Decolourization of Palm Oil by Nigerian Local Clay: A Study of Adsorption Isotherms and Bleaching Kinetics

J. T. Nwabanne[1] and F. C. Ekwu[2]

[1]Department of Chemical Engineering, Nnamdi Azikiwe University, P.M.B. 5025, Awka, Nigeria
[2]Department of Food Science and Technology, Ebonyi State University, Abakiliki, Nigeria

***Abstract*– The Mechanism of decolourization of crude palm oil using local clay obtained from Nteje town in Anambra State, Nigeria was studied in order to understand the bleaching mechanism. The raw clay was characterized to determine its properties. Chemical activation of the clay was done using sulphuric acid. The effect of parameters such as time, temperature, particle size and dosage on the bleaching of palm oil was investigated. It was found that bleaching efficiency increased with increase in time, temperature and dosage, and decreased with increase in particle size. Langmuir and Freundlich models were used to study the adsorption mechanism. The adsorption data conformed to Freundlich isotherm. The heat of adsorption was determined as 35.6KJmol^{-1} which showed that bleaching process was chemisorption. The rate constant was evaluated as 1.552, indicating that there is a high rate of adsorption during the bleaching of palm oil.**

***Keywords*– Clay, Palm Oil, Bleaching, Adsorption Isotherm and Kinetics**

I. INTRODUCTION

Crude palm oil is a vegetable oil rich in minor components which have nutritional attributes (Puah et al., 2004). An ideal crude palm oil contains about 600-1000mg/kg of tocopherols and 500-700mgl/kg of carotenoids, mainly a-and B- carotene (Goh et al., 1985). These compounds help in health maintenance, since carotenes play an important role in the prevention of cancer, cataracts and heart disease (Choo, 2000). Despite the health benefits derived from palm oil, it must be refined to improve the purity characteristics desirable in edible oil (Basiron, 1996).

The removal of pigment and other trace constituents by adsorption process (bleaching) is one of the most important steps in the vegetable oil refining and this process removes the carotenes, chlorophyll and other pigments as impurities (Salawudeen et al., 2007). The process makes the oil more appealing and convenient for use. Activated clay has been widely employed as an adsorbent. In recent years, Nigerian clay has been found efficient in the adsorption (bleaching) of palm oil (Salawudeen et al., 2007). Studying the isotherms and kinetics of the bleaching activities of our local clays with such oil as palm oil is a very critical and necessary step to developing the bleaching process.

The process of clay bleaching of palm oil is an adsorption process whereby bleaching clay accepts into its surface the particles of the coloring matter thereby decolorizing the palm oil (Foletto et al., 2006). There are two types of adsorption on surfaces (Laidler, 2005). One is physical adsorption or physisorption in which the forces are of a physical nature and the adsorption is relatively weak. The forces in this kind of adsorption are called vander Waal forces and this type of adsorption is also known as vander Waal adsorption. The heat evolved during vander Waals adsorption is usually small, less than 20KJmol^{-1}. In the second type of adsorption, the adsorbed molecules are held to the surface by covalent force of the same general type as those occurring between bound atoms in molecules. The mechanisms for adsorption in oil bleaching industry are diverse and different. Christidis and Kosiari (2003) reported that removal of B carotene from crude maize oil with acid activated low grade Bentonite from Cyprus is a chemical adsorption process. Adsorption Isotherm is the equilibrium relationship between the concentrations in the fluid phase and the concentration in the adsorption particles at a given temperature. Usually bleaching or purification of palm oil follows the Freundlich adsorption isotherm since they involve adsorption from liquids (Rohani, 2006). Langmuir isotherm follows the assumption that the process happens at uniform surface. Christidis and Kosiari (2003) reported that removal of B-Carotene from crude maize oil with activated low grade bentonite from Cyprus conformed to the Freundlich isotherm.

The purpose of this study is to determine the applicability of the Langmuir and Freundlich adsorption isotherms for the bleaching of palm oil with Nteje clay, to determine the rate constant and the heat evolved during adsorption and the effects of parameters such as temperature, time, dosage and particle size on the bleaching process.

