

## **Effects of Thermal Activation on The Physico-Chemical Properties Of Natural White Clay As A Local Adsorbent**

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**ABSTRACT :** Adsorptive capacity of an adsorbent is directly linked to its physicochemical properties such as moisture content, volatile matter content, specific surface area etc. In this research, the physicochemical properties and the effects of thermal activation on the specific surface area of white clay, an abundantly available local adsorbent from Enugu, South-eastern province of Nigeria were carried out. The moisture content, volatile matter content, fixed carbon, specific gravity, and bulk density were determined using standard gravimetric method. The pH value was determined with a pH meter. The specific surface area and the effects of thermal activation on the specific surface area were carried out with Methylene Blue Adsorption method. The result obtained showed moisture content of  $7.95 \pm 0.51\%$ , volatile matter content of  $2.46 \pm 0.04\%$ , fixed carbon content of  $0.84 \pm 0.08\%$ , specific gravity of  $2.57 \text{g/cm}^3$ , pH value of 5.7, and bulk density of  $1.56 \text{g/cm}^3$ . The specific surface area range of  $68.010$  to  $172.226 \text{m}^2/\text{g}$  for a temperature range of  $34^\circ\text{C}$  to  $800^\circ\text{C}$  was obtained. The results indicate that white clay has good adsorptive potentials and does not require much or expensive treatment to open up its pores.

**KEYWORDS:** Thermal activation, Physico-chemical properties, local adsorbent, White clay.

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### **I. INTRODUCTION:**

Adsorbents are solid substances, usually porous in nature, with a high surface area, that can adsorb chemical substances onto its surface by intermolecular forces, and the process of attracting chemical substances onto the surfaces of adsorbents is called adsorption (Warren)[1]. Adsorption is present in many natural, physical, biological and chemical systems, and is used extensively in industrial process for the purpose of separation and purifications. Though, there are many commercially available adsorbents for the removal of contaminants, most of these adsorbents are synthetic, with high cost implications. Such adsorbents as silica gel, carboxyl-methyl cellulose, dowex 10, and zeolite, are all synthetic adsorbents that may not be readily available in Nigerian market or may be very expensive. Other organic adsorbents such as activated carbon, involve physicochemical treatments that are also expensive and environmentally unfriendly, due to its thermal pollution. The most frequently applied adsorbent for the removal of organic pollutant in waste water is activated carbon (Nagham) [2]. The high cost of commercial adsorbents, especially activated carbons restricts their uses and applications (Malik) [3], and hence the need to substitute them with the unconventional, relatively cheaper, readily affordable, easily assessable, environmentally friendly and locally sourced adsorbent cannot be over emphasized

White clay (local adsorbent) deposits are found in several locations in south eastern Nigeria, especially in Enugu province of the country. The applications to which adsorbents can be put depends on its physicochemical properties such as pH, specific surface area, moisture content, volatile matter contents etc. Walter [4] observed that the mechanisms of adsorption are related to the surface properties of the adsorbent, pH of solution, particle size and the thermodynamic parameters which are important in the adsorbent process. Therefore, to access adequately the feasibility of white sand as a local adsorbent for the removal of contaminants and to design the most effective way in which it can be used as adsorbent, it will be necessary to quantitatively and qualitatively determine some of these physicochemical properties. Since adsorbent capacity is a function of its physicochemical properties, analysis of white clay for these properties are of immense significant for its optimal utilization as adsorbent. This is the underlying reason for this study-to analyse white clay for some of its physicochemical properties, with the aim of utilizing them in improving its adsorbent potentials. The research is in line with the Nigeria's economic objective of self reliance and motivation of local industries by embarking on local sourcing of raw materials for their operations. This, in effect, will help to conserve foreign exchange and also add value to white clay (natural resources). It will also create job opportunities for the teaming school leavers in the region and also create revenues, both for government and individuals.

A wide range of materials have been researched for that purpose (Nde-Age[5], Itodo [6], Kyziol, [7], Michael [8]). The utilization of locally available materials as a raw material for the production of industrial products such as adsorbent is in line with the economic transformation of Nigeria as a nation. Several techniques have been developed to measure different parameters of an adsorbent. Specific surface area, is a parameter of solids that could correlate significantly with many parameters or properties of solids. Clays vary widely in their reactive surface because of the difference in their mineralogical, organic compositions and their particle size distribution (Carter) [9] and the measured surface area is largely dependent upon the amount of particle surface exposed (Mortland) [10]. Several methods have been established to measure the specific surface area of materials and value obtained, to some extent, depends on the method adopted. Churchman [11], suggested that while absolute value of surface area may be difficult to measure, the relative merits of the various methods proposed could be assessed in terms of their different abilities to predict important adsorbent properties. Some of these methods are the application of the BET theory (Brunar) [12], Cetyl Pyridinium Bromide (CPB) (Greenland) [13], Internal Reflectance Spectroscopy (mulla) [14], Methylene Blue Adsorption (Hang) [15] and Salwa [16]. Some of those methods produce similar results. Some are time consuming or require expensive, specialized apparatus.

