DEVELOPMENT OF KINETIC MODEL FOR ADSORPTION OF CAROTENOIDS ON ACTIVATED CLAY IN THE BLEACHING OF PALM OIL

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Abstract

In this work the mechanism of adsorption for the bleaching of palm oil using activated clay as adsorbent was studied. Tetraoxosulphate (VI) acid was used to activate a local (Inyi) clay obtained from Oji River province in Enugu State. The sample of palm oil used in the study was obtained from Akpugo in the same 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 acid addition increases the bleaching efficiency of activated clay. The mechanism of palm oil bleaching with the activated clay was developed from the results obtained. The stability of the oil was measured in terms of Free Fatty Acid (FFA) 0.12%, Peroxide Value (PV) 3.0 m.eq/kg, Anisidine Value(AV) 4.55 m.eq/kg, Iodine Value (IV) 48, Iron (Fe) 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.*

Keywords: *Adsorption Kinetics, Mechanism of adsorption, Activation, Bleaching, Characterization, and Stability*

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1. 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, (Beare-Rogers, [1]). 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 (Pahl G, [2]). Palm oil is a flesh fruit fat with a distinctive orange-red colour, due to its high content of carotenoids. Raw palm oil, in addition to carotenoid pigments content, contains impurities like free fatty acid, fiber particles, Chlorophyll, among others. 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 volatiles, (Christidis et al, [3]). Many types of adsorbent have been tested for the removal of pigments from vegetable oils, Kamga et al, [4], Falara et al, [5], Topallar, [6], Proctor and Snyder,[7], Kheok and Lim, [8].

Adsorption is defined in [9,10,11], as the adhesion of atoms, ions, biomolecules, or molecules of gas, liquid or dissolved solids to a surface, with physical and chemical adsorptions as mmethods. A film of adsorbate (the molecules or atoms being accumulated) is created by this process on the surface of the adsorbent. This differs from absorption as described in [12]. Atoms on the surface of the adsorbent are partially covered by other adsorbent atoms and hence can attract adsorbates. Nevertheless, the exact nature of the bonding, according to [13] depends on the details of the species involved as the process may be classified as physiosorption (characteristic of weak van der Waals force), or chemisorption (characteristic of covalent bonding), and it may occur due to electrostatic attraction. Adsorption is widely used in industrial applications such as activated carbon or charcoal, adsorption chiller, water purification, ion exchange and chromatography.

Freundlich and Kuster, the progenitors of isotherm Adamson [10], produced a relationship given by,

$$\frac{x}{m} = KP^{1/n} \qquad 1$$

Where x is quantity adsorbed, m is mass of adsorbent, P , the pressure of adsorbate and K and n are empirical constants for each adsorbent – adsorbate pair at a given temperature.

Adamson[10], also reported that the amount adsorbed can be measured as a function of partial pressure or concentration at a given temperature. The result was expressed as an adsorption isotherm. The lrving Langmuir adsorption isotherm model assumes that the adsorbent has S sites per unit mass, of which S_o are not occupied and S_1 occupied by adsorbate molecules. Hence,$S = S_o+S_1$

He assumed that the rate adsorption, r_{ad} and desorption, r_d are equal and at equilibrium;

$$r_{ad} = k_2PS_o;\ r_d = k_1S_1\ ;\ \text{and}\ k_2PS_o = k_1S_1$$

$$k_2P(S_o - S_1) = k_1S_1 \qquad 2$$

By expressing the amount adsorbed as a fraction of the sites occupied, we have,

$$\theta = \frac{S1}{S}$$

$$k_2P(1 - \Theta) = k_1\Theta$$

$$\theta = \frac{k2P}{k1 - k2P} = \frac{KP}{1 - KP} \qquad 3$$

Where $K = k_2/k_1$ and K is equilibrium constant

The type of adsorbent used world-wide today by refiners are mainly activated montmorillonite clays. Christidis and Kosiari, [14], 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 Freundlich type. Some authors pointed out that bleaching process led to and increased the fatty acid content of the vegetable oil, (Habile et al, [15], Boki et al [16], Nnaedozie et al, [17]. Hymore R. and Ajay [18], have 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, [19], 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 [18], 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 present in abnormal quantities, hinder the performance of the clay as a bleaching agent when activated. These include the amount of moisture contained, the level of volatile matters and non hydratable materials. However, non of the studies mentioned above investigated the adsorption of free fatty acids during the decolourization process, and the mechanism of such adsorption process.