II. MATERIALS AND METHOD

A. Materials

The grey coloured clay sample was obtained locally from Nteje, in Oyi Local Government Area of Anambra State, Nigeria as dry lumped sample. The crude palm oil (C.P.O) used for this study was obtained from Onitsha main market in Anambra State. Petroleum ether and the sulphuric acid used were of analytical grade.

B. Clay and palm oil characterization

The clay sample was characterised using Atomic Absorption spectrophotometer and X-ray Fluorensce (PW 4030 X-Ray Spectrophotometer). The properties of the unbleached palm oil were determined according to the AFNOR method (1981).

C. Acid Activation of clay

Acid activation was done according to the method described by James et al (2008) and Vicente Rodriquez et al (1996). The clay was ground into powder using mortar and pestle, and sieved through 1100µm sieve. 50g of the clay sample was introduced into a 600ml beaker and 250ml of 1M sulphuric acid added. The mixture was homogenized in a thermostatic bath at temperature of 95^0C for 3 hours. After stirring for 3 hours, the resulting mixture was filtered, washed with distilled water severally to reduce the acidity. The activated clay sample was dried in an electric oven at temperature of 105^0C. The dried activated clay sample was passed through 1100µm sieve, labeled and stored in an air tight container.

D. Bleaching process

Bleaching of the palm oil was carried out according to the procedure described by Nde-Age et al. (2007). Initially, the activated clay was ground to fineness and then sieved with a laboratory test sieve of 5 different apertures (150, 300, 600, 850, 1100µm). 0.6, 0.9, 1.2, 1.5, 1.8, 2.1 and 2.4g representing 2%, 3%, 4%, 5%, 6%, 7%, 8% of the weight of oil respectively were used. These samples were labeled adequately and stored for subsequent use. 30g of degummed palm oil was poured into a 50ml beaker and then heated up to 100^0C on a magnetic hot plate. 0.6g activated clay sample was added to the hot oil. The temperature was maintained at 100^0C for 30 minutes. After 30 minutes, the mixture was filtered through Whatman no 1 filter paper. This process was repeated with dosage of 0.9, 1.2, 1.5, 1.8, 2.1 and 2.4g in order to determine the effect of dosage. The effect of temperature was studied at 40, 60, 80 and 100^0C. The effect of time was done by varying the time (5, 10, 15, 20, 30, 45, 60 and 75 minutes). The effect of particle size was studied using particle size of 150, 300, 600, 850, and 1100µm.

The absorbance of the palm oil was measured using a UV Spectrophotometer. 0.1g of bleached palm oil was measured and poured into a beaker containing 7.5ml of petroleum ether. The mixture was poured in the cuvette and the value of the absorbance was read at 445nm wavelength using petroleum ether as reference (Nde Aga et al., 2007). The percentage bleached was calculated using equation 1:

$$\% \text{ Bleached} = \frac{A_o - A_t}{A_o} \times 100 \text{ ------- (1)}$$

Where, A_0 = absorbance of unbleached palm oil and A_t = absorbance of bleached palm oil at time, t

E. Adsorption Isotherms

The Freundich and Langmuir equations as reported by Achife and Ibemesi (1989) were used for isotherm study. Freundlich adsorption equation is given as:

$$\frac{x}{m} = KX_e^n \text{---------------- --------(2)}$$

Taking log of both sides gives

$$log\frac{x}{m} = logK + nlogX_e \text{ ---------- (3)}$$

Where, x = the amount of substance adsorbed, m = the amount of adsorbent (clay), X_e = the residual amount at equilibrium which is mathematically equal to 1 – x. The plot of log $\frac{x}{m}$ versus x_e gives n as slope and logK as intercept.

Langmuir adsorption equation is given as equation 4:

$$\frac{X_e}{x/m} = \frac{1}{a} + \frac{b}{a}X_e \text{ --------------- (4)}$$

Where, a and b are Langmuir constants. The plot of $X_e/(x/m)$ versus X_e was used to evaluate the values of a and b.

