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Establishment of the particle size distribution of bleaching earth for palm oil refining

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ABSTRACT : *Palm oil has carotenoid pigments in them that limit their applications. The need to reduce the carotenoid pigments to improve the quality of the oil for industrial applications became serious concern to researchers. Chemical activated local clays have been used as adsorbents for adsorption bleaching to remove the carotenoid pigments, since Federal Government of Nigeria presently banned the importation of the adsorbent (fuller earth) and vegetable oil in the country. However, thermal activated local clay has not been popularly known but considered in this research as a better alternative. The clay sample was obtained from Umana – Ndiagu in Ezeagu L.G.A of Enugu State, Nigeria. The sample was pre-treated and classified into different particle sizes of 20µm, 40µm, 60µm, 80µm and 100µm using a set of vibrating sieves. Each particle size was thermally activated at different temperatures of 200°C, 400°C, 600°C, 800°C and 1000°C in a muffle furnace. The chemical properties were determined using Atomic Absorption Spectrophotometer (model;210VGP). The bleaching procedures were carried out and colour reduction of the oil at various particle sizes and activation temperatures were measure by tintometer. In conclusion, the result shows that, carotenoid pigment or colour reduction was obtained at particle size of 100µm activated at a temperature of 800°C which makes Palm oil suitable for industrial applications. Hence, it is recommended that the clay samples from the source for this research be packaged for commercial use in Nigeria.*

KEYWORDS: *Thermal activation, bleaching earth, clay, adsorption, adsorbent*

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I. INTRODUCTION

Palm oil is a vegetable and highly saturated acid oil obtained from palm fruit ELACIS GUINEESIS. The oil palm produces two different oils; the palm oil and palm kernel oil (PKO). The pulp contains palm oil which is highly coloured and composed mainly of C16 and C18 fatty acids. In its raw form, palm oil is dark red in colour due to the presence of a mixture of carotenoid pigments. These carotenes are designated as alpha, beta and gamma carotenes. The beta carotenoid is responsible for the red colouration of the palm oil and the most important source of vitamin A. Although Vitamin A is essential in our diet, but the presence of beta carotenoid reduces the shelf life of the oil due to rancidity and hence reduce its industrial application in manufacturing of chemicals and other edible products. Palm oil also contains trace metals and other impurities which must be removed to make it edible and good for industrial applications. However, refining becomes inevitable to remove the impurities [1] and to increase the shelf life of the oil. This research is therefore aimed at finding new ways of improving the quality of palm oil by developing low cost adsorbents used in the adsorptive bleaching that results in low refining cost and avoiding unwanted by- products. The bleaching earth used as adsorbent is a solid substance usually porous in nature with a high surface area that can absorb chemical substances onto its surfaces by intermolecular forces. The processes of adsorption are essentially concentrating the chemical substances at an interface, between solid and liquid or solid and gas.

Naghan [2] reported that the most frequently used adsorbent for the removal of organic pollutants from the oil is activated carbon. Malik et al [3] stated that the high cost of commercially adsorbent especially the activated carbon restricts their uses and applications and hence the need to substitute them with unconventional, relatively cheaper, readily affordable, easily accessible, environmentally friendly and locally sourced adsorbent. They concluded that activated carbon has a long history of use in edible oils, but they are more expensive, retain more oil, and very difficult to handle. Salawudeen et al [4] noted that impurities such as Fe2O3, CaO and MgO that cover part of the active sites in clay are washed away by activation and the number of active sites available for adsorption increased. However, the modification in the surface area of the clay is to enhance adsorption capacity and increased wide range of applicability. Dias et al [5] reported that increase in the surface area from inactivated to activated state is related to the elimination of the exchangeable cations, de-lamination of clays and the generation of micro-porosity during the activation process. Activated clay is therefore expected to give good result comparable to activated carbon in adsorptive bleaching.