In the present study, the kinetics for the adsorption of palm oil pigment, carotene and free fatty acid, (the adsorbate) unto the active site of Nigerian (Inyi) clay (adsorbent) was developed from data obtained from refining of local palm oil. The result conformed with the Freudlich and Langmuir Isotherms for adsorption.

2. MATERIALS AND 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°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.

Acid Activation of lnyi Clay: 50g of 150 mesh size pulverized clay was weighed into a 250ml beaker and 100ml of 1.0M of 80% H_2SO_4 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 0.5, 1.5, 2.0, 2.5, and 3.0 and 3.5M, in order to establish the optimum acid concentration for the activation.

2.2 Properties of Inyi Clay: Laporte, method, [20], was used.

2.2.1 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 sample 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

$$\text{Apparent bulk density (ABD)} = \frac{W_x - W_y}{V}\,\text{g/cm}^3 \qquad 4$$

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;

$$\text{Titratable acidity (mg) NaOH /g} = \frac{\text{Mole (gram) NaOH consumed}}{\text{Mass (g) of Clay}} \qquad 5$$

iv) Moisture content: This was done by heating 200g of the hydrated clay sample (natural or activated), in a furnace at a temperature of 110°C for 1 hour. The moisture content was calculated from the difference in the weight of the original sample and the dehydrated clay sample after heating and cooling in a desiccator. The percentage moisture content was then calculated as;

$$\text{Moisture content (\%)} = \frac{W_1 - W_2}{W_1} \times 100 \qquad 6$$

Where - W_1 - Weight of original clay sample
W_2 - Weight of original sample after heating

v) Loss on Ignition: Clay contains organic and volatile matters which occupy the adsorption sites in the clay and render it incapable of adsorbing the adsorbable materials. In addition, the presence of such substances reduces the adsorptive power of the clay as a bleaching agent.

2.2.2 Chemical Properties

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, 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

2.3 Particle Size Distribution of Bleaching Clay:

Methods of analysis of particle size of Coulson, and Richardson [21], was used. The aim was to determine the particle size of the prepared sample of the 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.

2.4 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 produced 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. 3and 4

2.5 Mechanism of Bleaching (Adsorption)

According to Languir adsorption isotherm, Ferrari et al [22], adsorption takes place by the following reaction,

$$A + S \rightleftharpoons AS \qquad 7$$

It has been assumed that adsorption of carotene from Palm oil follows the Langmuir Isotherm, and hence the reaction above can be used to develop a mechanism for the adsorption, namely,

$$A + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AS \qquad 8$$

$$2AS \qquad QS + RS \qquad 9$$

$$QS \underset{k_6}{\overset{k_5}{\rightleftharpoons}} Q + S \qquad 10$$

$$RS \underset{k_8}{\overset{k_7}{\rightleftharpoons}} R + S \qquad 11$$

Where A is the reactant (palm oil), Q and R are products; S, the adsorption site, QS and RS are adsorbed species. It was also assumed that the surface reaction, equation 8 is the rate determining step, and all other equations are at equilibrium, and are equal to zero.

From equation 8 - 11,

$$r_1 = k_1P_AC_S - k_2C_A \qquad 12$$

$$r_2 = k_3C_A^2 - k_4C_QC_R \qquad 13$$

$$r_3 = k_5C_Q - k_6P_QC_S \qquad 14$$

$$r_4 = k_7C_R - k_8P_RC_S \qquad 15$$

But $\frac{n}{V} = C, and \quad P = CRT$

Since the adsorbate is a liquid, the pressure is now related to concentration by PV = nRT

Or P = nRT/V.