F. Heat of adsorption

For the bleaching process, the heat of adsorption may be calculated from equation 5 (Topallar, 1998).

$$\ln X_e = \frac{-\Delta H_a}{RT} + C \text{ -------------- (5)}$$

Where, X_e = the residual amount at equilibrium, ΔH_a = heat of adsorption, R = gas constant (8.314J/molK), T = temperature and C = integration constant. From the plot of $\ln X_e$ against 1/T, ΔH_a is evaluated.

G. Determination of rate constant

According to Brimberg (1982) the speed of discolouration of vegetable oils is given by equation 6

$$\ln \frac{C}{C_0} = -k(t)^{0.5} \text{ -------------- (6)}$$

Where, t is the time of contact between the adsorbent and oil, C is the concentration of the pigments at time t, C_0 is the initial concentration of the pigments and k is the rate constant. According to the Beer Lambert law the absorbance is proportional to the concentration of the pigments in the oil. Hence equation 6 can be written as

$$\ln \frac{A}{A_0} = -k(t)^{0.5} \text{ ------------ (7)}$$

Where, A is the absorbance of the oil bleached at time t and A_0 the absorbance of crude or unbleached oil. From this equation the linear regression between $\ln A/A_0$ and $t^{0.5}$ is a straight line whose slope is equal to -k.

III. RESULTS AND DISCUSSION

A. Chemical properties of the clay

The chemical analysis of Nteje clay in Table1 shows a high silica content (SiO_2 = 52.70%) which suggests its high potential for the production of floor tiles. The resut also suggests the existence of calcium montmoritonite since the silica content is within the range of 50 to 70%(Foletto et al., 2006, Falaras et al., 2000, Njiribeakor and Nwanya, 2000). It is seen from Table 2 that Nteje clay contains aluminium and iron in major quantities and trace elements like zinc, potassium and copper in minor quantities.

Table 1: Chemical analysis of Nteje clay using X-ray flourescence

Oxide	Composition
Al_2O_3	16.6
SiO_2	52.7
CaO	2.06
TiO_2	2.53
FeO_3	19.53
V_2O_5	0.16
Cr_2O_3	0.10
MnO	0.29
NiO	1.45
CuO	0.08
ZnO	0.13

Table 2: AAS Characterization of Raw Nteje Clay

Element	Concentration (ppm)
Fe	23.6340
Al	35.4839
Na	11.5033
Cu	0.0264
K	0.0163
Zn	0.0190
Ca	0.1214
Mg	0.1265
Mn	0.2204
Ni	0.1059

B. Properties of the unbleached palm oil

The properties of the palm oil are shown in Table 3. The low value of the free fatty acid (7.473%) shows that the palm oil used is fresh. According to Rohani (2006), 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 (Abdul Azis, 2000).

The low value of the moisture content reveals the reason why the free fatty acid is low. Rohani (2006) reported that the moisture content affects the percentage of free fatty acid in the oil and it must be reduced to 0.15 to 0.25 percent to prevent increasing free fatty acid through autocatalytic hydrolysis of the palm oil.

The value of the iodine value shows that palm oil is nondrying oil. Non-drying oils have iodine value less than 125 and the higher the iodine value, the higher the level of unsaturated fatty acids present, thus palm oil find its use in applications where oxidation is undesirable. Saponification value of 201.550mgKOH/kg suggests that the palm oil can be used for soap production.

Table 3: Physical and Chemical Characterization of palm oil

Property	Value
Absorbance	2.251
Moisture content	0.220
Specific gravity	0.975
Density	975kg/m^3
Acid value	14.867mg/KOH/kg
% FFA	7.473
Refractive index	1.462
Iodine value	55
Saponification value	201.55mgKOH/g

C. Effect of dosage on the bleaching of palm oil

Fig. 1 shows that the percentage bleached increased with increase in dosage. The increase in bleaching power with increasing dosage is as a result of increase in active site available for adsorption. Diaz and Santos (2001) stated that darker oils like palm oil require as much as 2 – 4% or more to meet final colour requirements.