In this study:

- The physico-chemical properties of white clay, namely; Moisture Content, Volatile Matter, Fixed Carbon, pH Value, Bulk Density and Specific Surface Area, were determined.
- Effects of thermal activation on the specific surface area, adsorbing potentials and possible use of white clay as a local adsorbent were evaluated.
- An adsorbent with appropriate porosity was developed from white sand.

## II. MATERIAL AND METHODS:

The material for the research is Enugu White clay collected from Enugu in south East province of Nigeria. The adsorbent was collected during the peak of dry season (April) and stored in a polyethylene bag. The physico-chemical properties of the local adsorbent were determined using standard procedures. The adsorbent was characterized for moisture content, volatile matter content, fixed carbon, specific gravity, pH value, bulk density, specific surface area, and the effects of thermal activation on the specific surface area.

### THERMAL ACTIVATION OF WHITE SAND

**Aim:** Thermal activation is aimed at increasing the adsorptive capacity of the white sand.

**Materials and equipment:** White clay sample, Crucible, Weigh balance, Furnace, Sieve plates, Piston and mortar.

**Experimental procedure:** 100g of white clay sample sieved with a 150 mesh size sieve was weighed out into a crucible. The latter, with its content was put in a furnace set at a temperature of 650°C for 4 hours. The furnace was then turned off to cool the sample. The calcined clay was then size - reduced to 20, 40, 60, 80, and 100 mesh sizes and stored in a dry container to be characterized and for bleaching experiment. The above procedure was performed for temperatures of 200°C, 350°C, 650°C, and 1000°C, and different drying times of 10, 20, 30, and 40 minutes. The activated sample sizes and their combinations were used to bleach a given oil sample and the performance in terms of colour reduction was used to determine the optimum activation temperature for the sample.

**Observation:** Physical appearance changed from white to light grey after activation

**MOISTURE CONTENT DETERMINATION : AIM:** To determine the moisture content of white clay with a view to increasing the active site and hence improve the adsorptive capacity .

**Materials/ Apparatus:** White clay, digital balance, oven, desiccators, thermocouple, crucibles, and spatula.

**Procedure:** The moisture content was determined using gravimetric method (Abubakar) [17]. Three crucibles A, B and C were washed with distilled water and oven dried at a temperature of 120°C. The dry, clean crucibles were weighed and the weight of each recorded as  $w_1$ . A spatula was used to introduce a small quantity of the white clay to the crucibles and reweighed. The weight of the crucible plus the adsorbent was recorded as  $w_2$ . The sample was placed in an oven at 110°C (383K) for 24 hours, cooled in a desiccator and reweighed to a constant weight  $w_3$ .

$$\text{Moisture Content} = \frac{W_2 - W_3}{W_2 - W_1} \times \frac{100}{1} \text{-----1}$$

Where  $w_1$ =weight of empty crucible,  $w_2$  = weight of crucible + sample before heating,  $w_3$  = weight of crucible + sample after heating. The exercise was repeated for two more times and average percentages moisture content was recorded.

### **VOLATILE MATTER**

**AIM:** To determine the volatile matter content of white clay, so as to know the amount of devolatilization required to produce a good adsorbent

**Materials/ Apparatus:** White clay, oven, desiccator, digital balance, thermocouple, crucibles, and muffle furnace.

**Procedure:** The same gravimetric method was used in the determination of the volatile matter content of the adsorbent (Echegi) [18]. The demoinsturized sample was placed in a dry clean crucible of weight  $w_1$ . The crucible plus the sample was weighed and noted as  $w_2$ . The crucible with the sample was kept in a muffle furnace at temperature of 920°C (1193K) for seven minutes. At the end of the duration, the crucible with the sample was cooled in a desiccator and the weight taken as  $w_3$ .

$$\text{Volatile matter} = \frac{W_2 - W_3}{W_2 - W_1} \times \frac{100}{1} \text{-----2}$$

Where  $w_1$ =weight of empty crucible,  $w_2$  = weight of crucible + sample before heating,  $w_3$  = weight of crucible + sample after heating. The process was repeated two more times and the average percentage volatile matter taken.

### **FIXED CARBON**

**AIM:** To determine the fixed carbon content of white clay so that good porosity property of the adsorbent is good assured.

