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Research Article

The Effect of Activation Modelling of Nigerian Local Clay on the Adsorption Characteristics

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Abstract

The research work is on the effect of modeling of acid activation on the adsorption characteristics of local clay in Nigeria. The sample of the local clay which was obtained from Eha-Ndiagu clay deposit in Enugu State of Nigeria was subjected to pretreatment to obtain pulverized clay of average particle size of 500µm. The activation was carried out at different process conditions of temperature, contact time, dosage and mass percentage of acid using activating agent of HCl. From the result, it shows that each of the parameters investigated, the adsorption capacities of clay increase to a maximum and later decreased progressively while the sample coded S_2 exhibited the highest degree of performance. Similarly, the effect of adsorption on the refining of palm oil also displaced a spectacular performance. A high degree of bleaching efficiency ranging from 85 to 90% were recorded at the different controlling factors of adsorption. This, therefore, suggest that the local clay of Eha-Ndiagu can be classified as a high-ranking adsorbent if it is properly activated.

Keywords	*Activation Modelling; Acid Activation; Absorption Characteristic; Nigerian Local Clay; Eha-Ndiagu*
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Introduction

Clay is a group of hydrous aluminum silicate mineral with particles that are within the range of 2μm in nominal spherical diameter [Bello et al, 2018]. The mineralogical and chemical composition of clay which comprises various classification of Kaolinite, montmorillonite, elite chlorite and attapulgite depend to a large extent on the geographical location of its source. Nigeria, like other countries of the world is blessed with abundant deposits of different types of clay yearning for exploration and harnessing (Abdelfatth et al, 2018]. Clay and clay products are of great significant to humanity due to their natural characteristics for industrial and domestic utilizations. The inherent cost-effectiveness is one of the indispensable factors in preferential scale of acceptance for its various applications [Echegi, 2019].

Due to their extremely small particle size, clay has a large surface area per unit mass. It exhibits surface charges that attract negative and positive ions and water [Hart and Brown, 2014]. However, like other raw materials, clay has to undergo appropriate physical and or chemical treatments such as activation, ion exchange and heating in order to promote their surface properties and optimize its industrial potentials [Javed et al, 2018].

Clay activation involves the treatment of the clay precursor with activating agents and subjecting the mixture to process variables of temperature, contact time, concentration of activating agent, particle sizes, among others. During acid activation, interlayer cations are initially replaced with H^+ ions followed by partial destruction of aluminum octahedral sheets and subsequent dissolution of structural cations with the erection of permanent porosity [Ajemba and Onukwuli, 2013]. For a specific mode of activation, the efficacy of the activated clay is a function of interactive dictation of the above enumerated variables of activation.

One of the applications of activated clay is on the bleaching of vegetable oil. Bleaching is an adsorption process which improves the color, flavor, taste and stability of the residual oil. In adsorption process, the colored pigments of carotene, chlorophylls etc. are adsorbed onto the pore sites of the clay adsorbent and thus allowing the pure and colorless oil to separate out into a distinct phase. The adsorption capacity of any adsorbent is a function of specific surface area, surface charge, porosity, pore size distribution etc. This research is intended to carry out a dual purpose of investigating the effect of activation condition on the adsorption characteristics of local clay as well as the performance evaluation of these variables on the bleaching of palm oil.

Materials and Methods

The clay was obtained from Eha-Ndiagu in Ehalumona while the palm oil was sourced from Ede-Oballa main Market, both in Nsukka L.G.A of Enugu State, Nigeria. The analytical grades of these chemical reagents of HCl, NaOH, H_2SO_4, $Na_2S_2O_2$, H_3PO_4, etc. were procured from CONRAW Chemicals Ltd in Enugu, Nigeria.

Method

Preliminaries on Clay Activation
According to previous works (Abdelfattah et al, 2018; Mustapha et al, 2013) and preliminary tests conducted, it was established that:

i. Particle size of the clay had no significant effect on the kinetics of activation or pore properties of clay particles when the dimensions were equal to or less than 40μm.
ii. The agitation does not have much effect on the kinetics of acid attack from values of above 300 RPM.
iii. Acid activating agent of HCl produces much higher percentage performance in parameter adsorption characteristics than H_2SO_4 and HNO_3.

