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Beneficiation of Local Clay to Improve Its Performance in Adsorption of Carotene Pigments and Volatiles in the Bleaching of Palm oil

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ABSTRACT: *In this work a local clay was beneficiated and used for the adsorption of pigmented substances in palm oil bleaching. Tetraoxosulphate (VI) acid was used to activate the clay obtained from Oji River province in Enugu Stateof Nigeria. The sample of palm oil used in the study was obtained from Nkanu West Area of the state and was bleached with the activated clay. The oil was characterized before and after bleaching and the results used in the study. It was observed that the use of Tetraoxosulphate (VI) acid in activation increases the bleaching efficiency of activated clay. The stability of the bleached oil was measured in terms of Free Fatty Acid (FFA) 0.12%, Peroxide Value (PV) 3.0 m.eq/kg, Anisidine Value(AV) 4.85 m.eq/kg, Iodine Value (IV) 49, Iron (Fe) content, 4.3 x 10^3(Ppm), and Phosphorous content 0.015 (Ppm), all of which were compared with those of the American Oil Chemist Society (AOCS) standard values.*

KEY WORDS: *Clay, Beneficiation, Bleaching, Adsorption, Characterization, and Stability.*

I. INTRODUCTION

Vegetable oils and fats are lipid materials derived from plants. Physically, oils are liquid and fats solid at room temperature. Chemically, fats and oils are composed of triglycerides as contrasted with waxes which lack glyceride in their structure, [1] [19]. Fats and oils also contain free fatty acids, mono- and di-glycerides, and unsaponifiable lipids. They may be edible or non-edible; palm oil and soya bean oil, and linseed oil, tung oil and castor oil respectively. Vegetable oils find application in soap manufacture, cooking, margarine, shortening, lubricants and cosmetics and as biodiesel,[2]. Palm oil is a fleshy fruit fat with a distinctive orange-red colour, due to its high content of carotenoids. Raw palm oils, in addition to carotenoid pigments content, contains impurities like free fatty acid. During processing, bleaching stage is an important step which is devised to remove pigments, and other unwanted constituents such as those of mucilaginous matter and other volatiles, [3]. Beneficiation is the treatment of naturally mineral deficient material (clay) with mineral acid to improve its adsorptive capacity and performance in the removal of pigmented substances during bleaching. Many types of adsorbent have been tested for the removal of pigments from vegetable oils, [4], [5], [6], [7], [8] . The type of adsorbent used world-wide today by refiners are mainly activated montmorillonite clays. Christidis and Kosiari, [9],

Showed that removal of β-carotene from oil with acid activated low grade bentonite from Cyprus is a chemical adsorption process. They obtained isotherm of the Freudlich type. However, non of the studies mentioned above investigated the adsorption of free fatty acids during the decolourization process. Some authors pointed out that bleaching process led to and increased the free fatty acid content of the vegetable oil, [10] [11]. Hymore and Ajay, [13], had demonstrated that local acid activated clay could be used successfully for the adsorption of pigments and free fatty acid of palm oil. Egbuna and Aneke, [14] , have also shown that bleaching stage of palm oil refining and the nature of bleaching clay used play a vital role in the stability of the finished product. Hymore R. and Ajay also showed that clay, when analyzed, has the following chemical compositions; SiO_2, AI_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O and SO_3. There are other properties which, when they are present in abnormal quantities, hinder the performance of the clay as a bleaching material when activated. These include the amount of moisture contained, the level of volatile matters and non hydratable materials.

In the present study, Inyi clay was characterized before and after activation and used for the adsorption of carotene pigment and free fatty acid in palm oil bleaching.

II. EXPERIMENTAL METHODS.

2.1 Activation of Clay

Pre – activation treatments

The clay sample was first dehydrated by putting it in a muffle furnace set at about 105^{o}C for 24 hours. About 7kg of the said sample was crushed in a jaw crusher, and the crushed material was subsequently size - reduced with mortar and piston to obtain fine particles, enough to pass through a 150 ASTM, E11 – 70 mesh sieves. This clay sample was then stored air-tight in a reagent bottle to be used in activation experiments.

Before activation process, the physical and chemical properties of the clay sample were determined and compared with those of the standard Fuller's earth. The aim was to determine the level of activation required. The major properties determined, which play a leading role in the adsorptive power of clay include; SiO_2, Al_2O_3, Fe_2O_3, CaO, KO, MgO, Na_2O, TiO_2, SO_3, and Ignition loss.