Then
$$P_A = C_A RT$$
$$P_Q = C_Q RT$$
$$P_R = C_R RT$$

Equation 12,14 and 15 can be re-written as:

$$r_1 = k_1 C_A RTC_S - k_2 C_A \qquad 16$$

$$r_3 = k_5 C_Q - k_6 C_Q RTC_S \qquad 17$$

$$r_4 = k_7 C_R - k_8 C_R RTC_S \qquad 18$$

Equations 16 to 18 are not rate determining steps and ccording to Bodenstein steady state approximation theory, are equal to zero, Octave l, [23]. Hence,

$$k_1 C_A RTC_S - k_2 C_A$$
$$\frac{k_1}{k_2} = \frac{C_A}{C_A RTC_S} = K_2 \qquad 19$$
$$C_A = K_2 C_A RTC_S$$

Similarly,

$$k_5 C_Q = k_6 C_Q RTC_S$$
$$\frac{k_5}{k_6} = \frac{C_Q RTC_S}{C_Q} = K_3 \qquad 20$$
$$C_Q = \frac{C_Q RTC_S}{K_3}$$

And

$$k_7 C_R = k_8 C_R RTC_S$$
$$\frac{k_7}{k_8} = \frac{C_R RTC_S}{C_R} = K_4 \qquad 21$$
$$C_R = \frac{C_R RTC_S}{K_4}$$

Substitution of equations 19 to 21 in equation 13, we obtain,

$$r_2 = K_3 (K_2 C_A RTC_S)^2 - K_4 \left[\left(\frac{C_Q RTC_S}{K_3}\right)\left(\frac{C_R RTC_S}{K_4}\right)\right]$$

$$= K_3 (K_2^2 C_A^2 R^2 T^2 C_S^2) - \left[\left(\frac{C_Q C_R R^2 T^2 C_S^2}{K_3}\right)\right]$$

$$r_2 = C_S^2 \left[K_3 K_2^2 C_A^2 - \frac{C_Q C_R}{K_3}\right] T^2 R^2 \qquad 22$$

Equation 22 is made up of constants, measurable concentrations and temperatures, as well as non-measurable concentrations C_S. Since C_S is not measurable, it has to be eliminated. However, an adsorption site cannot just disappear; it either becomes vacant site or adsorbed site[10]. Assuming that the total sites are represented by L, such that:

$$L = C_S + C_A + C_R + C_Q, \qquad 23$$

Where, C_S – Vacant site
C_A – Site with A adsorbe on them
C_R – Site with R adsorbed on them
C_Q – Site with Q Adsorbed on them

If we substitute equations 19 to 21 in 23, we have,

$$L = C_S + K_2 C_A RTC_S + \frac{C_Q RTC_S}{K_3} + \frac{C_R RTC_S}{K_4}$$
$$L = C_S \left[1 + K_2 C_A RT + \frac{C_Q RT}{K_3} + \frac{C_R RT}{K_4}\right] \qquad 24$$

$$C_S = \frac{L}{\left[1 + K_2 C_A RT + \frac{C_Q RT}{K_3} + \frac{C_R RT}{K_4}\right]} \qquad 25$$

$$2\, C_S = \frac{LK_3K_4}{K_3K_4 + K_2K_3K_4C_A RT + K_4 C_Q RT + K_3 C_R RT} \qquad 26$$

Substitution of equation 26 in 22 gave,

$$r_2 = \left(\frac{LK_3K_4 / RT}{\frac{K_3K_4}{RT} + K_2K_3K_4C_A + K_4C_Q + K_3C_R}\right)^2 \left(k_3 K_2^2 C_A^2 - \frac{k_4 C_Q C_R}{K_3 K_4}\right) \qquad 27$$

For $K_2 = 0$,

$$r_2 = \left(\frac{LK_3K_4 / RT}{\frac{K_3K_4}{RT} + K_4C_Q + K_3C_R}\right)^2 \left(\frac{-k_4 C_Q C_R}{K_3 K_4}\right)$$

$$r_2 = \left(\frac{L}{1 + \frac{RTC_Q}{K_3} + \frac{RTC_R}{K_4}} \right)^2 \left(\frac{-k_4 C_Q C_R}{K_3 K_4} \right) \qquad 28$$

