

Full Length Research Paper

## Performance evaluation of local clays from northern Nigeria for the refining of palm oil

Mustapha S. I.<sup>1\*</sup>, Mohammed A. A<sup>2</sup>., Zakari A. Y<sup>1</sup>. and Mohammed H. A<sup>1</sup>.

<sup>1</sup>Department of Chemical Engineering, Ahmadu Bello University, Zaria, Nigeria.

<sup>2</sup>Department of Chemical Engineering, Federal University of Technology Minna, Nigeria.

Accepted 15 May, 2013

The effectiveness of adsorbents (unactivated and acid activated) developed from local raw materials - clay and diatomaceous earth samples - sourced from various geographical locations in northern Nigeria for use in the adsorptive bleaching of palm oil was studied. Two acids namely hydrochloric and sulphuric acids of varying strengths 20, 30 and 45% were used for the activation. A batch adsorption process of operation was employed in the bleaching step. Results obtained in which the performance of these locally prepared adsorbents were expressed in terms of percentage colour reductions showed that, the acid-activated samples were more effective in the adsorptive bleaching of palm oil. As much as 96.5 and 98% colour reductions were attained in the first and second sequences of the bleaching steps respectively. This performance compares very well with those of well-known commercial adsorbents (fuller's earth and activated carbon).

**Key words:** Adsorptive bleaching, acid-activated clay, palm oil refining, degumming, neutralization.

### INTRODUCTION

A number of attempts have been made in the refining of palm oil using locally sourced raw materials as adsorbents (Salawudeen et al., 2007; Nwabanne and Ekwu, 2013; Regina and Okechukwu, 2012; Usman et al., 2012). The aim was to develop good local substitutes for the commercially imported adsorbent (fuller's earth). The effectiveness of these locally prepared adsorbents is expressed as a measure of percentage colour reduction of the bleached palm oil. A good number of these adsorbents have been found effective in the adsorptive bleaching of palm oil.

Hymore and Iyayi (1989) investigated the effectiveness of local clays sourced from various locations of the old Bendel State (now Edo and Delta States) and applied them in the adsorptive bleaching of palm oil. The effectiveness of these local clays was found to have improved when two of them were selected and activated

using acids. A very high percentage colour reduction that compares favourably with those of commercial adsorbents was attained. Danjuma (2001) also investigated the performance of saw dust and rice husk prepared as adsorbents by activation of their carbonaceous materials with zinc chloride. These adsorbents were also found effective when applied in the adsorptive bleaching of palm oil and a good percentage colour reduction was also obtained. Ukpor clay from Enugu State was used by Okeke (1990) for the adsorption bleaching of sheanut oil at 140°C bleaching temperature with a good percentage colour reduction achieved. Oboh et al. (1987) investigated the study of activated bleaching power of some selected Nigerian clays which include clays found in Shagamu and Ewekoro, both in Ogun State; Calabar in Cross River State and Nsukka, Enugu State, with a view to initiating

\*Corresponding author. E-mail: [mushery2001@yahoo.com](mailto:mushery2001@yahoo.com). Tel: 080-6-718-6215.

the utilization for bleaching earth manufacture and reasonable percentage colour reduction was achieved (Salawudeen et al., 2007).

The increasing use of palm oil for the manufacture of oleo chemicals and edible products (for example, cosmetics, lubricants, margarine, shortenings, and cooking oils) along with the recent ban placed on the importation of bentonites (fuller earth) and vegetable oils by the Federal Government of Nigeria poses a great challenge for the provision of high quality local substitutes. There is therefore, the need to continuously find new ways and means of improving the quality of palm oil by developing low cost adsorbents that can be used in the adsorptive bleaching of palm oil resulting in low refining loss and avoiding unwanted by-products.

In this work however, local raw materials - clays and diatomaceous earth – have been sourced from a wide-range of varying geographical locations in northern Nigeria and have been prepared as natural and acid-activated adsorbents to be applied in the adsorptive bleaching of palm oil. These raw materials will be analyzed with the aim of determining those that will bleach well in their natural form and those that are activable, and also study and compare their effectiveness as adsorbents in the bleaching of palm oil.

## MATERIALS AND METHODS

The clays and diatomaceous earth samples were obtained from the central laboratory of the Federal Geological Surveys Barnawa, Kaduna South, Kaduna State. They were sourced from a wide range of varying geographical locations. Clay sample C<sub>1</sub> was obtained from Rido village (Kaduna State); Clay sample C<sub>2</sub> was obtained from Gambori Ngala (Borno State); Clay sample C<sub>3</sub> was obtained from Darazo (Bauchi State); Clay sample C<sub>4</sub> was obtained from Kaoje (Kebbi State) and Clay sample B<sub>1</sub> – diatomaceous earth was obtained from Fularaba (Yola State). The crude palm oil was purchased from the Kaduna central market, Kaduna State. Hydrochloric and Sulphuric acid used for activation were of analytical grade.