2.2 Acid Activation of (lnyi) Clay

50g of 150 mesh size pulverized clay was weighed into a 250ml beaker and 100ml of 5M of 80% Tetraoxosulphate (VI) acid, was introduced and the contents shaken vigorously to form a homogeneous slurry. The latter was then filtered and the residue washed with distilled water to eliminate any traces of acid on its surface. The washed clay was then oven dried at a temperature of 150°C for 2hours to a constant weight, reground and sieved to, 20, 30, 40, 60, 80, 100 mesh sizes, and stored in a clean container for bleaching experiments. The procedure was repeated for acid concentrations of 10, 15, 20, 25, and 30M, in order to establish the optimum acid concentration for the activation.

2.3 Properties of the Clay: Laporte, method, [15], was used.

a) Physical Properties

i) Non - clay residue:

Determination of percentage amount of non - clay residue in clay sample was done by first, soaking 100g of clay completely in distilled water for 24 hours. This mixture was then stirred vigorously and poured into a beaker through a screen. The percentage amount of the non – clay residue was then calculated as the difference in weight between the screen before and after pouring the solution through it.

ii) Apparent bulk density (ABD): The sieved clay (natural or activated), was put into a graduated cylinder of known weight and topped to a constant volume. The weight was then taken and the difference between the weight of the cylinder and the clay was calculated as

Apparent bulk density

$$(ABD) = \frac{W_x - W_y}{V} g/cm^3 \qquad 1$$

Where W_x - Weight of cylinder plus clay; W_y - Weight of cylinder; V - Total weight of clay used.

iii) Titratable acidity: 20g of the sample was soaked completely in a 100ml standard volumetric flask for 2 days with distilled water. The soaked clay was stirred vigorously to obtain a homogeneous mixture. A 20ml aliquot of the clay suspension was titrated against a 0.1N sodium hydroxide solution using 2 drops of Phenolphthalein as indicator. Titratable acidity was then calculated as;

$$\text{Titratable acidity (mg) NaOH /g} = \frac{\text{Mole (gram) NaOH consumed}}{\text{Mass (g) of Clay}} \qquad 2$$

b) Chemical Properties

Introduction: Two methods were used for this characterization experiment, occasioned by the two instruments available, namely, the Pye – Unican Spectrophotometer, for the analysis of SiO_2, AI_2O_3 and Fe_2O_3, and EEL Flame Photometer, for the analysis of CaO, MgO, Na_2O, K_2O and SO_3. The pre treated clay sample (natural or activated) was analyzed to determine its content of the compounds as indicated above, and the results are presented in tables 2 and 3

1.4 Particle Size Distribution of Bleaching Clay: Methods of analysis of particle size of [16] [17] [20], was used.

The aim was to determine the particle size of the prepared sample of the Inyi clay. The sieves were arranged into a nest of sieves with the coarsest on top and the finest at the bottom. About 150g of the clay sample was placed on the top sieve. To prevent loss of the particles, a lid was used to cover the top sieve and a solid tray at the bottom. The sieve nest was vibrated by gentle shaking of hand for 3 minutes. The nest was dismantled and the materials collected on each sieve weighed. The results are shown in Figs 1 and 2.

Bleaching of raw palm oil

The bleaching experiment was aimed at reducing the carotene pigments and FFA, so as to minimize the formation of hydro peroxides during deodorization and storage. The experiment was done with the pr oduced clay.

Procedure: One per cent (1%) by weight of the clay sample was added to l00g of the oil sample. The mixture was heated to a constant temperature of 373K, with stirring for 30 minutes. The oil was then filtered at the same temperature, and the filtrate characterized. The results of characterization are shown in tables 4, 5, 6, and 7, and Figs. 3, 4, 5, and 6,

III. RESULTS AND DISCUSSIONS

3.1 Oil characterization experiments:

Experiments were carried out in order to characterize the raw and bleached oils, even though the amount of oil needed in the test experiment for bleached oil was much less than that used for raw oil. However, similar equations were used in the calculation, AOCS. (2003). Tables 1 was generated from the characterization experiments of raw and bleached oils respectively. This table shows the physical and chemical properties of both oils.

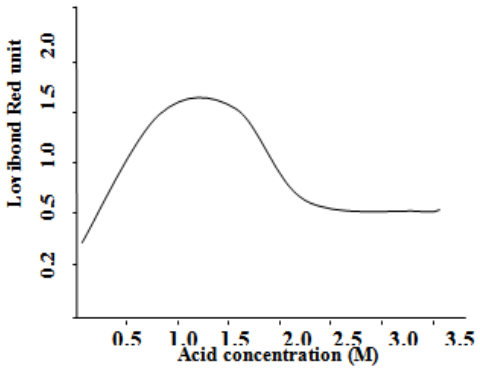

Fig. 1 The effect of concentration of activation chemical on the performance of the activated clay

From the table, it can be seen that there is a marked difference between the raw and bleached oils, in terms of their properties. However, while the difference is high in properties like, colour, taste, odour, moisture content, FFA, AV, PV, P, and Fe, it is low in others such as, specific gravity, melting point, refractive index, saponification value and iodine value.