When a sample of oil is bleached, the red pigment in the oil (mainly beta carotenoid) is removed to an extent. Adsorptive bleaching is a process of great important in the preparation of edible oil. Warren et al [6] stated that adsorption is present in many natural, physical, biological systems and it is used extremely in industrial processes for the purpose of separation and purification. The mechanisms of adsorption are related to the surface properties of the adsorbent, the pH of solution, particle size and the thermodynamic parameters which are important in the adsorption process. However, the bleaching earth or clay consists of various aluminum silicates which exhibit adsorption in their natural and more in activated state [7]. A number of physical and chemical methods have been investigated to undergo modifications in order to enhance the surface area and adsorption capacity of clay [8]. The modification of the surface area of clay includes the thermal and acid activation. [9-12]. Salawudeen et al [13] evaluated the effectiveness of clays from different parts of the Nigeria, Oyo and Osun states with the view to comparing the adsorptive power to that found in other parts of the country. The study of activated clay bleaching powder of some selected Nigerian clays found in Shagamu and Ewekoro, both in Ogun State, Calabar in Cross River, Nsusuka in Enugu State were also investigated and reasonable colour reduction of 80% was achieved[14].Many other studies have reported successful bleaching of oil using acid activated clays from across the world [15-19]. The bleaching performance of raw and acid activated clay in Yola, Adamawa was also studied and found to give high percentage of colour reduction [20]. Research has therefore concluded that clays are activated to generate micro-fissures that vastly increase its adsorptive surface area and its bleaching performance is found better than using activated clay. Thermal activation involves the use of heat only to create vacant sites for adsorption to take place. By increasing the temperature of activation, all mechanical properties have improved due to drying of clay minerals through dehydration and dehydroxylation process. At high temperature treatment, clay experiences series of physical and chemical changes that includes loss of water, changes in mass and density. It is observed that thermal activation has not been widely reported and this becomes a serious challenge which this research will investigate. Thermal activation has an advantage. It is cheaper and low risk compared to acid activation. Availability of clay in all parts of the country and low-cost technology using thermal activation will discourage the importation of fuller earth. Hence the research is poised at establishing the particle size distribution of the bleaching earth for palm oil refining.

A. THEORY: Adsorption Isotherms:

Freundlich: The Freundlich model is used to estimate the adsorption affinity of the adsorbents toward the adsorbate. The Freundlich isotherm coefficients were determined by plotting log X/m against logC. The constants k and n indicate the adsorption capacity and adsorption intensity. The linearity of the plots showed the representative nature of adsorption on adsorbents. It is possible to represent experimental results over a limited range of time by an empirical isotherm

$$X/m = Kc^n \tag{1}$$

Where: X = amount of pigment adsorbed, C = amount of residual pigment, m = amount of adsorbent

The equation which relates the above parameters gives a linear relationship when the ratio of the amount of substance adsorbed to the adsorbent is plotted on the logarithmic bases against the amount of residual colour.

Langmuir: This theory is restricted to cases where only one molecule can be adsorbed at the surface. Monolayer adsorption is distinguished by the fact that the amount adsorbed reaches a maximum value at moderately concentration and remains constant with further increase in concentration. The Langmuir isotherm can be derived from either kinetic or equilibrium argument and mostly applied to Chemisorptions of gases.

$$\theta = K_C/1+K_C/1+K_C \tag{2}$$

Where: θ is the fraction of the solid surface covered by adsorbed molecule and K is a constant temperature.

$$\theta = N/Nm \tag{3}$$

Where: N is the number of molecules adsorbed per gram of solid at an equilibrium solute concentration C and Nm is the number of moles per gram required to form a monolayer. Making this substitution and rearranging eqn. 2

$$C / N = c / Nm + 1 / kNm \tag{4}$$

However, if the Langmuir isotherm is an adequate description of the adsorption process, then the plot of C/N versus c will yield a straight line with slope 1/Nm.

If the area of 6 particles, occupied by an adsorbed molecule (on the surface) is known, the specific area A,

$$A = Nm \times N_0 \times 6 \times 10^{-20} \tag{5}$$

Where: N_0 is Avogadro's constant and 6 is given in square angstroms. If adsorption isotherm are determined at different temperatures, we predict that the slope of the C/N versus C plots should all be the same if the number of adsorption site is independent of temperatures, since k is a function of temperature.