### Purification of samples

Each of the clay samples was ground and then mixed with water to remove impurities. The mixture was stirred and the slurry was decanted leaving behind impurities such as sand and stones. The slurry was allowed to settle, the water was decanted off and the clay was dried.

### Activation of samples

For preparation of the activated clays, varying concentrations (20, 30 and 45%) of Hydrochloric and Sulphuric acids were used. 200 g of the purified sample was placed in a 500 mL beaker and pasty slurry of it was made with distilled water. Activation was carried out by adding the acid of a known concentration to the clay slurry and the mixture was boiled for 90 min at a regulated temperature of 100°C. After slow cooling, the slurry was filtered via a Buchner funnel to separate clay and acid. The filtered clay was thoroughly washed with distilled water to remove the residual acid. The

samples were then dried in an oven until the weight of the clay remained constant. The lumps of the prepared clays were ground using a mortar and pestle, sieved to 240 micrometer and stored for further use in the bleaching process. Each sample was thus subjected to 6 different conditions of activation.

### Refining of palm oil

Crude palm oil was refined with the aim of removing the free fatty acids, phosphatides, gummy materials, and also to improve its colour. The steps taken are; degumming, neutralization, and adsorptive bleaching.

### Degumming

The crude palm oil was degummed by adding hot water to the oil, stirring the mixture and removing the aqueous layer. The oil and water mixture was then allowed to settle after which the water was drain off via a separating funnel.

### Neutralization

The degummed oil was neutralized by adding an alkali (sodium hydroxide solution). The mixture was then stirred and then heated at a regulated temperature of 75°C for 20 min to break the emulsions formed. Two layers were formed after centrifuging, oil and soap. The soap stock was then filtered off. Neutralization of the free fatty acid (FFA) from the oil was carried out using varying strengths (0.5, 1.0, 1.5, 1.7, 2.0, and 3.0 M) of sodium hydroxide solution with the aim of determining the effect of alkali concentration on FFA, yield of neutral oil, and ease of separation. These varying concentrations were each, titrated against a known weight of oil (50 g). The volumes of alkali solution (NaOH) consumed in the neutralization process were in each case determined.

### Adsorptive bleaching

Adsorptive bleaching was achieved by charging 200 g per batch of the degummed, neutralized oil along with 4 g of sized activated clay into a 500 mL beaker. The feed charged was heated and stirred continuously on a hot plate regulated at a temperature of 130 to 140°C for 30 min. At the completion of the time, the mixture was filtered through a dry filter paper before measuring the absorbance. The bleaching efficiency of the activated clay samples was then determined by measuring the colour of the bleached oil using a Jenway colorimeter at an excitation wavelength of 710 nm. In this work, the efficiency of the adsorbents used have been expressed in terms of absorbance of light passing through the medium (crude and bleached palm oil), which are then converted into percentage colour reductions of the bleached oil, thus,

$$\text{Percentage colour reduction} = \frac{ABS_0 - ABS_1}{ABS_0} \times 100 \quad (1)$$

Where,

ABS<sub>0</sub> = absorbance of crude palm oil

ABS<sub>1</sub> = Absorbance of bleached palm oil

To study the effect of process variables on the bleaching efficiency of the adsorbents, the above experimental procedure was repeated at different adsorbent dosage (2, 4, 6, 8 and 10%); operating temperatures (100, 110, 120, 130, 140, 150, 160 and 170°C) and bleaching time (10, 20, 30, 40, 50 and 60 min). The effect of

activation parameters on the bleaching efficiency of the clay samples was investigated by using the samples activated with different acid concentration bleach palm oil.

### Solution adsorption isotherm

The Freundlich isotherm equation has been widely applied to adsorptions from dilute solutions. The equation was derived by assuming an exponential distribution of adsorption potential energies.

The equation takes the form,

$$x/m = kC^n \quad (2)$$

Where  $x$  is the amount of solute adsorbed by  $m$  grams of the adsorbents at concentration  $C$  in the solution.  $k$  and  $n$  are constants.

Expressing equation 2 in logarithmic form,

$$\log x/m = n \log C + \log k \quad (3)$$

A plot of  $\log x/m$  against  $\log C$  gives a straight line known as the adsorption isotherm plot having an intercept  $\log k$  and slope  $n$ .

### Clay characterization

The percentage composition of inorganic compound like  $Al_2O_3$ ,  $SiO_2$ ,  $TiO_2$ ,  $Fe_2O_3$ ,  $MgO$ ,  $CaO$ ,  $K_2O$ ,  $Na_2O$ ,  $MnO$ ,  $Pb_2O_5$  and  $H_2O^+$  were determined using gravimetry and colorimetry method.

## RESULTS AND DISCUSSION

### Characterization

Table 1 shows the results of the analysis of mineralogy content of the clay and diatomaceous earth samples investigated. Result shows the presence of  $SiO_2$ ,  $TiO_2$ ,  $Al_2O_3$ ,  $MgO$ ,  $CaO$ ,  $K_2O$ ,  $Na_2O$ ,  $Pb_2O_5$  and  $H_2O$  in varying amount. However no  $MnO$  was observed except in clay sample  $C_1$ , where it is found present in trace amount.