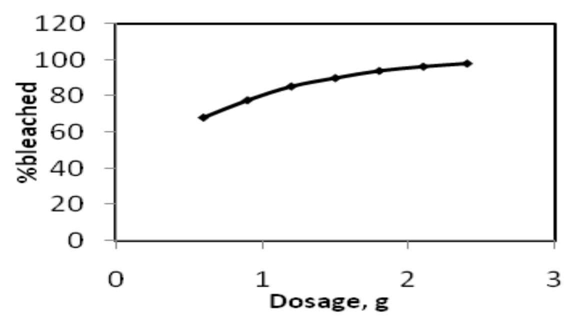

Fig. 1: Effect of dosage on the bleaching of palm oil

D. Effect of temperature on the bleaching of palm oil

It can be seen from Figure 2 that the percentage bleached increased with increase in temperature. The highest bleaching efficiency was obtained at a temperature of 100^{0}C. According to Berbesi (2006), bleaching temperature typically ranges from 90 – 125^{0}C. He also noted that oil viscosity decreases with increasing temperature resulting in better dispersion of particles, improved clay oil interactions, and flowability. James et al (2008) reported that the optimum bleaching temperature is specific for a particular adsorbent and oil which is between 100 – 120^{0}C for palm oil.

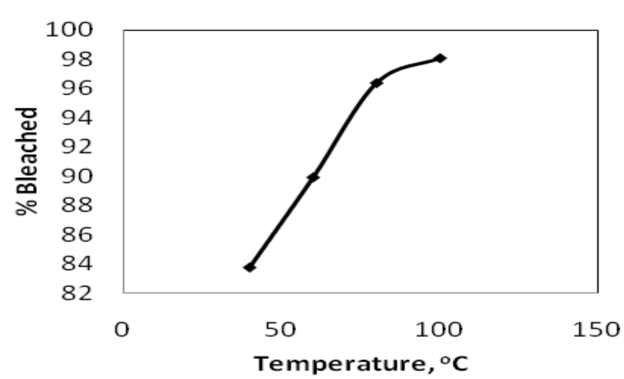

Fig. 2: Effect of temperature on the bleaching of palm oil

E. Effect of particle size on the bleaching of palm oil

The percentage bleached increased as the particle size decreased (Figure 3). The best bleaching efficiency was obtained using 150μm clay sample. As the clay particle size decreased, the rate of adsorption of the impurities increased, thus reducing the quantities of the impurities and subsequently increased bleaching of the palm oil.

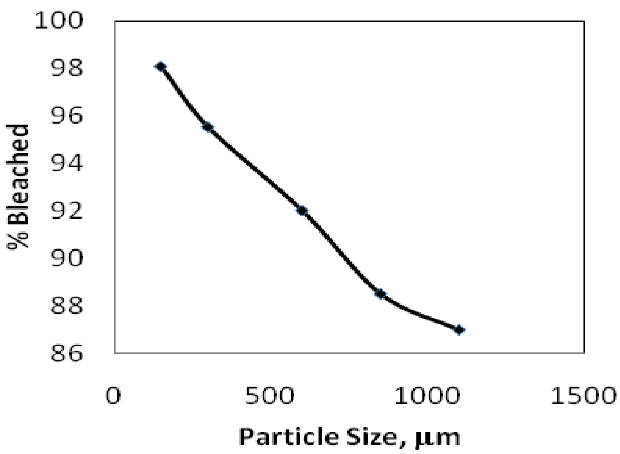

Fig. 3: Effect of particle size on the bleaching of palm oil

F. Effect of time on the bleaching of palm oil

Figure 4 shows that percentage bleached increased with increase in bleaching time. At 30 minutes, the highest bleaching efficiency was obtained which remained fairly constant thereafter. The result is in agreement with the report of Berbesi (2006) which stated that the contact time for effective bleaching typically ranges from 15 to 45 minutes, with 20 to 30 minutes being most common.