Brunauer – Emmett-Teller (BET): The theory gives a correct semi- qualitative description of the scope of the isotherm and provides a good means of evaluating V_m, which is used to obtain the surface area of solid. BET theory is the most reliable at low relative pressures where only a few complete layers have formed and be applied successful to the calculation of V_m even for porous solids. This theory is an extension and generalization of Langmuir's treatment of monolayer adsorption. In order to obtain an expression for θ as a function of the isotherms. The BET isotherm is obtained from such a derivation, thus:

$$\theta = n / 5 = \frac{cx}{\left(1 - x\left[1 + (c - 1\right]\right)x} \tag{6}$$

Where: 5 is the number of sites, n is the number of adsorbed molecules. X is relative pressure (p/p_6) and c is the dimensionless constant greater than unity and dependent on temperature only. Note that θ equals zero when x=0 and approaches infinity as θ approaches unity in agreement with eqn. (6) which can be rearranged to the usual form of the BET equation.

$$\frac{X}{V(1 - x)} = \frac{1}{V_{mc}} + \frac{(C - 1)x}{V_{mc}} \tag{7}$$

The plot of $\left\|\mu x / v(1 - x)\right\| vs \mu$ should be a straight line. In practice the derivation from linear plots are deduced below. From the slopes S and the intercept, I, both V_m and C can be evaluated.

$$V_m = \frac{1}{st}, C = 1 + \frac{s}{1} \tag{8}$$

The volume adsorbed is related to N, the number of moles absorbed by $V = PRT_0$

The total area of the solid is

$$A = N_0 N_m \delta \tag{9}$$

Where: N_0 is Avagadro's number and δ is the cross-sectional area of adsorbed molecules.

II. MATERIALS AND METHODS

A. Collection of clay samples

The clay used as bleaching earth was collected from Umana-Ndiagu in Ezeagu Local Government Area (6.38855°N, 7.2931°E) of Enugu State. The clay deposits at Umana -Ndiagu was originally used for pottery works. Data from the central laboratory of the Federal Geological Surveys Barnawa, Kaduna South reported sources of clay samples from varying geographical locations that produce good bleaching results; namely, clay sample from Rido village in Kaduna State, Gambori Ngala in Borno State, Darazo in Bauchi State,Kaoje in Kebbi State, Fularaba in Adamawa State.

B. **Clay preparation**:

The clay sample was ground, mixed with water to remove impurities. The mixture was stirred and the slurry was decanted leaving behind impurities. The slurry was allowed to settle and clay was dried in the oven at a temperature of 107°C for 1hour.

Sources and preparation of crude palm oil: The palm oil used for this research has its source from Ezeagu Local Government of Enugu State. Both the physical and chemical properties of the oil were determined.

C. Methodology

1. Loss on ignition: The loss on ignition was determined by placing one gram of dry clay sample in the oven for 12hours at a temperature of 107°C. This was done using crucible of known weight (Wd). The sample was subsequently heated at 1000°C in the muffle furnace for 1hours. The sample was reweighed (Wf) after cooling to room temperature. The loss in ignition was calculated in percentage. Thus;

$$\frac{Wd-Wf}{Wd}\times 100\% \qquad (10)$$

2. Thermal activation: About 200g of a well-prepared clay sample was weighed and placed in an oven maintained at 107°C for 5hours.

It was ground and shared in different crucibles and subjected to further heating at different temperatures of 200°C, 400°C, 600°C, 800°C and 1000°C for a constant time 40minutes before cooling to 40°C. With the help of the heating tong, the samples were transferred to the electromagnetic shaker where they are classified into different particle sizes (using set sieve) of 20, 40, 60, 80, and 100µm. The chemical compositions of clay were determined after activation. Each particle size was kept dry in the desiccator.

Bleaching of the oil sample with the activated clay:
30g of crude oil obtained from the local market was weighed in the conical flask. The content was heated to 120°C. 20g of the activated clay samples was added to the oil and stirred for 15minues on a hot plate at a temperature not below 800°C. The content was filtered with filter cloth. However, a clean bleached oil was obtained and percentage (%) colour reduction measured by tintometer. The experiment was repeated with different particle sizes of activated clay at different temperatures of activation which are: 200°C, 400°C, 600°C, 800°C and 1000°C.

III. RESULTS AND DISCUSION

Table 1 shows the chemical properties of thermally activated clay samples obtained from Ezeagu Local Government Area of Enugu, compared with the imported bleaching earth called fuller's earth. The results indicated that the clay has a property comparable to the fuller's earth which is a certified earth and widely used in adsorptive bleaching. Table1 further suggest that the thermally activated clay sample closes rank with the imported bleaching earth with high percentage of silicon IV oxide and alumina. The presence of other minerals like the MgO, Fe_2O_3 and SO_3 in some reasonable quantities shows that the local clay can respond to both chemical and thermal activation. Table 1 also show that loss on ignition of the clay sample is low depicting that the apparent bulk density of the clay is high and this in agreement with fuller's earth.