Let $\frac{k_4}{K_3 K_4} = K'; \frac{RT}{K_3} = K_A; \frac{RT}{K_4} = K_B$

$$r_2 = \left(\frac{L}{1 + K_A C_Q + K_B C_R} \right)^2 \left(K' C_Q C_R \right) \qquad 29$$

Expanding and simplifying, for, For $C_Q = C_{R,}$ we have,

$$C_S = \frac{-LK'CQ^2}{1 + 2CQ[K_A + K_B] + 2CQ^2 K_A K_B + 2CQ^2 \left[K_A^2 + K_B^2 \right]}$$

$$C_S = \frac{-LK'CQ^2}{1 + 2K''CQ + 2K'''CQ^2} \qquad 30$$

Where $K'' = K_A K_B ; K''' = K_A K_B + K_A^2 + K_B^2 ;$

3. RESULTS AND DISCUSION

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 and deodorized oils was much less than that used for raw oil. However, similar equations were used in the calculation, AOCS [24]. Tables 1 was generated from the characterization experiments of raw bleached and deodorized oils respectively. This table shows the physical and chemical properties of the oil

Table 1 Physio-Chemical Properties of the raw, bleached and deodorized Oils used in the investigation. (Temperature – 100^{o}C, Activated clay dosage 1%) [25]

Properties	**Raw Palm Oil**	**Bleached oil**	**Deodorized oil**
Colour (Physica Appearance)	Deep Orange	Orange yellow	Golden Yellow
Odour	...of Palm Oil	Palm fruit odour	Palm fruit odour
Taste	...of Palm Fruit	Bland taste	Bland taste
Specific Gravity	0.9182	0.9025	0.9282
Melting Point(°C)	38	40	35
Moisture (%)	1.3	0.3	0.05
Refractive Index	1.4514	1.4562	1.4562
Free Fatty Acid (%)	3.80	2.80	0.12
Lovibond Red Unit (1" Cell)	23	5.8	3.2
Anisidine Value (M.eq/kg)	8.2	6.40	4.55
Peroxide Value (M.eq/kg)	5.8	4.20	3.0
Phosphorous (Ppm)	9.0	0.5	0.015
Iron (Ppb)	350	20	4.3
Saponification Value	200	205	210
Iodine Value	45	45.2	48

From the table, it can be seen that there is a marked difference between the raw, bleached and deodorized 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,[26]. 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.

Table 2 Results of Physical characterization of raw (Inyi) Clay before activation

Properties	Dark Red Crude Inyi Clay	Milky Crude Inyi Clay	Int'l Standard [20]
Non Clay Residue (%)	3.55	9.56	4.0 – 7.0
Moisture content (%)	8.44	9.48	8 - 12
Apparent Bulk density g/cm^3	0.87	0.63	0.740 – 0.810
Ignition Loss (%)	6.26	7.47	6.0 – 7.0
Titratable Acidity (mol/g)	0.78	1.13	0.72

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

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 also good . 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,[27].

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

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 size), the smaller the weight of material retained.

The effect of activation chemical on the performance of activated clay is shown in Figure 1

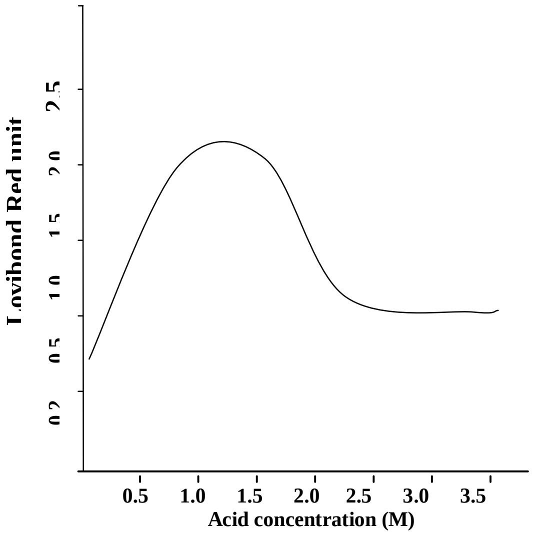

Fig 1 The effect of concentration of activation chemical on the performance of the activated clay.

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 between 1.0 and 1.5M, (the optimum), beyond which it began to decrease, and became constant towards the end.