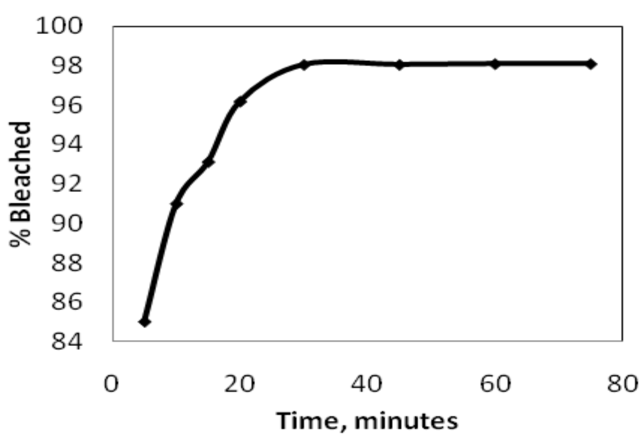

Fig. 4: Effect of time on the bleaching of palm oil

G. Freundlich and Langmuir Isotherms

Figure 5 shows the Freundlich isotherm. The slope of the plot, n was determined as 0.351 and K was evaluated as 1.479. The value of n depicts that the clay is a very good adsorbent. According to James et al (2008), when the value of n is below 0.5, it depicts that the clay is a very good adsorbent. Rossi et al (2003) stated that if the n is high, the adsorbent will be effective for removing the first portions of colour but less efficient for reaching highest bleaching degree. The value of K determines the decolourizing power or activity of the adsorbent for a specific solute (Topallar, 1998). The value of K shows that the clay has a high decolourizing power. Coefficient of determination, R^2 from the Freundlich model is 0.946.

From the plot of $X_e/(x/m)$ against X_e (Figure 6), a slope of 0.781 and intercept of 0.064 were determined, from where the values of 'a' and 'b' were evaluated as 15.625 and 12.203 respectively. The value of 'a' is a measure of the surface area of the clay. The high positive value of b indicates that the clay is good for the adsorption of carotene in the palm oil. The Freundlich isotherm is more applicable in this experiment because its value of R^2 is greater than R^2 value of 0.917 obtained for Langmuir Isotherm. This conforms to Rohani (2006) observation that Freundlich isotherm is more applicable to a liquid phase and Langmuir isotherm is more applicable to a gaseous phase.

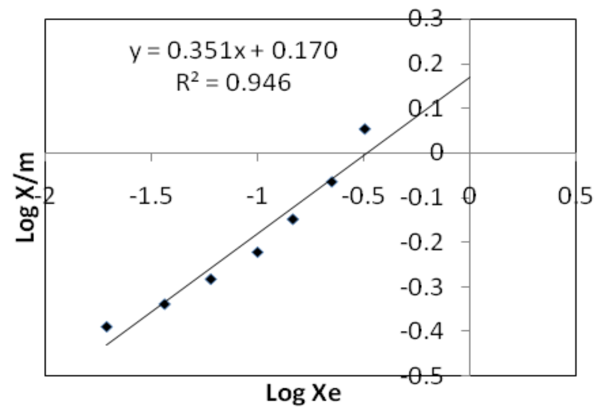

Fig. 5: Freudlich Isotherm for the bleaching process

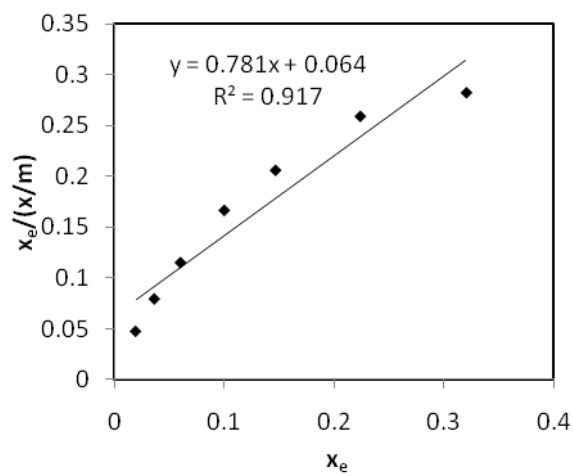

Fig. 6: Langmuir Isotherm for the Bleaching Process

H. Heat evolved during adsorption

The heat of adsorption is normally the heat evolved during the adsorption process. The negative value of the heat of adsorption (-35.62 KJ mol^{-1}) obtained from Figure 7 indicates that the adsorption process is an exothermic process. The high value of the heat evolved shows that chemisorption occured during the bleaching of palm oil. Topallar (1998) stated that when the heat of adsorption is greater than $20KJmol^{-1}$, it is a chemisorption process but when it is less than $20KJmol^{-1}$, it is a physical adsorption. This result is in agreement with that found by Christidis and Kosiari (2003) for the adsorption of B-Carotene from maize oil.