### Neutralization

Table 2 shows the result of the yield of neutral oil when crude palm oil was titrated against by varying concentrations of sodium hydroxide solution. The result shows an upward and then downward trend in the yield of the neutral oil as the concentration of sodium hydroxide solution used increases.

It was observed that the volume of alkali consumed was decreasing with increase in concentration from 0.5 to 3.0 M. Percentage colour reduction was also observed for all the neutralization. Colour reduction has been known to improve with increasing strength of alkali used in neutralization (Hamilton and Bhatti, 1980). A balance was however, sought between the strength of alkali (concentration) and the yield of neutral oil. The yields of

neutral oil were observed to be lower at higher concentrations of 2.0 and 3.0 M. This could be attributed to the fact that, most of the neutral oil as well as the FFA are converted to "foot" (soap stock) as a result of increase reactivity of sodium Hydroxide solution. This explains why FFA of neutralized oil at higher concentrations tends to be low. At the lower concentrations used 0.5 and 1.0 M, large volumes of alkali was consumed in the process. This causes the formation of emulsions between the soap stock and the neutral oil resulting in a significant loss of neutral oil. A concentration of 1.7 M Sodium Hydroxide solution used was observed to have the highest yield of neutral oil of 85% as well as a relatively low FFA of 3.0%. This concentration was therefore adopted for use in this work with the aim of establishing a balance between yield of neutral oil with low FFA and alkali (NaOH) concentration.

### Effect of bleaching time on adsorption

The effect of contact bleaching time for both unactivated and acid-activated samples was investigated as shown in Figure 1. The percentage colour reduction was observed to have improved from 10 to 50 min while bleaching with un-activated samples. No further improvement in percentage colour reduction was observed after this time. However, shorter bleaching times were observed while using acid-activated samples as adsorbents. The highest bleaching time established for both hydrochloric and sulphuric acid-activated samples were 30 and 40 min respectively. No further improvement in percentage colour reduction of palm oil was observed after these contact times. This 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 min.

Establishing optimum bleaching time is therefore important as prolonged bleaching time may lead to colour deterioration as was noticed with some of the acid-activated samples. Hymore and Iyayi (1989) made similar observation while bleaching palm oil using local clays and prepared as adsorbents.

### Effect of adsorbent dosage

The effect of adsorbent dose expressed in percentage weight of adsorbent dose to weight of oil was also investigated with the aim of establishing the most favorable dose of adsorbent to oil. The results clearly indicate that the bleaching efficiency of both Hydrochloric and Sulphuric acid-activated samples (AHC<sub>1</sub>20, AHC<sub>2</sub>20, ASC<sub>3</sub>30, ASC<sub>4</sub>45) increases to an optimum value at adsorbent dosage of 4% above which further increase in adsorbent dosage has no significant effect on it. The Percentage colour reduction increases to an optimum value for the un-activated samples (UC<sub>2</sub> and UC<sub>4</sub>) at adsorbent dosage of 6%. The effect is shown in Figure 2.

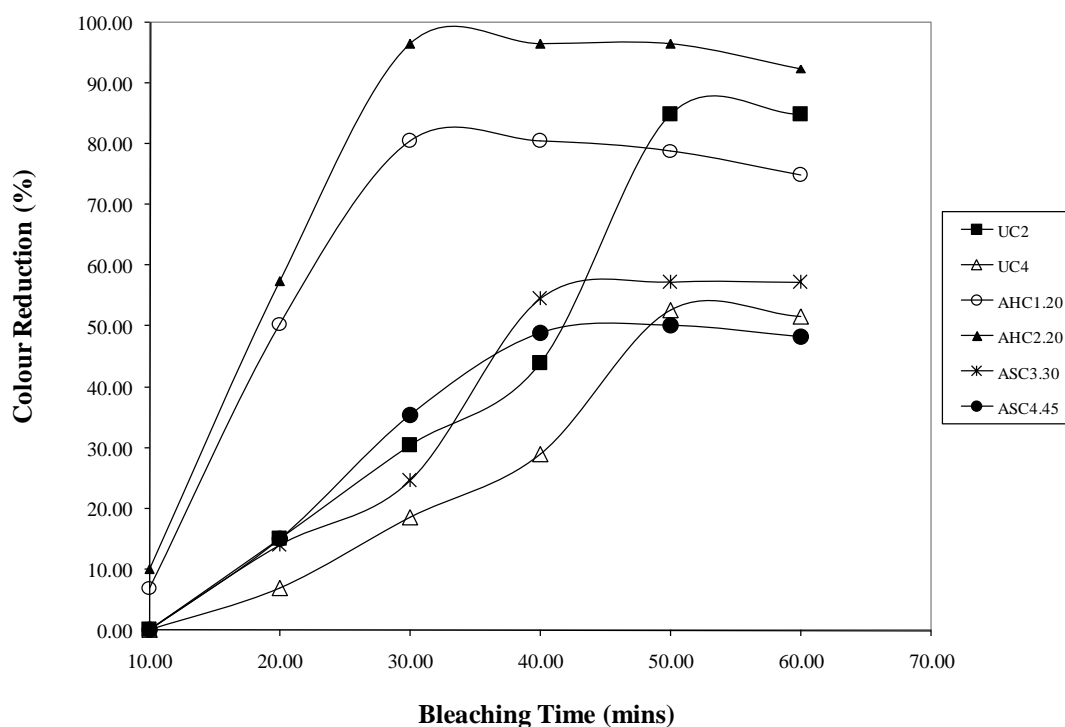
**Table 1.** Mineralogy content analysis of clays and diatomaceous earth samples.