**Materials/ Apparatus:** White clay, digital balance, furnace, desiccator, thermocouple and crucibles.

**Procedure:** The activated sample of the adsorbent was again subjected to gravimetric method to determine its fixed carbon content, (Echegi) [18]. The sample was placed in a crucible of known weight  $W_1$ , and reweighed  $W_2$ . The sample in the crucible was heated in a furnace at 800°C for 1hour, and subsequently at 815°C until two consecutive constant weights were obtained.

$$\text{Fixed carbon ( \% )} = \frac{W_2 - W_3}{W_2 - W_1} \times \frac{100}{1} \text{-----3}$$

Where  $w_1$ =weight of empty crucible,  $w_2$  = weight of crucible + sample before heating,  $w_3$  = weight of crucible + sample after heating. The process was repeated two more times and the average percentage fixed carbon content taken.

### **SPECIFIC GRAVITY (RELATIVE DENSITY)**

**AIM:** To determine specific gravity of white clay in order to know its density relative to water as a reference substance.

**Materials/ Apparatus:** White clay water, relative density bottle, shaker, digital balance.

**Procedure:** The method utilizes the Archimedes principle for a granular solid insoluble in water (Echegi) [17]. The clean, dry relative density bottle with stopper was weighed as  $w_1$ . It was then partially filled with the adsorbent sample and re-weighed as  $w_2$ . The remaining space in the bottle was finally filled with water and shaken gently to remove air bubbles. The stopper was inserted and the bottle cleaned, dried and weighed again as  $w_3$ . After emptying the contents of the bottle, it was washed thoroughly with water and then again filled with water. The stopper was inserted, excess water wiped off and the bottle with its content weighed as  $w_4$ . The relative density of the sample was calculated using the relationship.

$$\text{Relative density, (R.D)} = \frac{w_2 - w_1}{(w_4 - w_1) - (w_3 - w_2)} \dots\dots\dots 4$$

Where  $w_1$  = weight of empty relative density bottle  $w_2$  = weight of relative density bottle + sample,  $w_3$  = weight of relative density bottle + sample + water,  $w_4$  = weight of relative density bottle + water.

**pH MEASUREMENT**

**AIM:** To determine pH of white clay to know its level of acidity or alkalinity in the white claysample.

**Materials/ Apparatus:** White clay beaker, shaker, **pH** meter

**Procedure:** The pH of a 10% suspension of the adsorbent sample (white clay) was determined using Hanna H<sub>1</sub> 981-digital pH meter at room temperature. Initially, the pH meter was standardized in a buffer solution of pH of 4, 7, 9.

The 10% suspension was prepared by dispensing 1g of the adsorbent sample in 10cm<sup>3</sup> of distilled water and shaken very well. The pH electrode was dipped into the solution and the value read from the meter.

**BULK DENSITY**

**AIM:** To determine bulk density of white clay so as to establish its weight relative to a given weight of water.

**Materials/ Apparatus:** white clay, measuring cylinder, spatula and bench

The bulk density of the adsorbent was measured using the method of (Yoshiyuki) [19], by placing 100cm<sup>3</sup> cylinders on a balance and the weights noted as  $W_1$ . The cylinder was filled with the adsorbent and the weight recorded as  $W_2$ . The sample was compacted by tapping on the bench top until the mass (g) occupied the volume (V Cm<sup>3</sup>). The cylinder was tapped on the bench until the volume of the sample stopped decreasing.

$$\text{Bulk Density} = \frac{\text{Mass of Sample}}{\text{Volume occuoied aftertapping}} \dots\dots\dots 5$$

Where  $w_1$  – weight of empty cylinder, and  $w_2$  –weight of cylinder + adsorbent

**SPECIFIC SURFACE AREA (m<sup>2</sup>/g)**

**AIM:** To determine specific surface area with a view to producing an adsorbent of good adsorptive capacity .

**Materials/Apparatus:** White clay, methylene blue, distilled water, filter paper, digital balance, beakers, burette, stirring rod, measuring cylinder

**Procedure:** This was determined by titrametric method after Salwa [16]. Two grams (2g) of the dried sample (at 34°C) was transferred into a conical flask and stirred in 100 ml-distilled water for titration with standard methylene blue solution.

The methylene blue solution was prepared by dissolving one gram of dry methylene blue (with relative molecular weight, 319.9) in 250 ml of distilled water. The end point of titration of the methylene blue adsorption was determined with the halo method (Kahr[20], and Yukselen[21]. Small quantity of the methylene blue solution was gradually added from a burette to the stirred sand suspension in the conical flask and drops of this suspension were put with a glass rod on a filter paper. First, a colourless waterfront spread in a circle on the filter paper, Fig. 2(A); whereas the blue- coloured sand in the centre stuck to the paper. At the end point a light blue halo appeared Fig.2(B). The sand suspension was then stirred two more minutes and the dotting test carried out to show whether a blue halo shape was formed again which marked the end point of the test; otherwise further titration was carried out carefully until the halo did not disappear any longer after two minutes.

