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

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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\textsuperscript{-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 500-700mg/l/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\textsuperscript{-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 conform 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 Rodriguez 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°C 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°C. The dried activated clay sample was passed through 1100μm sieve, labeled and stored in a 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°C on a magnetic hot plate. 0.6g activated clay sample was added to the hot oil. The temperature was maintained at 100°C 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°C. 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:

\[ \% \text{ Bleached} = \frac{A_0 - A_t}{A_0} \times 100 \text{ ------ (1)} \]

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

E. Adsorption Isotherms

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

\[ \frac{x}{m} = Kx^n \text{--------------------------- (2)} \]

Taking log of both sides gives

\[ \log \frac{x}{m} = \log K + n \log x_e \text{ ----------- (3)} \]

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 \( \log K \) as intercept. Langmuir adsorption equation is given as equation 4:

\[ \frac{X_e}{X} = \frac{1}{a} + \frac{b}{a} X_e \text{ ------------------ (4)} \]

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, \( \Delta H_a \) = heat of adsorption, \( R \) = gas constant (8.314J/molK), \( T \) = temperature and \( C \) = integration constant. From the plot of \( \ln X_e \) against \( 1/T \), \( \Delta H_a \) is evaluated.

G. Determination of rate constant

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

\[ \ln \left( \frac{C}{C_0} \right) = -kt^{0.5} \text{ --------------- (6)} \]

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

\[ \ln \left( \frac{A}{A_0} \right) = -k(t)^{0.5} \text{ --------------- (7)} \]

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 (SiO₂ = 52.70%) which suggests its high potential for the production of floor tiles. The result also suggests the existence of calcium montmorittonite since the silica content is within the range of 50 to 70% (Foleto 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 fluorescence

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>16.6</td>
</tr>
<tr>
<td>SiO₂</td>
<td>52.7</td>
</tr>
<tr>
<td>CaO</td>
<td>2.06</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2.53</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>19.53</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>0.16</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.10</td>
</tr>
<tr>
<td>MnO</td>
<td>0.29</td>
</tr>
<tr>
<td>NiO</td>
<td>1.45</td>
</tr>
<tr>
<td>CuO</td>
<td>0.08</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.13</td>
</tr>
</tbody>
</table>

### Table 2: AAS Characterization of Raw Nteje Clay

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>23.6340</td>
</tr>
<tr>
<td>Al</td>
<td>35.4839</td>
</tr>
<tr>
<td>Na</td>
<td>11.5033</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0264</td>
</tr>
<tr>
<td>K</td>
<td>0.0163</td>
</tr>
<tr>
<td>Zn</td>
<td>0.0190</td>
</tr>
<tr>
<td>Ca</td>
<td>0.1214</td>
</tr>
<tr>
<td>Mg</td>
<td>0.1265</td>
</tr>
<tr>
<td>Mn</td>
<td>0.2204</td>
</tr>
<tr>
<td>Ni</td>
<td>0.1059</td>
</tr>
</tbody>
</table>

### 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.

### 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°C. According to Berbesi (2006), bleaching temperature typically ranges from 90 – 125°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°C for 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.

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.

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 0.664 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.

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 occurred
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.

![Graph](image)

**Fig. 7.** A plot of lnX against 1/T

**I. Rate constant**

The rate constant (k) of 1.552 was obtained from the plot of ln A/Ao against t⁰.⁵ 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°C respectively using an adsorbent activated with 1M Sulphuric acid.

![Graph](image)

**Fig. 8.** A plot of ln A/Ao against t⁰.⁵

**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**