Table 2 shows the result of oil characteristics which may influence the bleaching activities. The low percentage of free fatty acid and acid value indicated that the oil has not degraded by oxidative reactions which would have affected the bleaching process and colour reduction. In order words, the carotenoid pigments that are removed during bleaching have not been affected by external factors that may likely affect the chemical nature of the pigments.
The tables 3(a-e) show an increase in % colour reduction with corresponding increase in particle size distribution at various temperatures of thermal activation.

Table 1: Chemical composition of thermal activated Clay (at 800°C) compared to fuller's earth.

% chemical Composition	Local Clay	Fuller' earth
SiO_2	60.63	61.7
Al_2O_3	13.0	21.0
Fe_2O_3	4.0	5.7
CaO	0.3	0.2
MgO	2.0	2.3

Na_2O	0.19	0.2
K_2O	0.50	0.6
TiO_2	1.00	0.6
SO_3	5.0	6.2
Loss on ignition	7.0	6.2

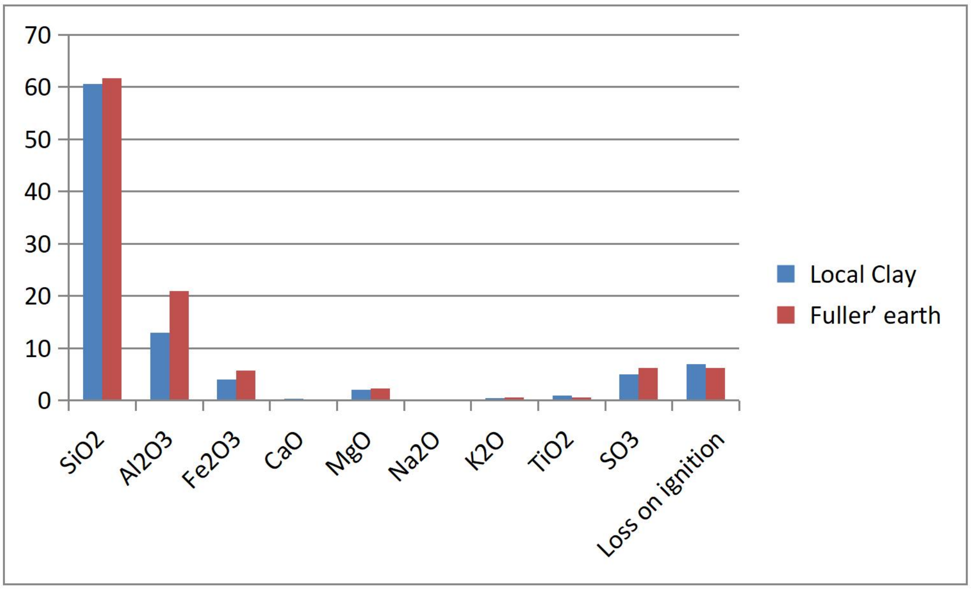

Fig 1. Chart of Chemical composition of activated clay and fuller's Earth.

Fig 1 compares the chemical composition of the local clay and imported fuller's earth. It however shows that both the local and fuller's earth has high percentages of silicates and alumina and this serves as an advantage in absorptive bleaching and possible colour reduction.

Table 2: Characterization of Palm oil used

Characterization of palm oil.	Chem. Properties
Free fatty acids (% FFA)	4.9
Acid value	5.85
Saponification Value	197.9

Table 3(a): Particle Size and Percentage Colour Reduction (200°C)