Hence, these factors are noted and the following conditions are therefore adopted in this work;

i. The stirring has been adjusted to a maximum value of a laboratory stirrer in order to ensure the homogenization of the reaction mixture.
ii. Acid activating agent of HCl was employed.

iii. Consequently, the study was conducted using only four major factors: reaction/interacting temperature (T), strength of acid (Wt%), contact time (t) and liquid to solid mass ratio (R) or dosage.

Sample Collection and Preachment

The clay sample was collected from Eh-Ndiagu clay deposit in sacks by manual method of mining using digger and shovel. The clay was in lumps of about 5-7cm. The collected clay sample was soaked in excess water for three days, stirred vigorously to ensure proper dissolution of any deleterious materials present in them and also to form slurry. The slurry was then sieved with 180µm mesh size to remove the deleterious materials and other contaminating foreign substances. The filtrate was allowed to settle for three days after which excess water was decanted. The clay was then oven dried at 110^{0}C for 24 hours. The dried clay sample was pulverized in a locally fabricated grinder at the Industrial Centre of in IMT Enugu and sieved to an average particle size of 100µm.

Activation

Based on the preliminary tests and from the literature reviews stated above, the samples for activation were prepared according to the following ranges: Temperature (60^0 – 90^{0}C), Contact time (1.5 – 6.0h), dosage or liquid/solid mass ratio (4-7) and mass percentage of acid (15 – 50%).

Three samples of activation model were prepared as follows:

I. Sample 1 (S_1): T = 60^{0}C, t = 1.5h, Wt% = 15%, R = 4
II. Sample 2 (S_2): T= 75^{0}C, t = 3.75h, Wt% = 32.5%, R= 5.5
III. Sample 3 (S_3): T = 90^{0}C, t = 6.0h, Wt% = 50%, R = 7

The Activation for each of the Samples was Conducted as Follows:

100g of raw clay with particle size less than 50µm, was mixed with an aqueous solution of HCl. The slurry was stirred at maximum speed by the laboratory agitator. Then, slurry was air-cooled and filtered with glass fiber. The filter cake was washed with distilled water several times until the wash water was neutral with no traces of acid. The pH of the filtrate was monitored using universal pH test strips. Finally, the clay product was dried in an oven at 110^{0}C for 24 hours. The dried samples were stored in a tight container. All the activated samples (S_1, S_2 and S_3) were prepared with the same procedure as described above.

Characterization of Activated Clay

The chemical composition of clay was determined according to the procedure outlined by Iloabuchi et al. (2020). The samples were analyzed for the major oxides of elements such as Sio_2, Al_2O_3, MgO, CaO, Na_2O, K_2O, MnO, at National Steel and Raw Materials Exploration Agency (NSRMEA), Kaduna, Nigeria, using a Perkin Elmer Atomic Absorption Spectrophones (AAS). P_2O_5 and TiO_2 were determined by colorimetric method while Loss on Ignition (LOI) was determined by heating in a furnace to a temperature of 1000^{0}C for 30 minutes. The final mass of the sample was measured after the duration of 30 minutes. The loss in weight was used for the evaluation of loss in ignition (LOI). Other parameters such as surface area was determined in line with the procedure described by Sars (2018), Pore volume, Porosity and titratable acidity were evaluated in accordance with the methods described by Echegi and Okoye (2019). Similarly, the analysis of the raw clay which is coded sample S_0 was carried out to provide a bench mark for the intrinsic evaluation of the adsorptive potentials of the activated ones.