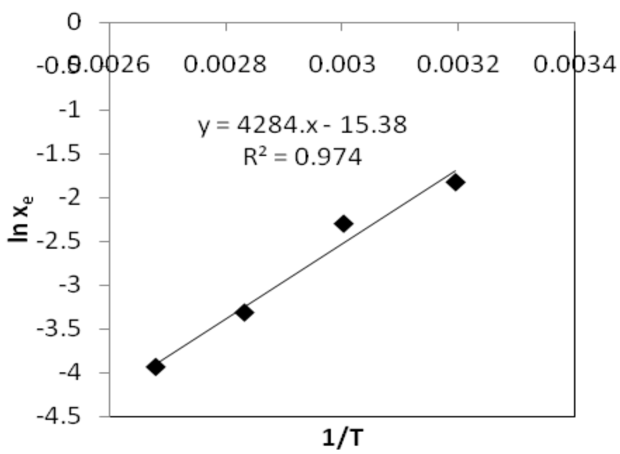

Fig. 7. A plot of lnX_e against 1/T

I. Rate constant

The rate constant (k) of 1.552 was obtained from the plot of ln A/Ao against $t^{0.5}$ as shown in Figure 8. The high value of K shows that the adsorption of the pigments of the palm oil is very rapid. Nde Aga et al. (2007) obtained rate constant values of 0.031, 0.072 and 0.199 at temperatures of 65, 80, and 90^0C respectively using an adsorbent activated with 1M Sulphuric acid.

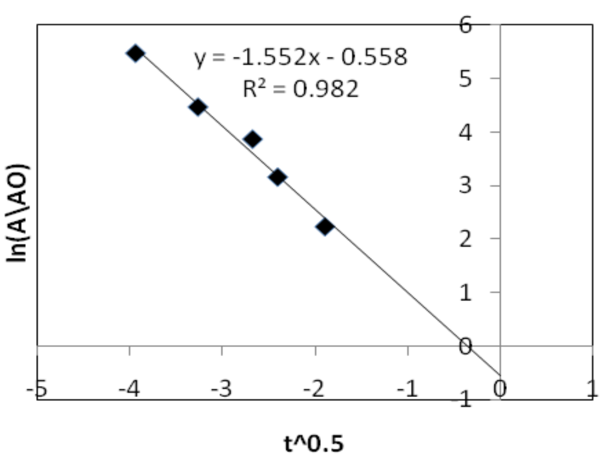

Fig. 8. A plot of In A/Ao against $t^{0.5}$

IV. CONCLUSION

The adsorption isotherms and kinetics of the bleaching of palm oil have been investigated. The effect of the variables such as temperature, time, dosage and particle size on the bleaching of palm oil was also studied. It was observed that the adsorption data conformed to Freundlich isotherm model. The heat evolved during adsorption was recorded as -$35.6kJmol^{-1}$ showing that the bleaching process was chemisorptions. As temperature, time and dosage increased the percentage bleached increased while the increase in particle size led to decrease in the percentage bleached.

REFERENCES

[1] Abdul-Azis, A. The Effect of CPO Quality Parameters (FFA, M & 1, IV, PV, AV, DOBI and colour) on the Refinery Production Efficiency. Proceedings of the 2000 National Seminar on palm oil Milling, Refining technology, Quality and Environment. July 3 – 4, Malaysia, 79 – 88,(2000).

[2] Achife, E. C and Tbemesi, J.A . Applicability of the Freundlich and Langmuir adsorption isotherms in the bleaching of rubber and melon seed oils. J. Am. Oil Chem. Soc; 66 (1989), 247 – 253.