3.2 Characterization of local Clay

Tables 2 and 3 are the results obtained by characterizing natural Inyi clay, before activation, Mag, (1990). The properties of the activated clay were compared with the literature values of Fulmont AA, a brand of activated clay from Malaysia and Fuller's earth . The chemical properties of the clay as analyzed proved it to be montmorillonite with large amount of alkaline metals. These are shown in table 4.

From tables 3 and 4, it is observed that SiO_2 of crude Inyi clay is very good compared to Fuller's earth and Fulmont AA. Al_2O_3 and Fe_2O_3 contents are good also. However, alkali metal oxides are on the higher side, but do not contribute so much to the bleaching action of clay. Activation, however, improved the quality of the clay as an adsorbent.

3.3 Particle Size Analysis

The particle size analysis of acid activated Inyi clay is shown in table 5.

From the table, it is observed that the bigger the particle size the more the weight fraction, i.e. the weight fraction increases linearly with average particle size. From the same table it can be seen that the higher the sieve number (mesh number), the smaller the weight of material retained. The effect of activation chemical on the performance of activated Inyi clay is shown in Figure 1

From Fig 1, it is observed that the performance of the activated clay measured in terms of colour reduction,is increased until the concentration of 1M,

The effect of particle size distribution of the acid treated Inyi clay on the colour reduction in palm oil bleaching is shown in figure 2

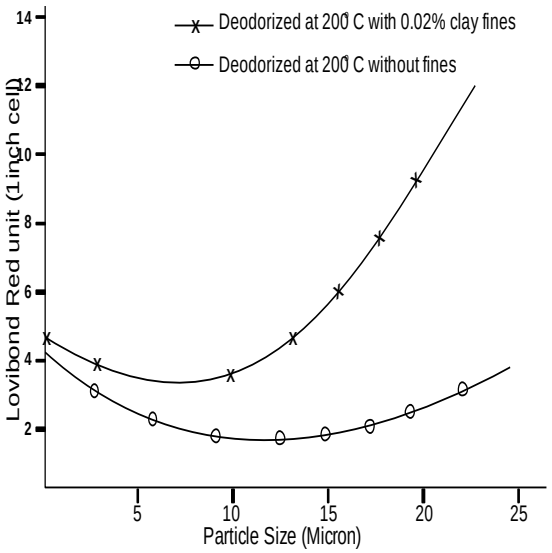

Fig. 2 The effects of particle size on the colour of physically refined palm

From the figure, it is observed that;

a) The smaller the particle size, the lower the colour until the particle size of between 10 and 15 micron is reached. Beyond this point, colour rises probably due to fines in the oil.

b) Colour rises sharply when 0.02% clay fines were introduced in the oil during deodorization.

3.4 Bleaching Experiment

The results of laboratory bleaching experiments are presented in tables 6, and 7.

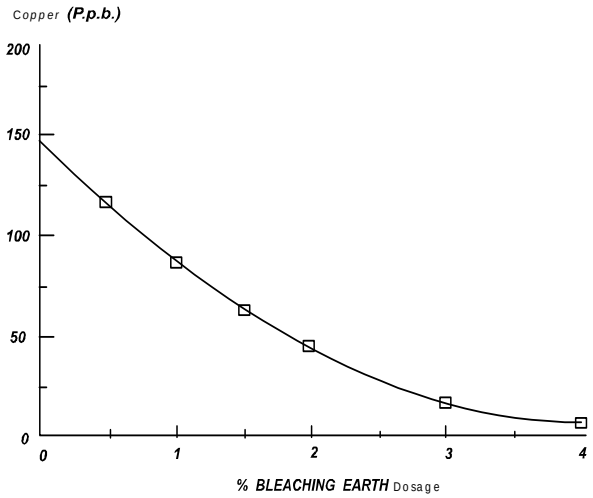

Figure 4 The effect of earth dosage on the copper content of physically refined Palm oil.

From table 6, it is observed that the variables; colour, PV and AV are higher relative to the internationals standards, but FFA of bleached oil is lower than the standard value.