Adsorption Experiment (Bleaching of Palm Oil)

Based on the preliminary studies conducted and in reference to previous works [Akinwande et al, 2015], the optimum bleaching efficiency of vegetable oil with activated clay is achieved within the range of these adsorptive parameters:

i. Temperature is 80^0 – 130^{0}C
ii. Contact time ranges from 20 – 40 minutes
iii. Dosage of clay is from 0.20 – 2.0%, while
iv. the particles sizes of clay ranges from 0.05 – 0.5mm.

These guiding principles were therefore effectively utilized in this adsorption research using sample S_2 of the activated clay from activation experiment. The selection of sample S_2 is predicated on the overriding performances of its adsorptive properties over other samples after evaluation.

Adsorptive bleaching was carried out by charging 100g per batch of degummed crude palm oil with 2g of sieved activated clay in a 500ml beaker. The feed charged was heated and stirred continuously on a hot plate regulated at a temperature of 80^0C for 20 minutes. At the completion of the time, the mixture was filtered through a dry filter paper to obtain the bleached oil. The bleaching efficiency of the activated clay sample, S_2 was then evaluated by measuring the colour of the bleached oil using UV – VIS spectrophotometer (Model WFJ 525) at 450nm. The bleaching efficiency (BE%) was determined from each of the experiments as thus;

Bleaching efficiency (BE %) = $\frac{A_u - A_b}{A_U} \times \frac{100}{1}$

A_U and A_b = Absorbance of unbleached and bleached oil respectively.

The above experimental procedure was conducted with the activated clay sample. Sample S_2 at the above enumerated ranges of process variables of temperature of 90^0-140^0C at 15^0C intervals clay dosage from 0.10 -5.0g, contact time of 10-60minutes at 10minutes interval and particle sizes of 0.05, 0.10, 0.20, 0.30, and 0.40 mm.

Results and Discussion

The results of the experiment are shown below

Table 1: Mineralogical Content Analysis of Activated Clay from Eha-Ndiagu

Compound	*SiO_2*	*Al_2O_3*	*Fe_2O_3*	*MgO*	*CaO*	*K_2O*	*Na_2O*	*MnO*	*TiO_2*	*LOI*
% composition of activated clay (sample S_2)	58.53	20.43	3.89	1.46	0.32	1.57	0.36	0.74	1.18	11.53
% composition of Raw Clay (Sample S_0)	45.63	16.24	8.76	1.87	4.12	1.79	3.01	0.86	1.64	16.08

Table 2: Adsorptive Properties of Activated and Raw Clay Samples

Properties	*Clay Samples*			
	S_0	S_1	S_2	S_3
Surface area (m^2/g)	90.16	188.4	324.06	207.58
Pore Volume (cm^3/g)	0.82	0.92	1.15	1.03
Bulk density (Kg/m^3)	1089.68	98.35	710.32	861.99
Porosity (ε)	0.31	0.40	0.57	0.48
Acidity ($\frac{mg.NaOH}{g}$)	0.01	0.05	0.16	0.09
pH	8.6	6.6	2.8	4.2

The Performance of Activated Clay of Sample S_2 on Bleaching Efficiency (%B.E) of Palm Oil