The Methylene Blue Adsorption Value (MBA) can be calculated as:

$$\text{MBA}(\frac{\text{g}}{100\text{g}} \text{ of sample}) = \left(\frac{A}{B}\right) \times C_n \left(\frac{D}{100}\right) \dots\dots\dots 6$$

Where A – the weight of dry methylene blue, B – Volume of methylene blue solution (1 Litre),  $C_n$  – the volume of methylene blue (MB) added to the sample until the end point is reached. D – the weight of dry powdered sample.

$$SSA (m^2/g) = \frac{mM_B \times A_V \times A_{MB}}{319.9 \times M} \dots\dots\dots 7$$

Where SSA – Specific surface area, mM<sub>B</sub> – the mass of adsorbed methylene blue at the point of complete cation replacement (end point). A<sub>v</sub> – Avogadro’s number = 6.02 x10<sup>23</sup>/mol A<sub>mB</sub> – the area covered by one methylene blue molecule, typically assumed to be 130A<sup>02</sup> (Hang[15])., M – Mass of Adsorbent (2g),A – Weight of methylene blue to be dissolved in 1 litre of distilled water. The same was repeated at temperatures of 100 °C, 200 °C, 300 °C, 400 °C, 500°C, 600<sup>io</sup>C, 700°C, and 800°C.

**BLEACHING EXPERIMENT :** The aim of bleaching is to reduce the level of residual pigment in the oil sample. The activated White clay was used for the bleaching experiment, and the efficiency of the activated clay was measured in terms of colour reduction obtained after bleaching.

**III. RESULTS AND DISCUSSION**

The results of these experiments are presented in tables 1-5 and figures 1-5. Tables 1 and 2 show the results of the analyses of raw and activated white clay samples.

<i>PARAMETER</i>	<i>VALUE</i>
Moisture content %	7.95 ±0.51
Volatile matter %	2.46 ± 0.04
Fixed carbon %	0.84 ± 0.08
Specific Gravity g/cm <sup>3</sup>	2.57
pH	5.7
Bulk density g/cm <sup>3</sup>	1.56
Non Clay Residue (%)	3.55
Bulk density g/cm <sup>3</sup>	1.56
Ignition Loss (%)	11.26
Titrateable Acidity (mg NaOH/g	0.78
SiO <sub>2</sub>	63.39
Al <sub>2</sub> O <sub>3</sub>	4.42
Fe <sub>2</sub> O <sub>3</sub>	0.11
CaO	1.62
MgO	2.33
Na <sub>2</sub> O	4.10
K <sub>2</sub> O	3.48
Ignition loss	11

**Table I: Physico-chemical properties of raw white clay.**

It was observed that natural white clay was ideal in terms of non-clay residue, moisture content, ignition loss and titrateable acidity, but low in bulk density. Nutting, [22], noted that physical properties of clay influence their ability to adsorb carotenoids. Richardson [23], indicated that Low moisture content is an indication of good adsorptive capacity, while high oil retention indicates a high apparent bulk density. Low ignition loss and non clay residue of the white clay, indicate that the clay is free from inorganic substances which would naturally hinder its adsorptive properties. Soon, [24], in his experiment on natural clays, observed that high level of SiO<sub>2</sub> (about 65%), in a clay sample proves it to be montmorillonite. And hence, the chemical properties of the clay presented hereunder as analyzed, proved it to be montmorillonite. The physico-chemical properties of adsorbent usually affect its adsorptive property, since they have profound influence on the specific surface area. The results of the physico-chemical properties of white clay as shown in table1 shows that the moisture content is comparable to those of the other adsorbent but volatile matter and fixed carbon are by far less than those obtained from organic based adsorbent (Echegi ) [18] .This may probably be the reason why specific surface area of organic based adsorbents are greater than those obtained for white clay after thermal activation. The specific gravity, pH value and bulk density are comparable to those in the literature for soil based materials. Physical and chemical properties of fine grained clay may be greatly influenced by the amount of its specific surface areas (Amy) [25]. Differences in the surface area of adsorbents may be predominantly as a result of texture, grain size distribution, types and amount of different materials present in the adsorbent. The surface area of the adsorbent as observed may be due to irregular shapes, and, or surface roughness of the grains and so the relative high surface area of the adsorbent as observed may be due to the presence of high surface materials, irregular grain shapes and, or the surface roughness of the grain. From the table, it was observed that

the clay has higher SiO<sub>2</sub> and a lower Alumina than the fuller's earth. Fe<sub>2</sub>O<sub>3</sub> is also lower than that of the fuller's earth. Going by these three properties, the natural white clay is a good adsorbent material as it compares well with the standard fuller's earth. The low Fe<sub>2</sub>O<sub>3</sub> content also proved it to be a good material of adsorption compared to fuller's earth. The chemical composition of white clay after activation as compared with Fuller's earth and Fulmont AA, is shown in table 2.