Compound	% Composition				
	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	B <sub>1</sub>
SiO <sub>2</sub>	50.49	58.65	49.91	54.16	87.15
TiO <sub>2</sub>	0.04	1.42	0.31	0.40	0.22
Al <sub>2</sub> O <sub>3</sub>	28.71	22.34	32.99	29.11	3.91
Fe <sub>2</sub> O <sub>3</sub>	3.55	2.41	1.49	2.37	1.20
MgO	0.68	0.63	0.80	0.72	0.46
CaO	0.23	1.19	0.46	0.29	0.52
K <sub>2</sub> O	3.14	0.66	0.52	0.64	0.86
Na <sub>2</sub> O	1.87	0.64	0.32	0.42	0.59
MnO	0.02	-	-	-	-
P <sub>2</sub> O <sub>5</sub>	0.31	0.20	0.62	0.51	0.31
H <sub>2</sub> O <sup>+</sup>	10.71	11.84	12.49	11.36	4.76

**Table 2.** Comparisons of the yield of neutral oil using varying concentration of sodium hydroxide solution.

Concentration of NaOH (M)	Volume of NaOH consumed cm <sup>3</sup> /g oil	FFA%	Yield of neutral oil (%)
0.50	0.62	3.50	62.00
1.00	0.58	3.25	65.00
1.50	0.57	3.20	70.00
1.70	0.50	3.00	85.00
2.00	0.45	2.50	58.00
3.00	0.39	2.20	39.00

FFA- free fatty acid.

**Figure 1.** Variation of colour with bleaching time.

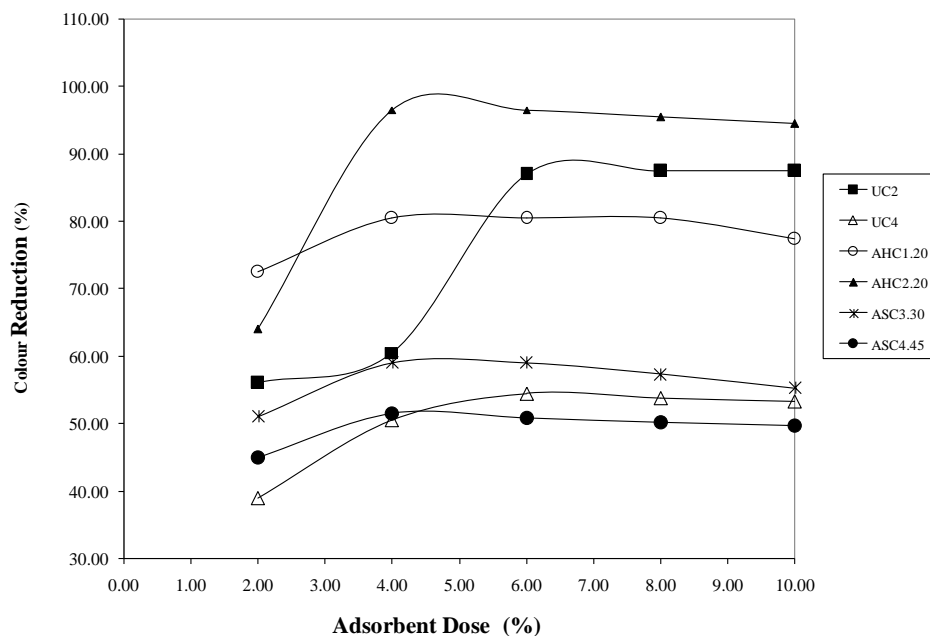


Figure 2. Variation of colour with adsorbent dose to oil of some selected adsorbent.