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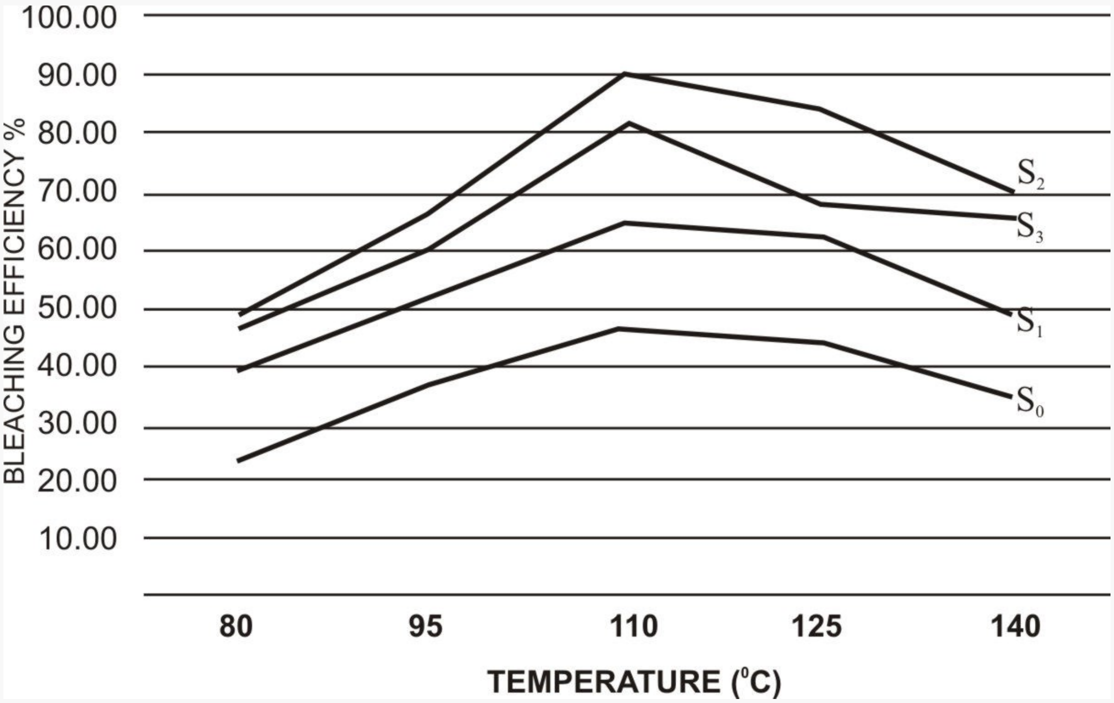