[3] AFNOR (French Association of Norm). Fat Materials, Oleaginous grains and derivatives. Collection of French Norms. 2nd Edn., AFNOR, Paris (France)(1981),438.

[4] Basiron, Y. Palm oil, in Bailey's Industrial Oil and Fat Products, edited by Y.H. Hui, John Wiley & Sons, New York, 2 (1996), 271 – 373.

[5] Berbesi, R. Achieving Optimal Bleaching Performance. Oil Mill Gazetteer, 112 (2006) 1-5.

[6] Brimberg, U.I. Kinetics of bleaching of vegetable oils. J. Am. Oil chem.Soc., 59 (1982) 74 – 78.

[7] Choo, Y.M. Specialty Products: Carotenoids. Advances in oil palm Reaserch (Basiron, Y., Alani, BS and Chan, K. eds). Vol. II. MPOB, Bangi P., 1036 – 1060, (2000).

[8] Christidis, G.E. and Kosiari, S. Decolourization of vegetable oils: A study of the mechanism of adsorption of β-carotene by acidactivated bentonite form Cyprus. Clay Miner., 51 (2003), 327 – 333.

[9] Diaz, F. R. and Santos, P. Studies on the Acid Activation of Brazilian Smectite clays, Quim Nova, 24 (3) (2001), 345 – 353.

[10] Falaras, P., Lezou, F., Seiragakis,G. and Petrakis, D. Bleaching properties of alumina-pillared acid activated montmorillonite clays. Clay Miner., 48 (2000), 549 - 556.

[11] Foletto, E.L., Volzone, C. and Porto, L.M. Clarification of cotton seed oil: how structural properties of treated bentonites by acid affect bleaching efficiency. Latin American Applied Research. 36, (2006), 37 – 40.

[12] Goh, S.H., Choo, Y.M. and Ong, S.H. Mineral constituents of palm oils, J. Am. Oil Chem. Soc. 62 (1985), 237-240.

[13] James, O.O., Mesubi, M.A., Adekola, F.A., Odebunmi, E.O., Adekeye, J.I.D. and Bale, R.B. Bleaching performance of a Nigerian (Yola) Bentonite. Latin American Applied Research. 34 (2008), 45 – 49.

[14] Laidler, K.J. Chemical Kinetics, 3rd Edn., Pearson Education Publishers, India, (1987),230.

[15] Nde-Aga, B. J, Kamga, R. and Nguetnkam, J. P. Adsorption of palm oil carotene and free fatty acids onto acid activated Cameroonian clays. Journal of Applied Sciences. 7 (2007), 2462 – 2467.

[16] Njiribeakor, J.A. and Nwanya, L.N. Enhancing the Adsorptive performance of natural bleaching earths from limestone/clay mixture. Journal of the Chemical Society of Nigeria, 25 (2000), 54.

[17] Puah, C. W., Choo Y. M., Ma, A. N. and Chuah, C. Deguming and Bleaching: Effect on selected Constituents of palm oil. Journal of Oil Palm Research 16 (2) (2004), 57 – 63.

[18] Rohani, B M. Z. Process Design of Degumming and Bleaching of palm oil. Thesis. Ministry of Science, Technology and Innovation, Malaysia. 12 – 69, (2006).

[19] Rossi M., Gia naza M., Alan Presc., Stanga F. The Role of Bleaching clays and synthetic silica in palm oil physical Refining. Food Chemistry, 82 (2003), 291 – 296.

[20] Salawudeen, T.O., Dada, E.O. and Alagbe, S.O.. Performance Evaluation of Acid Treated Clays for palm Oil Bleaching. Journal of Engineering and Applied Sciences 2(11) (2007), 1677 – 1680.

[21] Topallar, H. The Adsorption Isotherms of the bleaching of sunflower-seed oil. Tr. J. of Chemistry, 22 (1998), 143 – 148.

[22] Vicente – Rodriquez, M.A., M. Suarez, M., de Dios Lopes-Gonzalez, J. and Banares –Munoz, M. A. Characterization, surface area and porosity analyses of the solids obtained by acid leaching of a Saponite. Langmuir, 12 (1996), 566 – 572.