Particle size (µm)	20	40	60	80	100
% colour reduction	10	20	35	45	50

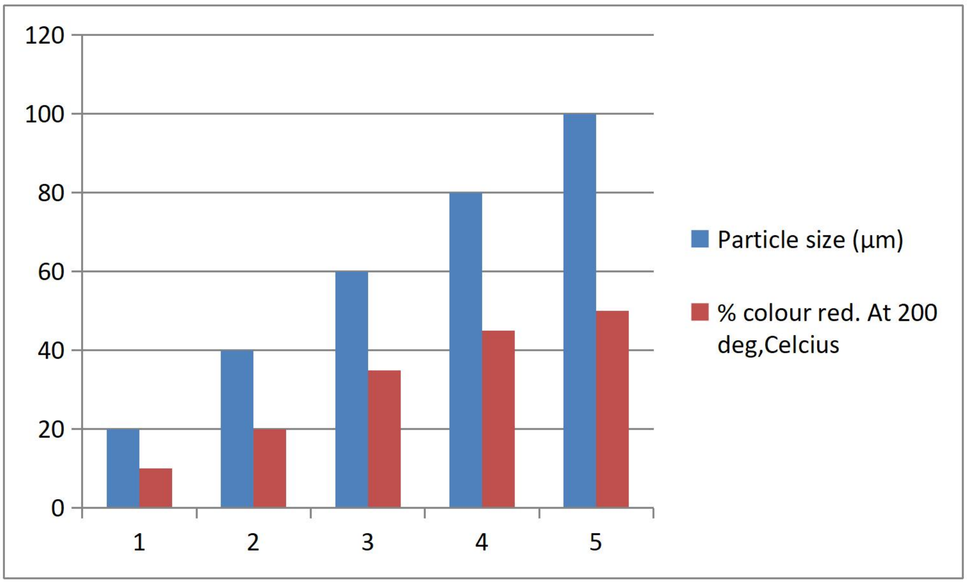

Fig 3(a): Particle size and % Colour reduction at 200°C Clay activation

Fig 3(a) shows that the highest colour is 50% at the particle size of 100μm when the clay is thermally activated at 200°C. The bar chart also affirms that the lowest colour reduction occurs at 20μm of thermal activation, the graph confirmed the low percentage in the colour reduction

Table 3(b): Particle Size and Percentage Colour Reduction (400°C)

Particle size (μm)	20	40	60	80	100
% colour reduction	15	20	30	40	60

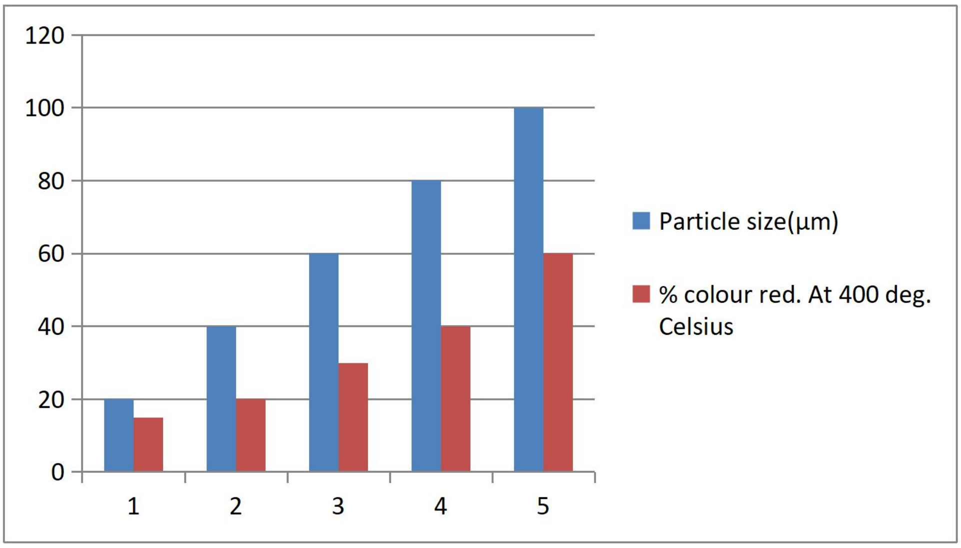

Fig 3(b): Particle size and % Colour reduction at 400°C Clay activation

Fig 3(b)shows that at 400°C of activation, the highest colour reduction is 60% when the particle size is 100μm. The least reduction of 18% occurs when the particle size is 20μm.

Table 3(c): Particle Size and Percentage Colour Reduction (600°C)