Figure i: Effect of Temperature

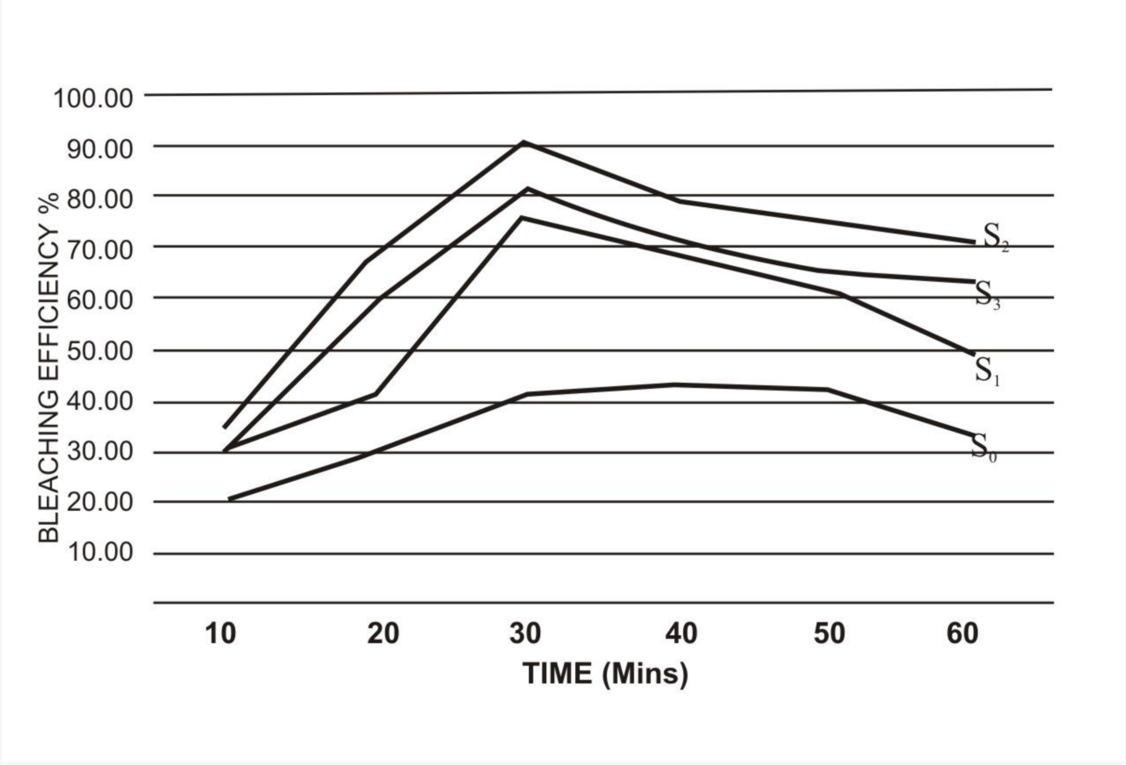

Figure ii: Effect of Contact Time

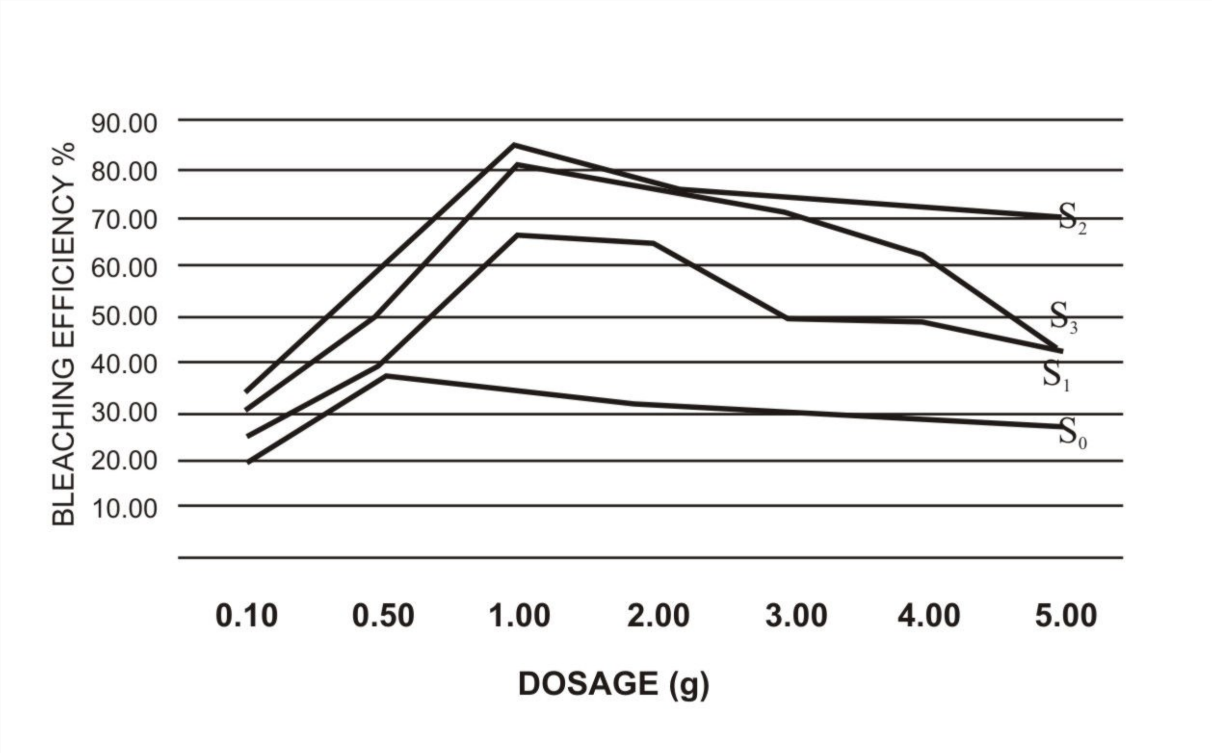

Figure iii: Effect of Dosage

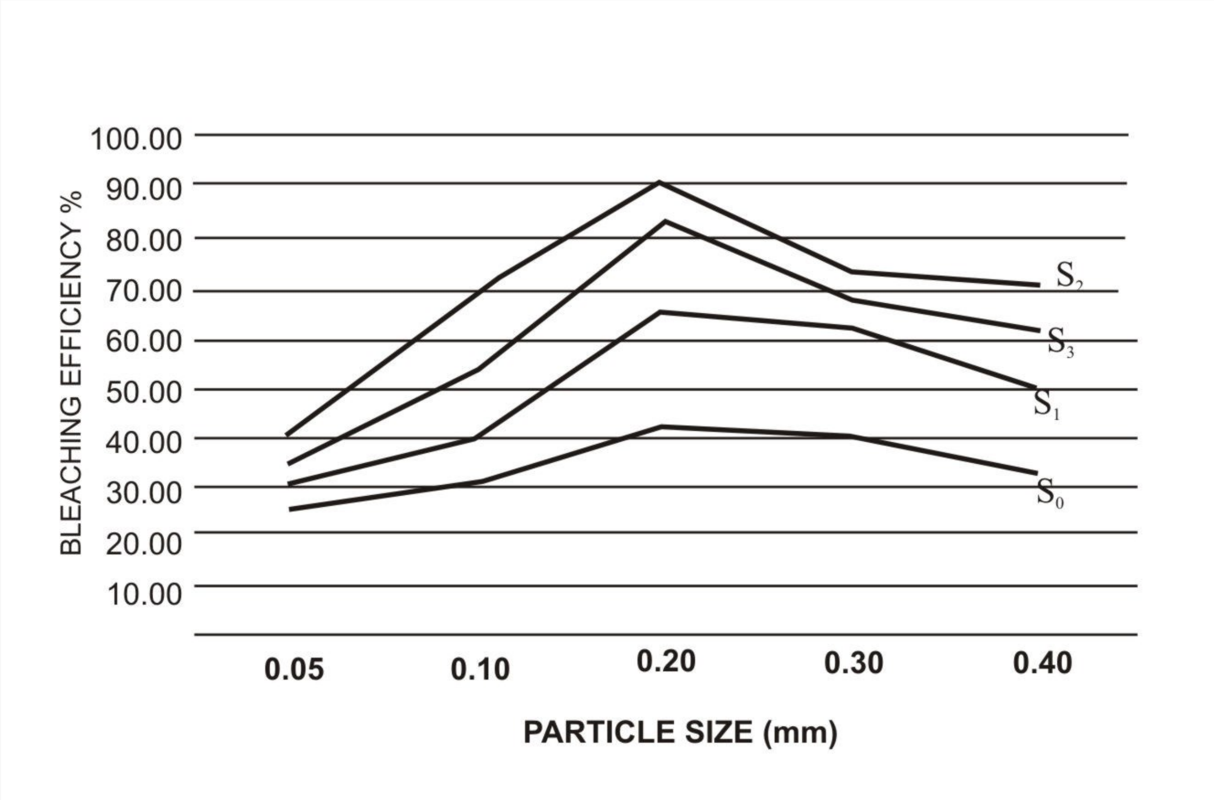

Figure iv: Effect of Particle Size

Discussion

Chemical Composition of Activated Clay Samples

The results of the chemical composition of the activated clay using hydrochloric acid is shown in Table 4.1. It was observed that from the result that sillica (SiO_2) and alumina (Al_2O_3) constitute the major composition of the clay with other metallic oxides present in smaller amounts. The chemical properties of the clay as analysed proved it to be montmorillonite with large number of alkaline metals. The silica and alumina contents satisfied the required content of the clay for the higher adsorptive (bleaching) capacity of the clay. When compared with highly rated adsorbent such as Fulmont, a brand of activated clay from Malaysia and Fullers earth from U.S, it is observed that there is no significant deviation as regard to these major components that are responsible for the bleaching of clay (Egbuna and Omotioma, 2013). However, alkali metallic oxides are relatively high but not enough to bring about the destructive effect on adsorption characteristics of the activated clay samples.