**Table II: Chemical Composition of Activated white Clay compared with fuller's Earth, and Fulmont AA**

<i>Properties</i>	<i>Thermal Activated White clay</i>	<i>Fuller's Earth</i>	<i>Fulmont AA</i>
SiO <sub>2</sub>	61	52.26	61.7
Al <sub>2</sub> O <sub>3</sub>	8.75	14.33	12
Fe <sub>2</sub> O <sub>3</sub>	0.10	3.04	5.7
CaO	2.14	3.02	4.1
MgO	1.5	-	2.3
Na <sub>2</sub> O	0.55	0.40	0.2
K <sub>2</sub> O	2.25	0.48	0.32
Ignition loss	8.6	-	6.2

From table 2, it is observed that SiO<sub>2</sub> of activated white clay is very good compared to Fuller's earth and Fulmont AA. Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> contents are good also. 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. From the table also, it was observed that the silicate content of the thermally activated white clay compares very well with the Fulmont AA, decreased from 63.39 to 61, showing it to be a standard adsorbent. The removal of more soluble constituents vastly increased the specific surface area of the clay. Gregg, [26], showed that these factors favour bleachability as the efficiency of the earth sample is proportional to their surface area. Time of activation (contact time), which gave the best result was 30 minutes. It was also observed that there was a certain amount of disintegration during calcinations of the sample which was lost as dust powder. Overheating is therefore not necessary in order not to lose the adsorptive power of the clay. The optimum temperature for thermal activation was found to be 650°C. Any attempt to heat the clay sample beyond this temperature would result in complete loss of moisture. Ethre-Snell, [27], noted that this results in sintering, which leads to drastic reduction of porosity.

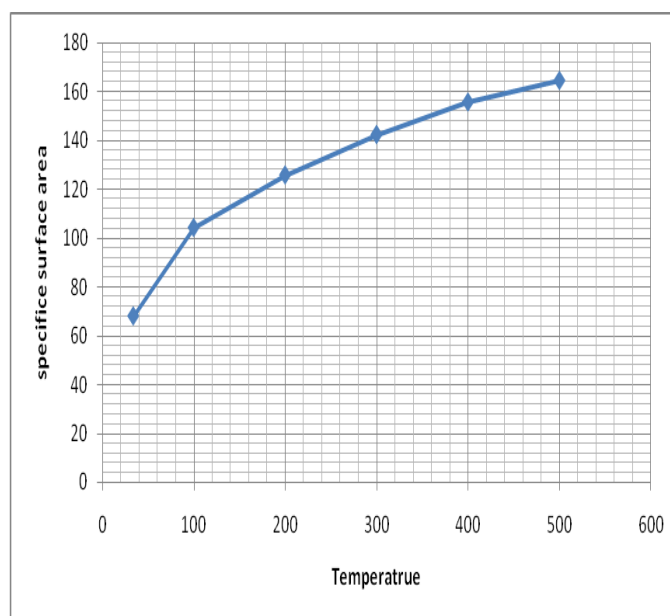
The effect of temperature on the specific surface area of the adsorbent is shown in table 3

**Table III: Effect of temperature on the specific surface area of the adsorbent**

<i>Temperature (°C)</i>	<i>Methylene blue adsorbed (g)</i>	<i>Specific surface area SSA (m<sup>2</sup>/g)</i>
34	0.0556	68.010
100	0.0852	104.216
200	0.1028	125.744
300	0.1164	142.280
400	0.1272	155.590
500	0.1344	164.397
600	0.1404	171.737
700	0.14132	172.862
800	0.1408	172.226

The adsorptive capacity of an adsorbent is a function of its specific surface area, since this property determines the degree of porosity of the adsorbent, Table 3. The more pores in an adsorbent, the more will be the adsorbing sites. The result shows a significant impact of temperature on the specific surface area. At 34°C, the SSA, was 68.010m<sup>2</sup>/g, and increased to 172.862m<sup>2</sup>/g at 700°C, a difference of 104.852, representing 154.17%. Thus the adsorptive capacity and specific surface area are temperature dependent. The specific surface area obtained is comparable to those obtained from soil material in the literature. Amy[25]

Figure 1 shows the effect of thermal activation on the specific surface area of white sand.



**Figure 1: Graph of specific surface area against temperature in °C**

From figure 1, the impact of temperature was significant up to 600°C. Above that temperature, the effect of increasing temperature was insignificant.

The surface area expressed as the ratio of the total surface of a porous or dispersed substance in a given medium to its volume or mass, is always proportional to the particle size of the dispersed phase. The adsorptive capacity of adsorbents, the effectiveness of solid catalyst and the properties of filter materials, all depends on the magnitude of their surface area. The shape of adsorbent grain sample is of immense importance, as the surface area per unit volume or mass depends on changes with the shape of the grain. A specific grain having the shape of sphere has the smallest surface area, but will exhibit the greatest surface area when deformed into extremely thin disc or shapes (Suess) [28]. (De Kimpe), [29] had observed that surface area increases with decreasing particle size.