3.5 Variation of Temperature.

The effect of bleach temperature on colour, PV, AV, and FFA, are shown in table 7

From table 7 also, it is observed that;

1) Colour and PV decrease linearly with temperature for bleached oil.
2) Colour and FFA decrease marginally with temperature for deodorized oil until a temperature of 100^{o}C, beyond which it starts to rise.
3) AV increases marginally, until a temperature of 100^{o}C, beyond which it rises sharply.

3.6 Variation of Clay dosage

In Fig 3 and 4, the effects of bleaching clay dosage on colour and Fe/Cu contents respectively, are shown

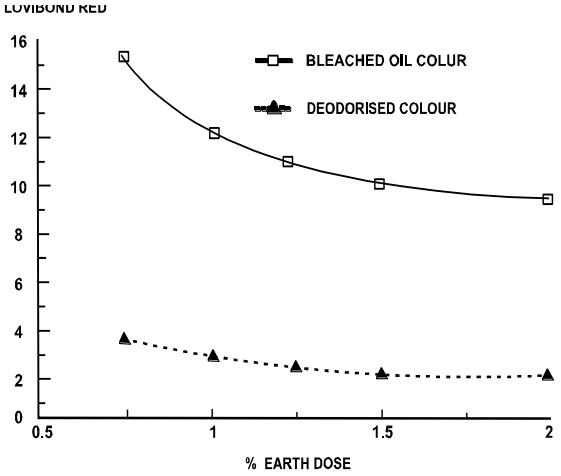

Figure 3 The effect of earth dosage on the colour of physically refined palm oil.

From Fig. 3, the bleached and deodorized colours are reduced with increase in clay dosage, but the deodorized colour is at low value compared to the bleached colour. This is due to heat effect at high temperature of deodorization.

The Fe or Cu content is reduced linearly as bleaching clay dosage is increased, as shown in Fig.4.

The effect of clay dosage on phosphorous is shown in Fig. 5

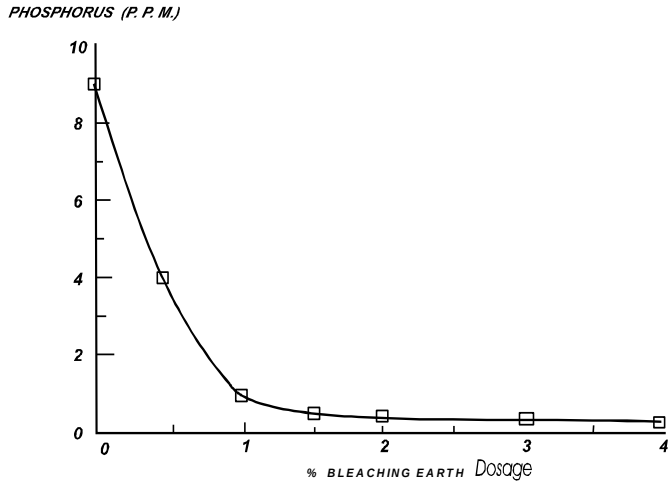

Figure 5 The effect of earth dosage on the phosphorus content of physically refined palm oil.

Figures 6 give the effects of bleaching clay on the PV and AV of refined oil.

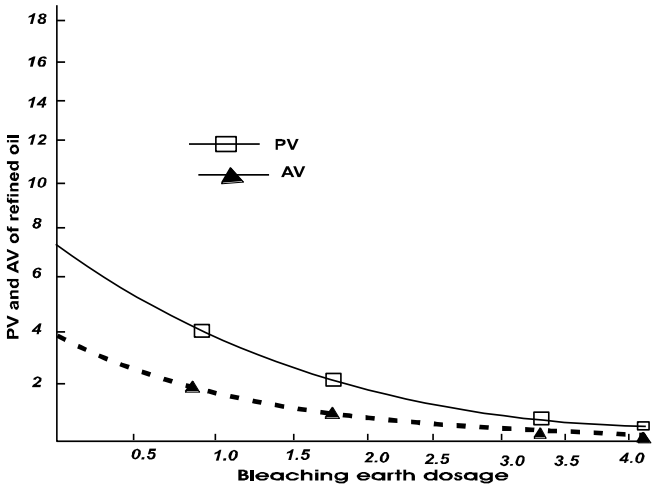

Fig 6 Reduction of PV and AV at increase earth dosage.

It is observedin Fiig 6 that both Pv and AV of finished productare reduced as the bleaching clay increases up to 2.5%, beyond which it increases marginally.