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

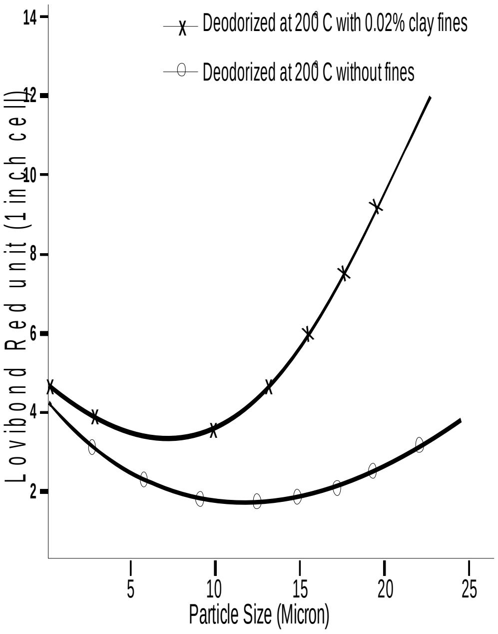

Fig. 2 The effects of particle size on the colour of physically refined palm

From the figure, it is observed that;

a) The smaller the particle size, the lower the colour until the particle size of between 5 and 10 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.

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	4.55	6.0	3.7

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. This might be due to the quality (grade) of the raw oil used and the conditions under which they were processed.

3.5 Variation of Temperature.

The effect of bleach temperature on colour, PV, AV, and FFA, are shown in table 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	13.0	3.7	6.0	3.65	0.60
60	12.5	3.8	5.5	3.70	0.48
80	11.0	3.6	5.0	3.80	0.50
95	8.2	3.5	4.3	3.85	0.40
100	5.8	3.2	3.0	4.55	0.12
110	5.0	3.5	2.8	6.00	0.13
120	4.5	4.8	1.2	6.50	0.40
140	4.0	5.1	1.0	10.50	0.50
160	3.6	5.5	0.9	14.50	0.60

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, the effects of bleaching clay dosage on Fe/Cu contents respectively, are shown.

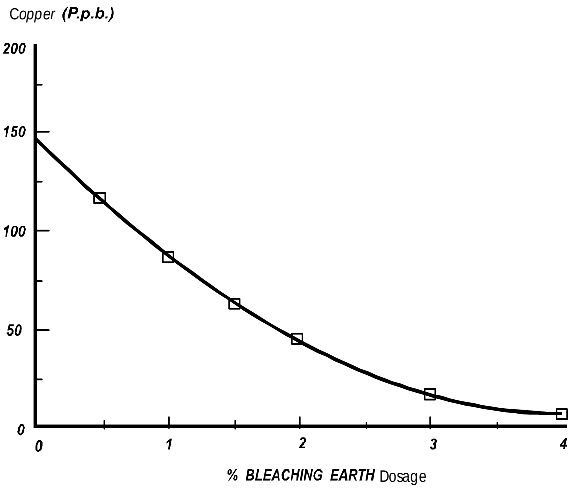

Figure 3 The effect of earth dosage on the copper content of physically refined Palm oil.

From the figure. 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. 4. Phosphorous is reduced linearly with clay dosage until a dosage of 1 per cent is reached, beyond this point, any increase in earth dosage has no corresponding reduction in phosphorous, and hence an asymptotic behaviour of the graph.

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

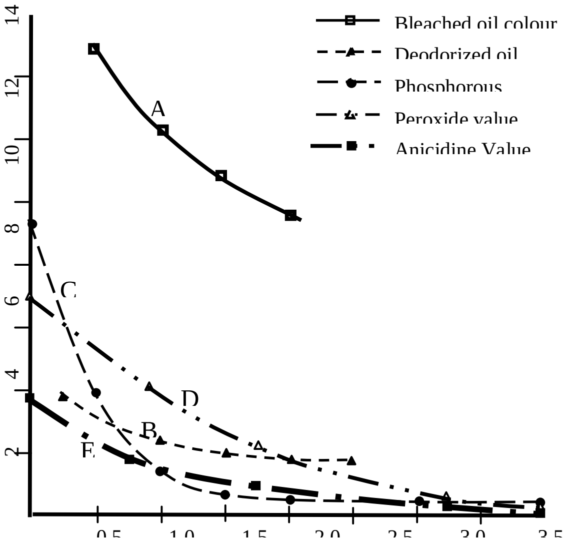

Fig.4. The relationship between bleaching clay dosage and: A – Bleached colour(Red unit, in 1 inch cell); B – Deodorized colour(Red unit, in 1 inch cell); C – Phosphorous(Ppm); D –Peroxide value(M.eq/kg); E– Anicidine value(M.eq/kg)