The contributions of organic matters to the specific surface area of soil materials are difficult to evaluate (Thompson) [30], but organic matter and inorganic colloids possess specific surface area which contributes to the overall surface area of soil materials. Specific surface area is related to the porosity of the adsorbent. That is, it is the porosity that yields the surface area on which the adsorbate attaches. Therefore, the higher the specific surface area, the higher the porosity of the adsorbent. High specific surface area is an indication that the adsorbent has high tendency to adsorb material.

Moreover, the specific surface area is affected by the activation. The activation process modified the surface chemistry of the adsorbent by the formation of more functional groups which surely enhanced the performance of the adsorbent. Also, activation helped to open up the pores of the adsorbent. Table 4 shows that an increase in the temperature of the adsorbent will lead to a corresponding increase in its specific surface area.

**Table IV: Methylene Blue adsorption value at different temperatures.**

Temperature (°C)	Volume of methylene blue used cm <sup>3</sup>	MBA (g/100g sample)
34	13.90	2.78
100	21.30	4.28
200	25.70	5.14
300	29.10	5.82
400	31.80	6.36
500	33.60	6.72
600	35.10	7.02
700	35.33	7.066
800	35.20	7.04

The increased adsorption of methylene blue at elevated temperature is probably because elevated temperature increases the escaping tendencies of moisture and gases trapped in the pores of the adsorbent. It could also be that chemisorption was involved in the adsorption of methylene blue by the adsorbent. This is shown in Fig.1. Table 4 also shows the relationship of methylene Blue adsorption at different temperatures

In the table, it is observed that volume of methylene blue used increases linearly with temperature, but the MBA increases marginally with temperature from a temperature of 400°C.

Fig. 2 shows the physical appearance of Methylene Blue before and at the end of reaction with White clay suspension.

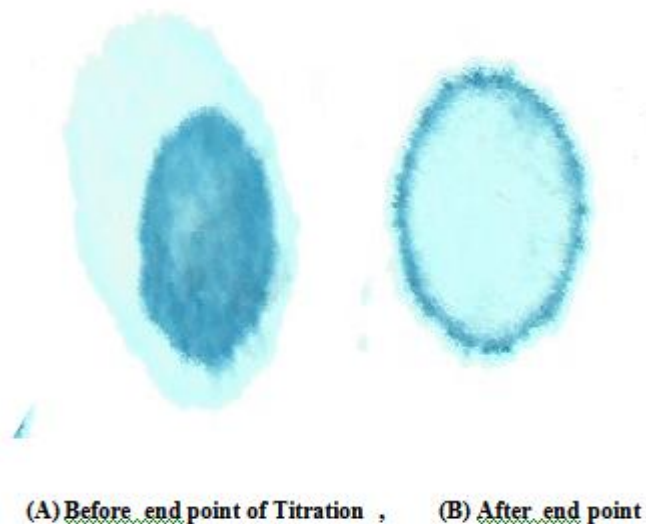
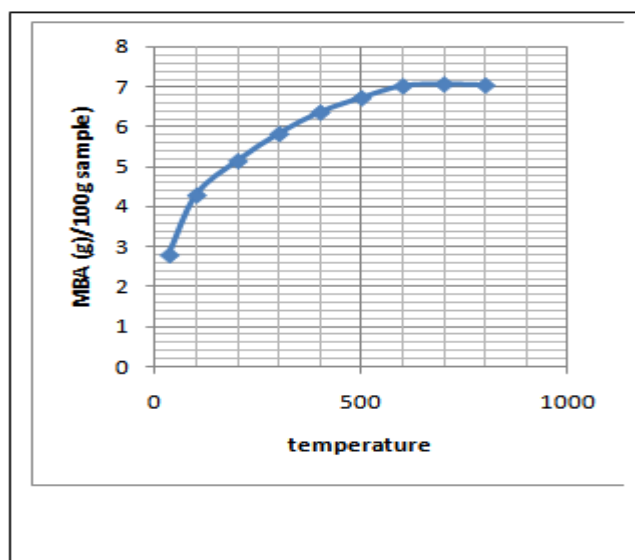


Figure 2: End point of titration

At first, a colourless water front spread in a filter paper, whereas the blue coloured clay stopped at the center as shown in figure 2. At end point of the titration, a light blue halo appeared as in figure 2 (B).