Particle size (µm)	20	40	60	80	100
% colour reduction	20	25	40	70	80

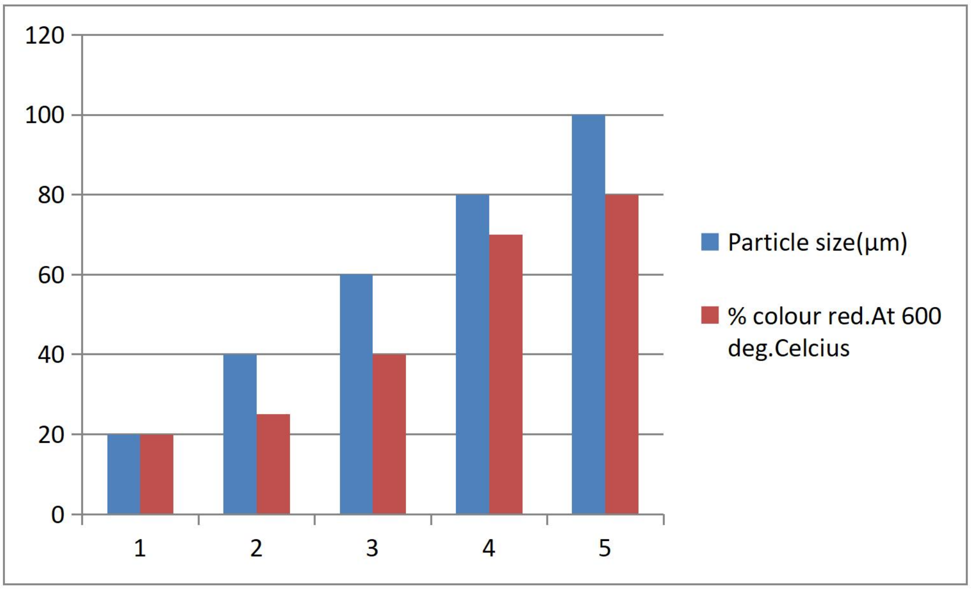

Fig 3(c): Particle size and % Colour reduction at 600°C Clay activation

Fig 3(c) shows that at 600°C, the highest colour reduction of 80% when the particle size is 100µm while the least 20% occurs at 20µm.

Table 3(d): Particle Size and Percentage Colour Reduction (800°C)

Particle size (µm)	20	40	60	80	100
% colour reduction	25	40	50	85	90

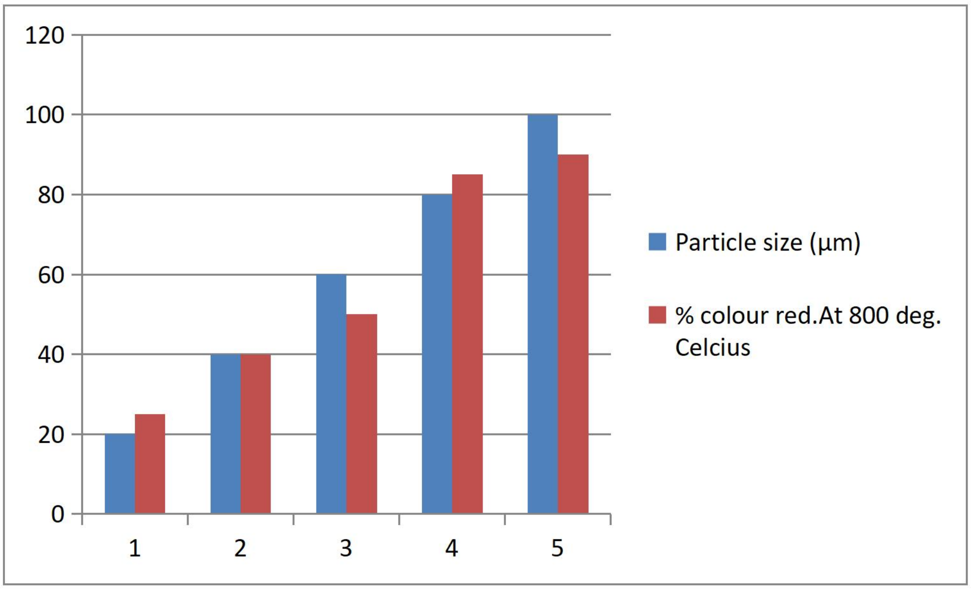

Fig 3(d): Particle size and % Colour reduction at 800°C Clay activation.

Fig 3(d) shows that at 800°C, the highest colour reduction of 90% at a corresponding particle size of 100µm. Despite this increase, an interesting trend is observed at the particle size of 80µm. The percentage colour reduction increases to 83% as represented in the bar chart. This means that more vacant sites are created for adsorption of the carotinoids. The trend also occurred at 20µm as shown in Fig.3(d).