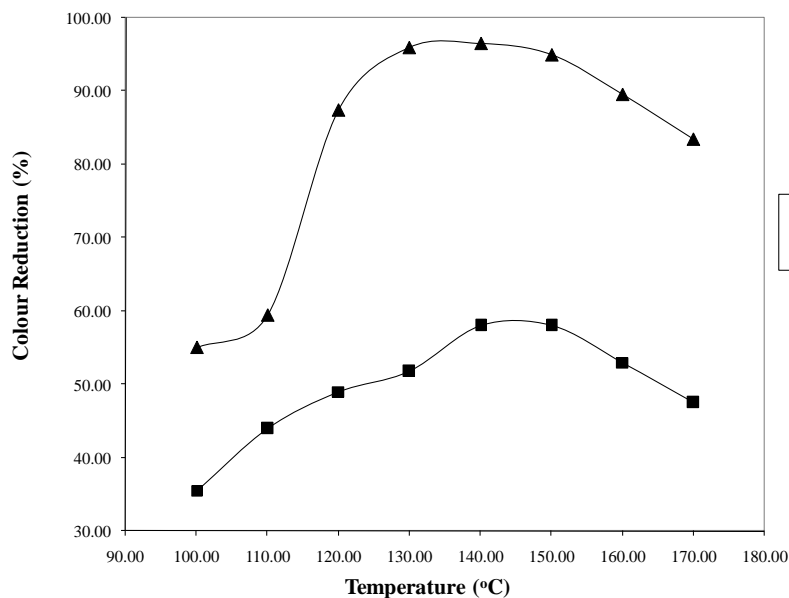


Figure 3. Variation of colour with operating temperature.

Further increase in dose of adsorbents does not seem to improve percentage colour reduction. This could be explained by the fact adsorption equilibrium has been reached between the adsorbent/oil mixtures, thereby, preventing further colour removal by the excess adsorbent dosage. Diaz and Santos (2001) stated that darker oils like palm oil require as much as 2 to 4% or more to meet final colour requirements.

### Effect of temperature on adsorption

It can be seen from Figure 3 that the percentage colour reduction was found to have increased with increasing temperature from 100 to 140°C for the acid – activated clay sample (AHC<sub>2</sub>20). The bleaching efficiency increased with increase in temperature until it reaches a maximum (140°C), then it starts to decrease. Berbesi

**Table 3.** Performance of unactivated clay samples in the bleaching of palm oil.

Adsorbent type	ABS <sub>1</sub>	Colour reduction (%)
UC <sub>1</sub>	1.27	36.56
UC <sub>2</sub>	0.19	90.59
UC <sub>3</sub>	1.35	32.23
UC <sub>4</sub>	0.84	58.85
UB <sub>1</sub>	1.36	32.00

UC- Unactivated clay samples C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub>. UB- Unactivated diatomaceous earth sample B<sub>1</sub>. ABS<sub>1</sub>- Absorbance of bleached oil.

**Table 4.** Performance of acid-activated clay samples C<sub>1</sub> in the bleaching of palm oil.

Adsorbent type	Acid strength	ABS <sub>1</sub>	Colour reduction (%)
AHC <sub>1</sub>	20	0.39	80.29
AHC <sub>1</sub>	30	0.44	78.00
AHC <sub>1</sub>	45	0.67	66.67
ASC <sub>1</sub>	20	0.59	70.49
ASC <sub>1</sub>	30	0.48	75.99
ASC <sub>1</sub>	45	0.82	58.82

AHC- Hydrochloric Acid – Activated Clay Sample C<sub>1</sub>. ASC- Sulphuric Acid – Activated Clay Sample C<sub>1</sub>. ABS<sub>1</sub>- Absorbance of bleached oil.

**Table 5.** Performance of acid-activated clay samples C<sub>2</sub> in the bleaching of palm oil.

Adsorbent type	Acid strength	ABS <sub>1</sub>	Colour reduction (%)
AHC <sub>2</sub>	20	0.07	96.5
AHC <sub>2</sub>	30	0.44	77.89
AHC <sub>2</sub>	45	0.55	72.66
ASC <sub>2</sub>	20	0.57	71.74
ASC <sub>2</sub>	30	0.72	63.88
ASC <sub>2</sub>	45	0.72	63.98

AHC- Hydrochloric Acid – Activated Clay Sample C<sub>2</sub>. ASC- Sulphuric Acid – Activated Clay Sample C<sub>2</sub>. ABS<sub>1</sub>- Absorbance of bleached oil.

(2006) noted that oil viscosity decreases with increasing temperature resulting in better dispersion of particles, improved clay oil interactions and flowability. The highest bleaching efficiency was obtained at a temperature of 150°C for the un-activated sample (UC<sub>4</sub>). Further increase in temperature tends to darken the colour of the bleached oil.

The most favourable temperatures established for the adsorptive bleaching of palm oil using acid-activated and unactivated samples used in this work were 140 and 150°C respectively. Also, it can be deduce from Figure 3

that the acid activated clay show a much higher bleaching capacity when compared to the unactivated sample. Regina and Okechukwu (2012) reported that acid activation of clay usually cause some modifications in the structure of the clays. During acid activation, initially interlayer cations are replaced with H<sup>+</sup> ions followed by partial destruction of aluminum octahedral sheets with subsequent dissolution of structural cations. The increase in the surface area from unactivated to activated sample is related to the elimination of the exchangeable cations, de-lamination of clays, and the generation of micro-porosity during the activation process (Dias et al., 2003).