Table 1. Physio-Chemical Properties of the raw and bleached Oil used in the Investigation

Properties	**Raw Palm Oil**	**Bleached oil**
Colour (Physical Appearance)	Deep Orange	Orange yellow
Odour	...of Palm Oil	Palm fruit odour
Taste	...of Palm Fruit	Bland taste
Specific Gravity	0.9182	0.9025
Melting Point(°C)	38	40
Moisture (%)	1.3	0.3
Refractive Index	1.4514	1.4562
Free Fatty Acid (%)	3.80	2.80
Lovibond Red Unit (1" Cell)	23	5.8
Anisidine Value (M.eq/kg)	8.2	6.40
Peroxide Value (M.eq/kg)	5.8	4.20
Phosphorous (Ppm)	9.0	0.5
Iron (Ppb)	3.0	20
Saponification Value	200	205
Iodine Value	45	45.2

Table 2. Results of Physical characterization of raw Inyi Clay before activation

Properties	**Dark Red Crude Inyi Clay**	**Milky Crude Inyi Clay**
Non Clay Residue (%)	3.55	9.56
Moisture content (%)	1.44	3.48
Apparent Bulk density g/cm^3	0.87	0.63
Ignition Loss (%)	11.26	17.47
Titratable Acidity (mg NaOH/g	0.78	1.13

Table 3. Results of Chemical characterization of raw Inyi Clay before activation

Components	SiO_2	AI_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Ignition loss
Values	63.39	4.42	0.11	1.62	2.33	4.10	3.48	11

Table 4. Chemical Composition of Activated (Inyi) Clay compared to fuller's Earth, and Fulmont AA

Properties	**Acid activated Inyi Clay**	**Fuller's Earth**	**Fulmont AA**
SiO_2	65	52.26	61.7
AI_2O_3	9.56	14.33	12
Fe_2O_3	0.08	3.04	5.7
CaO	3.25	3.02	4.1
MgO	2.20	-	2.3
Na_2O	0.24	0.40	0.2
K_2O	2.00	0.48	0.32
Ignition loss	9.5	-	6.2

Table 5. The results of particle size analysis of activated (Inyi) clay

Sieve numbers	Aperture(mm)	Weight retained(g)	Average size	Weight fraction	Cumulative Weight fraction
20	0.840	82.33	0.6300	0.5489	0.5489
40	0.420	42.61	0.3350	0.2841	0.8330
60	0.250	14.45	0.2135	0.09963	0.9293
80	0.177	6.40	0.1630	0.0427	0.9720
100	0.149	2.36	0.1370	0.0157	0.9897
120	0.125	1.00	0.0625	0.0057	0.9944
150	0.095	0.85	0.0475	0.0057	1.0001

Table 6. Laboratory bleaching experimental results compared with the international standard. (Test temp. is 110^{o}C, and bleaching earth doage is 1%)

Parameters	Laboratory experiment		International standard	
	Bleached Oil	Deodorized oil	Bleached Oil	Deodorized oil
Colour in1inch cell	11.5Red units	3.4Red units	10.5Red units	2.5 Red units
FFA%	2.8	0.12	3.5	0.1
PV m.eq/kg	4.2	3.00	3.2	1.0
AV m.eq/kg	6.4	4.05	6.0	3.7

Table7.The effect of bleach temperature on Colour, PV, AV and FFA of physically refined palm oil

Temperature ^{o}C	Colour in 1 inch cell		Peroxide value	Anisidine value	Free fatty acid
	Bleached oil	Deodorized oil			
20	14.2	3.8	6.5	3.60	0.62
40	13.8	3.7	6.0	3.65	0.60
60	13.5	3.8	5.5	3.70	0.48
80	13.3	3.6	5.0	3.80	0.50
95	12.6	3.5	4.3	3.85	0.40
100	11.5	3.4	3.0	4.05	0.12
110	9.6	3.5	2.8	6.00	0.13
120	9.2	4.8	1.2	6.50	0.40
140	8.5	5.1	1.0	10.50	0.50
160	8.0	5.5	0.9	14.50	0.60

IV. CONCLUSION

The adsorption of carotenoids on activated clay has been investigated in this work. The clay obtained from Inyi in Oji River Province of Enugu State was activated using Tetraoxosulphate (VI) acid. The results of the characterization of the clay showed it to be montmorillonite with more of metallic oxides than the standard activated Fulmont AA bleaching earth. The physical properties of Bulk Density, Moisture content, percent of non clay residue and Ignition loss, and the chemical properties like Silica, Alumina, and Ferric oxide were found to be in agreement with the standard values. However, the metal oxides were found to be somewhat higher than the standard values, although with little or no contribution to the bleachability of the activated clay. The bleaching performance of the activated clay in terms of colour reduction showed that it is a veritable material in the bleaching of palm oil.

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