Table 3(e): Particle Size and Percentage Colour Reduction (1000°C)

Particle size (µm)	20	40	60	80	100
% colour reduction	15	20	35	40	50

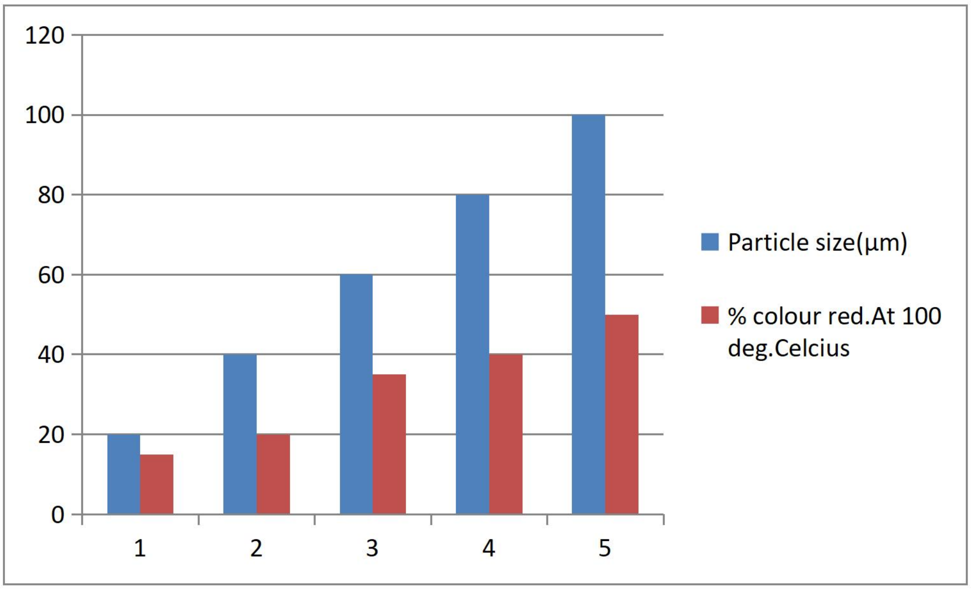

Fig 3(e): Particle size and % Colour reduction at 1000°C Clay activation

Fig 3(e) shows that at 1000°C, the highest colour reduction is 50% at a corresponding particle size of 100µm. The least colour reduction occurs at a particle size of 20µm.

The plots in Fig 3(a-e) show an increase in color reduction with a corresponding decrease in particle size, that is from 20 - 100µm. However, there is slight increase in colour reduction (50 - 90%) as the temperature of activation increases from 200°C to 800°C. At temperature of 1000°C, there is a reverse in the trend. The percentage colour reduction is 50%, the same with 200°C. The increase in percentage colour reduction as the particle size increases (20 - 100µm) may be attributed to gradual increase in the surface area due to increase in activation temperature. In addition, the porosity of the clay gradually increases when activated from 200°C to 800°C. Above 800°C, there is a sharp decrease in colour adsorbed. The decomposed and the residual carbonaceous matter are burnt away over a range of temperature say 350°C – 850°C. At this point, the constitutional water which holds the clay layers together starts being evaporated, causing collapse of the clay structure and thus increasing the surface area available for adsorption. Within 900°C – 1000°C, vitrification range starts and extends to 1500°C. During the vitrification period, the porosity of the clay decreases due to a marked decrease in external site. This is because loss of shape becomes increasingly difficult to prevent as the firing temperature increases. The consequence at 1000°C due to vitrification period is the reduced percentage (%) of colour reduction.

IV. CONCLUSION

Thermal activated clay from Enugu State of Nigeria serves as a good adsorbent in palm oil refining, for the removal of carotenoid pigment. The procedure was successfully carried out at different temperatures of 200°C, 400°C, 600°C, 800°C and 1000°C using the muffle furnace. Different particle sizes of the thermally activated clay were used as adsorbent to remove betacarotenoid pigments from definite quantity of the oil. The process of bleaching followed the recommended procedure that yielded a good result with thermal activation which has not been widely reported. From the results and for the purpose of providing solutions of improving the quality of palm oil using our local clay as adsorbent, the conclusion can be stated. Thus;

Table 3(a-e) shows that the most favourable temperature established for the adsorptive bleaching of palm oil using thermal activated clay samples used in this work is 800°C with particle size of 100µm.
The results showed that as the particle size increases, the tendency for adsorption increases due to increase in porosity. The surface area of particles however increases as the temperature of activation increases until it reaches vitrification at 1000°C where there is sharp decrease in colour reduction. The colour reduction is best achieved at 800°C thermal activation of local clay obtained from Ezeagu LGA of Enugu State and particle size ranging between 80µm-100 µm.

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