### Performance of adsorbents samples in the bleaching of palm oil

Table 3 shows the results of the performance of unactivated clay and diatomaceous earth samples applied in the bleaching of palm oil as investigated.

Adsorptive bleaching of the neutralized palm oil was effected using unactivated samples of clays labelled UC<sub>1</sub>, UC<sub>2</sub>, UC<sub>3</sub>, UC<sub>4</sub>, and a diatomaceous earth sample UB<sub>1</sub>. The effectiveness of this prepared adsorbents were found to be low and colour reduction expressed in percentage ranges from 32 to 59%, except for the sample labelled UC<sub>2</sub> in which as high as 90% colour reduction was attained. Diatomaceous earth sample record the lowest colour reduction of 32%. This may be attributed to the fact that though diatomaceous earths have large surface areas, they are found to exhibit low adsorptive capacity and as such are more effective when used as filter aids (Stanley et al., 1975).

Tables 4 to 8 show the results of performance of acid-activated clay and diatomaceous earth samples applied in the bleaching of palm oil. The results show a general improvement in the performance of these sample adsorbents except for the acid-activated diatomaceous earth sample in which the performance was low. A general improvement in the performance of the samples was observed. Percentage colour reduction was improved from as low as 32% (un-activated adsorbent) to as high as 96.5% (acid-activated adsorbents) as presented in Tables 4 to 8.

The samples (4 clay types and diatomaceous earth) were activated using Hydrochloric acid and sulphuric acids of varying strengths (20, 30, 45%). Each sample was subjected to 6 different conditions of activation. Analysis of results presented in these tables also shows that, effective overall performances of Hydrochloric acid-activated samples are higher than that of sulphuric acid-activated samples. Same conditions applied to samples activated using dilute acids of 20% strength than those activated using concentrated acids of 45% strength. The improved performance as found in the acid-activated samples may be attributed to the improved physical characteristics such as pore size, particle porosity and

**Table 6.** Performance of acid-activated clay samples C<sub>3</sub> in the bleaching of palm oil.

Adsorbent type	Acid strength	ABS <sub>1</sub>	Colour reduction (%)
AHC <sub>3</sub>	20	0.42	79.22
AHC <sub>3</sub>	30	0.82	58.85
AHC <sub>3</sub>	45	0.89	55.44
ASC <sub>3</sub>	20	0.75	62.38
ASC <sub>3</sub>	30	0.79	60.06
ASC <sub>3</sub>	45	0.37	31.72

AHC- Hydrochloric Acid – Activated Clay Sample C<sub>3</sub>. ASC- Sulphuric Acid – Activated Clay Sample C<sub>3</sub>. ABS<sub>1</sub>- Absorbance of bleached oil.

**Table 7.** Performance of acid-activated clay samples C<sub>4</sub> in the bleaching of palm oil.

Adsorbent type	Acid strength	ABS <sub>1</sub>	Colour reduction (%)
AHC <sub>4</sub>	20	0.24	88.22
AHC <sub>4</sub>	30	0.46	77.20
AHC <sub>4</sub>	45	0.58	70.88
ASC <sub>4</sub>	20	0.11	94.75
ASC <sub>4</sub>	30	0.61	69.48
ASC <sub>4</sub>	45	0.96	31.72

AHC- Hydrochloric Acid – Activated clay sample C<sub>4</sub>. ASC- Sulphuric Acid – Activated clay sample C<sub>4</sub>. ABS<sub>1</sub>- Absorbance of bleached oil.

**Table 8.** Performance of acid-activated diatomaceous earth samples B<sub>1</sub> in the bleaching of palm oil.

Adsorbent type	Acid strength	ABS <sub>1</sub>	Colour reduction (%)
AHB <sub>1</sub>	20	1.10	45.00
AHB <sub>1</sub>	30	1.10	45.00
AHB <sub>1</sub>	45	1.20	40.20
ASB <sub>1</sub>	20	1.16	42.10
ASB <sub>1</sub>	30	1.24	38.10
ASB <sub>1</sub>	45	1.30	35.00

AHB- Hydrochloric acid – Activated diatomaceous earth sample B<sub>1</sub>. ABS<sub>1</sub>- Absorbance of bleached oil. ASB- Sulphuric Acid – Activated diatomaceous earth sample B<sub>1</sub>.

increase surface area for adsorption as a result of leaching out of organic matters from the samples (Regina and Okechukwu, 2012). These same observations were made by Salawudeen et al. (2007) while evaluating the effectiveness of acid treated clays for palm oil bleaching. Proctor and Palaniappan (1989) and Brace (1973) attributed the high adsorptive power of HCl activated clays to the complete removal of aluminium, magnesium

and calcium ions within the crystal of the clay. Based on these explanations, it may be inferred that impurities such as Fe<sub>2</sub>O<sub>3</sub>, CaO and MgO e.t.c that cover part of the active sites are washed away by acid activation and the number of active site available for adsorption increased (Salawudeen et al., 2007).

