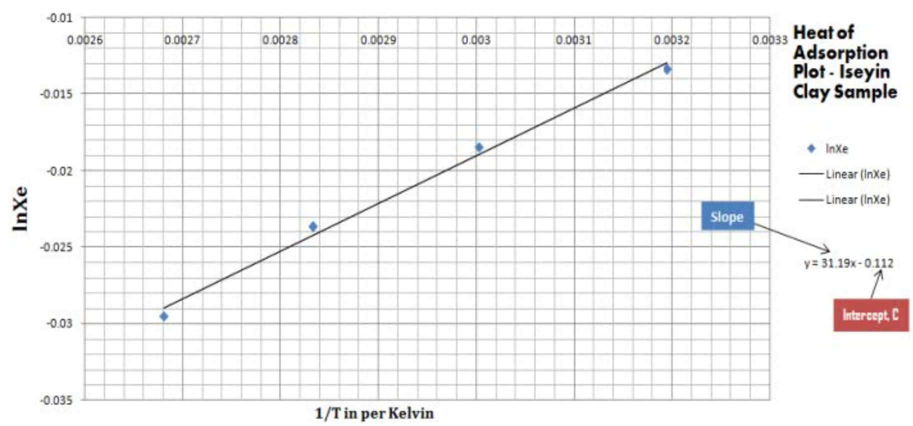

Fig. 5: Plot of the natural logarithm of the residual amount of palm oil adsorbed at equilibrium against the reciprocal of temperature

the adsorption data of crude palm oil on activated Iseyin clay samples. A line of best fit is drawn to determine the slope and intercept of the curve. By Langmuir type of adsorption theory, the isotherm plot is given in Fig. 4.

For each of the temperature values of measurement, a plot of the natural logarithm of the residual amount of palm oil adsorbed at equilibrium against the reciprocal of temperature is shown in Fig. 5.

From Fig. 3, the best line of fit shows a better correlation for the plotted point and from this, the Freundlich isotherm parameters K and n were determined as K = 0.01019 and n = -12.327. The value of n determines the degree of decolourization or intensity within which the adsorbent is relatively inefficient as an agent to be used. Since the value of n is relatively low, it shows a better efficient clay sample. Also, the k-value is a general measure of the activity or capacity of the adsorbent.

From Fig. 4 as well, a moderate line of fit is assumed to be the best that can be drawn and the Langmuir parameters a and b were determined as $\alpha = -0.00117$. From Fig. 4, the heat of adsorption value $-\Delta ha$ is evaluated as $0.259\ kJ\ mol^{-1}$ and presented as follows. For low value of, it shows that the adsorption of the pigments of the crude palm oil on the Iseyin local clay takes place via chemsorption (i.e., activated adsorption).

CONCLUSION

From this project research, the use of low cost adsorbents (local clay) in the adsorptive bleaching/refining of palm oil was studied, i.e., local clay samples from within our country (Nigeria) can be used to obtain bleaching earth of very good quality. Acid activation increases the bleaching power of iseyin claysamples. The adsorption of pigments onto the clay surfaces was observed to increase with temperature, adsorbent dosage and contact time.

The results of this study also clearly indicates that Iseyin clay is clearly a good adsorbent for the purification/refining of palm oil and thus a recommended local substitute for industrial application and further research.

Moreover, the experimental data make a better correlation with the Langmuir Adsorption Isotherm model (R^2 = 0.9035) than reundlich Adsorption Isotherm model (R^2 = 0.8954) although, both models are suitable. Furthermore, the thermodynamic parameters evaluated reveal the spontaneous and exothermic nature (since -Δha value is positive) of colour pigment adsorption onto acid activated Iseyinclay and the adsorption takes place with increase of entropy.

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