The relationship between methylene blue adsorption value MBA(g/100g of sample) with temperature is given in figure 3, while methylene blue adsorbed at different specific surface area is shown in figure





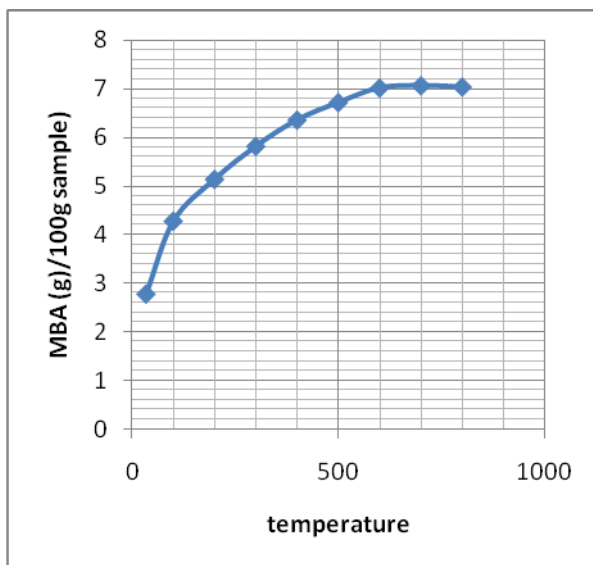


Figure 3. Graph of methylene Blue at different temperatures

The adsorption of Methylene Blue increases curve-linearly at first, but at a temperature of 600°C, it increases marginally.

Fig. 4 shows the relationship between Methylene Blue adsorbed and specific surface of adsorbed

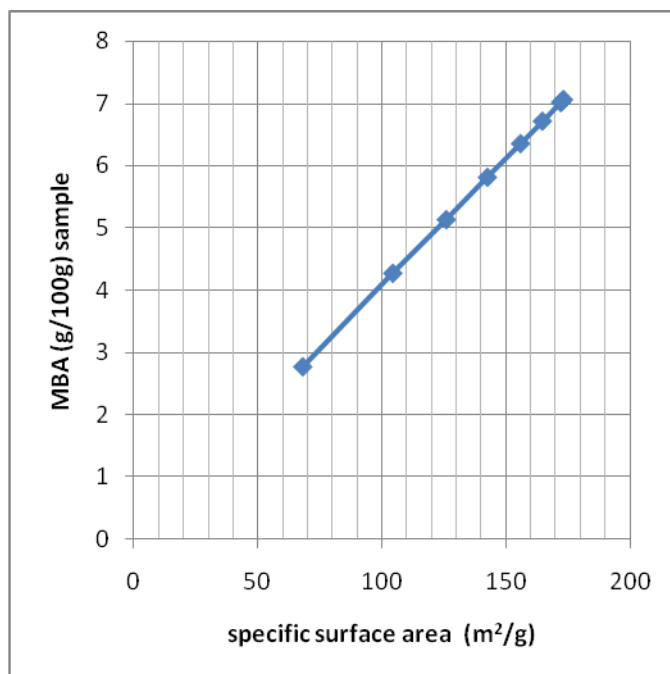


Figure 4: Graph of Methylene Blue Adsorbed at different specific surface area.

Figure 3 shows that there is a positive correlation between methylene blue adsorption and temperature. At temperature above 600°C, the increase in methylene blue adsorption value becomes insignificant. Figure 4 shows a linear relationship between methylene blue adsorption value and specific surface area.

**pH:** Hydrogen and hydroxide ions are adsorbed strongly. The adsorption of other ions is influenced by the pH of the solution. Moreover, the ionization of acidic or basic compounds affects its adsorption. pH affects adsorption, in that it governs the degree of ionization of compounds. According to Walter[4], polar solute will be strongly adsorbed from a non-polar solvent by polar adsorbent. The polarity of compound is a function of charge separation within the molecule. The degree of ionization is affected by the pH (a weak acid or a weak

base), which in turn affects adsorption process and particularly on the adsorption capacity (Malik) [3]. White clay shows a pH value of 5.7 the weakly acidic nature of the adsorbent may likely be due to the chemical composition of the adsorbent. According to Lai [31], charges in low pH adsorbent surface changes with the change in pH value. That is, increasing pH value increases the number of hydroxyl group thus increasing the number of negatively charged sites and enlarges the attraction between the adsorbent and basic dyes (adsorbate). As hydroxyl group increases, repulsion between the adsorbent surface and the adsorbate decreases. It is known from chemistry that surface of sand ends with Si –O (Mohammed) [32]. The presence of this functional group in the adsorbent surface in liquid phase may easily dissociate and serve as sorption or ion exchange site. That is, the negative entities might bind metal ions, via the coordination. The binding of metal ions on a surface might be influenced by the nature of the surface. Therefore, the polarity of the adsorbent is an indication that it may work best for polar solutes in non-polar solvents.

**Specific Gravity:** Specific gravity of an adsorbent depends not only on the nature of the starting material, but also on the preparation process. Specific gravity and particle size of an adsorbent are important adsorbent properties which must be known before its application. High specific gravity provides greater volume and normally indicates better quality adsorbent since higher density adsorbent need not be regenerated as frequently because it holds more adsorbate per unit volume (Itodo) [5 ].The relatively high specific gravity of 2.57 of table 1 for the adsorbent is an indication that the adsorbent is good and cannot easily be suspended in aqueous medium.