The performance of the best acid-activated local clay prepared as adsorbent was compared with those of some well known adsorbents in the oil refining industry; fuller's earth and a mixture of fuller's earth with activated carbon as presented in Table 10.

### Adsorption isotherm

The Freundlich isotherm coefficients were determined by plotting log x/m against log C and the results are shown in Table 9. The Freundlich model is used to estimate the adsorption affinity of the sorbents towards the adsorbate (Jimoh et al., 2011). The constants k and n indicate the adsorption capacity and the adsorption intensity. The linearity of the plot showed the representative nature of adsorption on the adsorbents.

From the solution adsorption isotherm plots, the amount of colour pigments adsorbed was found to be proportional to change in concentration of solute in the solution as measured before and after adsorption has occurred. 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. In view of these therefore mentioned points, an evaluation of the constants k and n as presented in Table 9 indicates that, the activated sample (AHC<sub>2</sub>20) is the most effective adsorbent in the adsorptive bleaching of palm oil. Freundlich isotherm model adequately described the adsorption data for all the clay samples investigated with regression coefficient values greater than 0.80. The same conclusion was reported by Nwabanne and Ekwu (2013). This conforms to Rohani (2006) observation that Freundlich isotherm is more applicable to a liquid phase (Figure 4).

Percentage colour reductions of 97 and 98% were obtained with fuller's earth and a mixture of fuller's earth with activated carbon respectively. The 96.5% colour reductions obtained with the best activated local clay compares favourably with the results obtained from the commercial adsorbents. In addition to this, an improved percentage colour reduction was further obtained when the filtered bleached oil was vigorously agitated with a fresh batch of 2% adsorbent to oil dose of the acid-activated clay for a period of 5 min, at a temperature of

**Table 9.** Evaluated value of k and n from the solution adsorption isotherm plots.

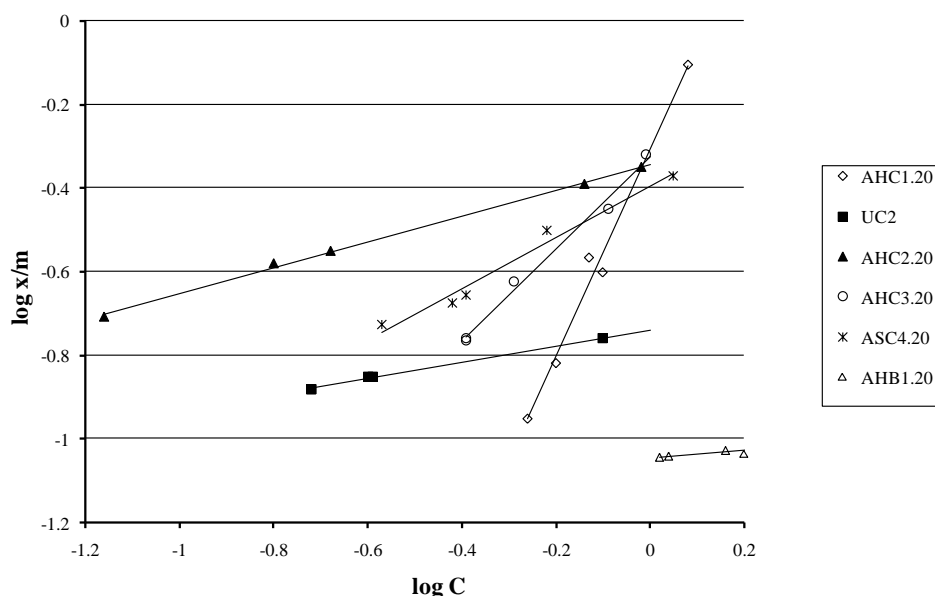
Adsorption type	Equation of graph	n	k	R <sup>2</sup>
UC <sub>2</sub>	$\log x/m = 0.191\log C - 0.739$	0.191	0.182	0.995
AHC <sub>1</sub> 20	$\log x/m = 2.484\log C - 0.305$	2.484	0.495	0.984
AHC <sub>2</sub> 20	$\log x/m = 0.308\log C - 0.343$	0.308	0.454	0.998
AHC <sub>3</sub> 20	$\log x/m = 1.108\log C - 0.324$	1.108	0.474	0.990
ASC <sub>4</sub> 20	$\log x/m = 0.613\log C - 0.395$	0.613	0.403	0.973
AHB <sub>1</sub> 20	$\log x/m = 0.088\log C - 1.045$	0.088	0.090	0.802

UC- Unactivated Clay Samples C<sub>2</sub>. AHC- Hydrochloric acid – Activated clay sample C<sub>1</sub>, C<sub>2</sub>, and C<sub>3</sub>. ASC- Sulphuric acid – Activated clay sample C<sub>4</sub>. AHB- Hydrochloric Acid – Activated diatomaceous earth sample B<sub>1</sub>.