Adsorptive Characteristics of Activated Clay

The result of the activation shows that acid HCl-Activation led to the remarkable modifications of the adsorptive properties of the clay. With the increase in concentration of HCl, the activated samples exhibited a general increase in surface area, pore volume and porosity until the weight percentage of 32.5% is exceeded. The analysis of the result from the dosage of acid employed for activation revealed the same pattern of progression for all the assessed parameters of the activated samples. In this case, the optimum values of these properties were recorded at about the ratio of 5 of HCl to clay sample. In the same vein, all the adsorptive properties investigated increased with temperature up to about 75^0C. Thereafter, a downward trend takes its turn and a reversion of decrease begins to emerge. Above the optimum, further increase in any of these parameters investigate may extend the limit of distortion of the adsorption characteristics of activated clay to a maximum.

The modifications of these adsorptive parameters may arise from the elimination of exchangeable cations, de-lamination of clay and generation of micro-porosity during the activation process. However, the decrease as observed at higher values of activation parameters might be due to the process of passivation [Ojemba and Onukwuli, 2013]. At higher temperature ranges and long contact time, the activation can cause the destruction of the octahedral structure, leading to the passage of cations into the solution while the silica generated by tetrahydral sheet remains in the solids due to insolubility. The tetrahydral sheets from the initial destruction are polymerized by the effect of high acid concentrations and deposited on the silicate fractions which protect them from further attack and thereby covering the existing pore structure and reducing the surface area, porosity among others [Diaz et al; 2013]. The cumulative effect leads to drastic reduction in most of the essential adsorptive potentials.

Bleaching (Adsorption) of Oil

Effect of Temperature
The effect of temperature is highly pronounced on the bleaching of oil by clay adsorbent. As the temperature of bleaching is increased for a specific activation with clay, the degree of bleaching of the oil also increases. From the results obtained in figure (i), a bleaching efficiency (% B.E) of about 48% was achieved at the temperature of 80^0C. But as the temperature increased to 110^0C, a tremendous improvement was recorded as the BE percentage increased to about 90%.

However, at above this temperature range, the reversed trend sets in and it decreases accordingly. This observation is in agreement with the reported works on the bleaching of vegetable oils by adsorbents [Akinwande et al, 2015]. At higher temperature the structural octahedral sheet of the clay is permanently destroyed leading to blockage of pore structures and reduction in adsorptive properties.

Effect of Time on Adsorption
As observed from the results obtained in figure (ii), there is a similar phenomenon to the time-controlled adsorption of coloured substances from vegetable oil by the clay adsorbent. The B.E percentage rises with the increase in time

to an optimum value but later decreases. The maximum value was obtained at the range of 30minutes mark. This results concord with the values obtained from various researchers [Mustapha et al., 2013] and further reaffirms the efficacy of this activated clay to the adsorbent rating.

Effect of Clay Dosage
The same trend as recorded on the preceding two factors is prevalent on the amount clay per given quantity of oil used for bleaching process. From figure (iii), the optimum bleaching efficiency obtained is about 85% at the clay dosage of 1.0. This is a recommendable result in view of oil retention which occurs at larger values of clay dosage which is envisaged to occur from the particle size of 0.30mm and onwards.

Effect of Particle Sizes of Clay
This effect was investigated at the range of particle sizes of 0.05 – 0.40mm. From figure (iv), the results shows that the B.E percentage of the activated clay increases as the particle size decreases. This effect may be due to the increase in surface area and modified pore structural network in activated clay. Reduced particle sizes create more adsorption sites as well as cation exchange sites that are exposed to the adsorbate. However, this positive effect of particle size reduction should be properly harnessed on or before the optimum mark in order to checkmate oil retention and other associated irreversibilities of the process.

Conclusion
Eha-Ndiagu clay has proved to be a high ranked adsorbent which is capable of achieving a high efficiency in the application of adsorption processes. However, like most of all the adsorbents, it should be activated in order to enhance its adsorptive potentialities. These high values of adsorption parameters vis-a-viz the BE recorded in all the conditions investigated suggest that it is comparable to those high classes of activated clay elsewhere across the globe.

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