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3.7 Adsorption Mechanism

Adsorption of carotene pigments on activated clay during bleaching is a surface phenomenon, and hence follows both Frundlich and Langmuir adsorption isotherms. Practically, all bleaching processes follow Langmuir/Freundlich adsorption isotherm, which expresses the relationship between the concentrations in the fluid phase to that in the adsorbent particle phase at a given temperature.

Frundlich isotherm, is particularly for adsorption from Liquid. However, in this study, langmuir isotherm was used to derive the mechanism, because, one of the assumptions of this isotherm is that all adsorptions occur through the same mechanism [13]. In the development, it was assumed that the adsorbent (clay) has S sites per unit mass, of which S_o are unoccupied and S_1 are occupied by the adsorbate, (Caroteenoids). Hence

$$S = S_o + S_1 \qquad 31$$

Now rate of adsorption on the site is proportional to the product of the number of unoccupied sites and gas pressure,

$$r_{ad} = k_2 P S_o = k \frac{n}{V} RT S_o \qquad 32$$

Adsorption is also assumed to be proportional to the number of occupied sites,

$$R_d = k1 S_1 \qquad 33$$

At equilibrium $r_{ad} = r_d$, and

$$k2 C S_o RT = k1 S1$$

$$k2 CRT(S - S1) = k1 S1 \qquad 34$$

Adsorbed amount is given as a fraction of the sites that are occupied

$$\theta = \frac{S_1}{S}$$

$$k2 CRT(1 - \theta = k1\theta$$
$$\theta = \frac{k2 CRT}{k1 - k2 CRT} = \frac{KCRT}{k1 - KCRT} \qquad 35$$

Where $K = \frac{k2}{k1}$

Hence K is the ratio of the adsorption rate constant and the dsorption rate constant with unit of the reciprocal of concentration.

CONCLUSIONS

The kinetic rate of adsorption of carotenoids on activated clay has been developed in this work. The clay obtained from Inyi in Oji River Province of Nigeria, 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 are in conformity with the standard values, while the chemical properties like Silica, Alumina, and Ferric oxide were found to be in agreement with the standard values. 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.

REFERENCES

[1]. Beare-Rogers, J.L, H.H. Draper. Ed. Tras and positional isomers of common fatty acids, Advances in Nutritional Research (Plenum Press< New York), 5: 171 – 200. PMID 6342341.
[2]. Pahl G, (2005), Biodiesel growing a new energy economy,White River Junction VT; Chelsea Green Publishing Co.
[3]. Chritidis G.E, P.W Scott, and A.C Duhnam, (1997), Acid activation and nleaching capacity of Bentonite from the islands of Milos and Chios. Aegan. Applied Clay Sci, 12: 329- 347.
[4]. Kamga R., G.J, kayem and P.G Reuxhet, (200), Adsorption of Gossypol from cotton seed oil on oxide. J. Colliod Interface Sci., 232: 198-206.
[5]. Falaras P., F. Lezou, G. Seiragakis and D.Petrakis, (200), Bleaching properties of alumina – Pillard acid
[6]. Topallar, H, (1998), Bleaching Kinetics of Sunflower oil. J. Amer. Oil Chem. Soc,75: 531 – 533.
[7]. Proctor, A and H.E Snyder, (1988), Adsorption of lutein from soybean oil on Silicic acid II Kinetics. J Amer. Oil Chem. Soc; 65:761-763.
[8]. Kheok S. C and E.E Lim, (1982), Mechanism of Palm oil bleaching by montmorillonite clay activated at various concentrations. J Amer. Oil Chem. Soc. 59: 129-131.
[9]. The Brownfield and land Revitalization Technology Support Center. http://www.brownfieldstsc.org/glossary.cfm?q=1. retrieved,2012-12-21
[10]. Adamson, A.W, (1990), Physical Chemistry of Surfaces, 5th Ed. John Wiley and sons, New York.
[11]. Israelachvili, J (1991), Intermolecular and Surface forces, 2nd ed., academic press, New York.
[12]. "absorption (chemistry0". Memidex (WorldNet) Dictionary/Thesaurus. http://www.memidex.com/absorption+chemistry. Retrieved 2011-11-02.
[13]. Henderson, A. P.; Seetohul, L.N.; Dean, A. .;Russell, P.; Pruneanu, S.; Ali, Z.(2009)," A Novel Isotherm, Modelling Self – Assembled Monolayer Adsorption and Structural Changes". Langmuir **25** (2):931 –938. doi:10.1021/1a802677n