**Table 10.** Comparison of the performance of the best refined palm oil with those of commercial adsorbents.

Adsorbent type	ABS <sub>1</sub>	Colour reduction (%)
AHC <sub>2</sub> 20	0.07	96.50
Fuller earth	0.06	97.50
Fuller earth + Activated carbon	0.04	98.00

AHC- Hydrochloric acid – Activated clay sample C<sub>2</sub>; ABS<sub>1</sub>- Absorbance of bleached oil.



**Figure 4.** Freundlich adsorption isotherm plot of some selected adsorbents.

140°C. A much clearer oil of 98% colour reduction was thus obtained.

**Conclusion**

The use of low cost adsorbents developed from local raw materials-clays and diatomaceous earth-for use in the adsorptive bleaching of palm oil have been studied. The

results indicate the great potential of some local clays (prepared as adsorbents) in the removal of colour pigments from palm oil. The percentage colour reduction of 98% achieved during the bleaching step competes with those of the commercial adsorbents-fuller’s earth and a combination of fuller’s earth with activated carbon used.

The effective overall performance of hydrochloric acid-activated samples was found higher than those of sulphuric acid-activated samples. Also, the effective



overall performance of samples activated with dilute acids was found higher than those activated with concentrated acids.

The various  $k$  and  $n$  values evaluated from the solution adsorption isotherm plots using Freundlich equations shows that the acid-activated samples were very effective in the adsorptive bleaching of palm oil.

## REFERENCES

- Berbesi R (2006). Achieving Optimal Bleaching Performance. *Oil Mill Gazetteer* 112:1-5
- Brace B (1973). Vegetable Oil Processing, Bleaching and Deodorization Process, pp. 249-250.
- Danjuma MN (2001). Performance of locally prepared adsorbent. Proceedings of National Engineering Conference of the College of Engineering, Kaduna Polytechnic.
- Dias MI, Suarez BM, Prates S, Martin JM (2003). Characterization and acid activation of Portuguese special clay. *Appl. Clay Sci.* 18:537-549.
- Diaz FR, Santos P (2001). Studies on the acid activation of Brazilian Smectite clays. *Quim Nova.* 24(3):345-353
- Hamilton RJ, Bhatti J (1980). Fats and Oil, Chemistry and Technology. Appl. Sci. Publishers limited, London, pp. 40-45.
- Hymore FK, Iyayi AF (1989). Use of local clays in the refining of palm oil. *N. S. Che. J.* 8(2):161-171.
- James OO, Mesubi MA, Adekola FA, Odebunmi EO, Adekeye JID, Bale RB (2008). Bleaching performance of a Nigerian (Yola) bentonite. *Lat. Am. Appl. Res.* 38:45-49.
- Jimoh OT, Muriana M, Izuelumba B (2011). Sorption of Lead (II) and Copper (II) ions from Aqueous Solution by acid modified and unmodified *Gmelina arborea* (Verbenaceae) leaves. *J. Emerg. Trends Eng. Appl. Sci.* 2(5):734-740.
- Nwabanne JT, Ekwu FC (2013). Decolourization of palm oil by Nigerian local clay: A study of adsorption isotherms and bleaching kinetics. *Int. J. Multidiscipl. Sci. Eng.* 4(1):20-25.
- Oboh AO, Aworh OC, Agagu OK (1987). The Use of Nigerian Clays in Vegetable oil refining: Evaluation of some Nigerian clays as potential bleaching earths. *Nig. Food J.* 5:42-51.
- Okeke JA (1990). Adsorption Bleaching of Sheanut oil. Proceedings of N. S. E., pp. 14-19.
- Proctor A, Palaniappan S (1989). Soil Oil Lutein Adsorption by Rice Hull Ash. *J. Am. Oil Chem. Soc.* 66:1618-1621.
- Regina OA Okechukwu DO (2012). Adsorptive removal of colour pigment from palm oil using acid activated Nteje clay: Kinetics, equilibrium and thermodynamics. *Physicochem. Probl. Miner. Process* 49(1):369-381.
- Rohani BMZ (2006). Process Design of degumming and Bleaching of palm oil. Thesis. Ministry of Science and Technology, Malaysia, pp. 12-69.
- Rossi M, Gianazza M, Alamprese C, Stanga F (2003). The role of bleaching clays and synthetic silica in palm oil physical refining. *Food Chem.* 82:291-296.
- Salawudeen TO, Dada EO, Alagbe SO (2007). Performance Evaluation of acid treated clays for palm oil bleaching. *J. Eng. Appl. Sci.* 2(11):1677-1680.
- Stanley JL, Robert BH, Reo L, James CB (1975). Industrial Minerals and rocks (non-metallic other than fuels), Port City press, Baltimore, Maryland, U.S.A., pp. 519-635.
- Topallar H (1998). Bleaching kinetics of sunflower seed oil. *J. Am. Oil Chem. Soc.* 75(4):531-533
- Usman MA, Ekwueme VI, Alaje TO, Mohammed AO (2012). Characterization, acid activation and bleaching performance of Ibeshe clay. *ISRN Ceram.* 20(12):1-5.