[14]. Chritidis G.e and S. kosiari, (2003), Decolorization of Vegetable oils: A study of the Mechanism of adsorption of β – Carotene by acid activated bentonite from Syprus clays. Clay Miners, 51: 327 – 333.
[15]. Habile M, J. P Barlow and M. Hole, (1992), Adsorptive bleaching of Soybean oil with Non – montmorillonite Zambian Clays. J Amer. Oil Chem. Soc. 69:379-383.
[16]. Boki K, M kubo; T Wada, and T. Tamura, (1992), Bleaching of alkali-refined vegetable oils with clay minerals. Ibid 69: 233-236.
[17]. Nnaedozie N.N., T.A Arowolo and H.J Akpan, (1989), Quality of Nigerain Palm oil after bleaching with local treated cllays. J Amer. Oil Chem. Soc. 66: 218-222.
[18]. Hymore F.k and Ajayi A. F, (1989), Use of local clay in the refining of Palm Oil. J. Nig. Soc of Chem. Engrs. Vol 8,2.
[19]. Egbuna S. O and Aneke N.A.G, (2005), Evaluation of the Quality Stability in the Physically refined Palm Oil. Preceding of the 35th annual Conference and AGM of the NSChE, kaduna. Pp 146-152.
[20]. Laporte Inorganics (1993), Fulmont, Activated bleaching Earths, Moorfield Road, Widnes, Cheshire, England.
[21]. Coulson, J. M., Richardson, J.F. (1993), Chemical Engineering, Vol. 2, 6th ed. Butherwork-Heinemann. 724 - 737
[22]. Ferrari, l.; Kaufmann, J.; Winnefeld, F.; Plank, J. (2010). Inteeraction of Cement Model Systems with Superplasticizers Investigated by Atomic Force Microscopy, Zeta Potential, and Adsorption Measurements. J.Colloid Interface Sci 347 (1): 15 – 24. doi : 10.1016/j.jcis.2010.03.005. PMID 20356605.
[23]. Smith , J. M. (1982). Chemical Engineering kinetics, 3rd Ed. McGraw–hill International Book company, New York. 314–322
[24]. Egbuna S.O, Aniokete T .C, Ozonoh M, (2013), Beneficiation Of Local Clay To Improve Its Performance In Adsorption Of Carotene Pigments And Volatiles In The Bleaching Of Palm Oil, IJESI, India (Accepted for publication).
[25]. AOCS. (2003), Sampling and Analysis of Commercial fats and oils. AOCS Official Method Cd 8 - 53. Surplus peroxide Value Acetic acid – Chloroform method Definition; AOCS Cold Spring Harbour, New York, NY, U.S.A
[26]. Mag, T (1990), Bleaching – Theory and Practice en David R.(Ed), Edible fats and oils processing, 107. J Amer. Oil Chem. Soc., Champaign U.S.A.
[27]. VanderWiel, D. P.; Pruski, M.; King, T. S. (1999). A Kinetic Study of the Adsorption and Reaction of Hydrogen on Silica- Supported Ruthenium and Silver-Ruthenium Bimetallic Catalyst during the Hydrogenation of Carbon Monoxide.Journal of Catalysis 188 (1): 186 – 202.doi:10.1006/jcat.1999.2646.