**Moisture, volatile matter and Fixed Carbon:** Most effective adsorbent must possess low moisture content, volatile matter and ash content. The reason may be that they block the active sites of the adsorbent. Therefore, the relatively low moisture, volatile matter and ash content of the adsorbent as observed is an indication that it is a good adsorbent. The lower adsorption of methylene blue at lower temperatures may be due to the physical constrictions and activation energy barrier from volatile matters as well as narrow pore mouths and necks. The increased adsorption at elevated temperature may be due to increase in pores accessibility which is in line with (Bae) [33], that higher temperature increases pore accessibility. The high thermal stability of the adsorbent is an indication that the adsorbent can withstand high temperature in which some adsorption processes are carried out. Silica as an adsorbent can be used to purify different chemicals without actually reacting with those chemicals.

**Performance of Thermally activated white clay :**Table 5, is the Physico-Chemical Properties of the raw and refined Oils used in testing the bleaching performance of the thermally activated white clay From the table, it can be seen that there is a marked difference between the raw and bleached 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. Since these values are close to the standard values, they can be accepted as true representative values and can be used in bleaching experiments

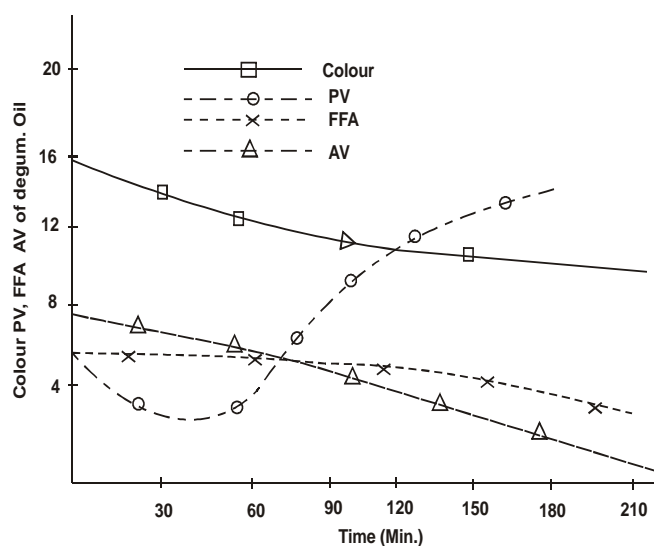
**Table V: Physio-Chemical Properties of the raw and bleached Oils used in testing the performance of the thermally activated natural white clay**

<i>Properties</i>	<i>Raw Palm Oil (RPO)</i>	<i>Bleached Palm Oil (BPO)</i>
<i>Colour (Physical Appearance)</i>	<i>Deep Orange</i>	<i>Light Orange</i>
<i>Odour</i>	<i>...of Palm Oil</i>	<i>... of palm fruit</i>
<i>Taste</i>	<i>...of Palm Fruit</i>	<i>Bland</i>
<i>Specific Gravity</i>	0.9182	0.9282
<i>Melting Point(°C)</i>	38	35
<i>Moisture (%)</i>	1.3	0.05
<i>Refractive Index</i>	1.4514	1.4562
<i>Free Fatty Acid (%)</i>	3.80	4.2
<i>Lovibond Red Unit (1" Cell)</i>	23	3.2
<i>Anisidine Value (M.eq/kg)</i>	8.2	4.05

Peroxide Value (M.eq/kg)	5.8	3.00
Phosphorous (Ppm)	9.0	5.01
Iron (Ppb)	3.0	4.3
Saponification Value	200	210
Iodine Value	45	48

**Activation Time (Contact Time) :** The effect of time of activation on the bleaching ability of the activated clay was also observed. It was noted that the optimum contact time during activation was 4 hours. In thermally activated white clay, it was observed that moisture was greatly reduced, and organic matters burned. This has the effect of increasing the surface area and pore volume available for adsorption. The optimum activation temperature for thermally activated clay was 650°C, beyond which the bleaching potential of the activated clay was reduced. This is in accordance with the observation of (Belaw, [34]).

**Performance of activated clay :** By observing the bleaching operations with the thermally activated clays, it was found that thermally activated lay has a lower performance when compared to chemically activated one, (Ibemesi, ([35])). This was as a result of the changes in structure and composition of the activated clay. The acid treated clay leads to leaching out of excess mineral composition of the clay samples, thereby increasing the adsorptive properties. The thermal mode of activation merely destroys the organic substances and evaporates the moisture of the clay sample, leaving unaffected the metal oxides, (Bumberg, [36]). The effect of contact time on the colour, PV, AV and FFA of Palm oil bleached with thermally activated White Clay is shown in Fig 5. Bleach temperature is constant.



**Fig. 5. The effects of contact time on the colour, PV, AV and FFA of Palm oil bleached with thermally activated White Clay**

In the figure, colour of bleached oil is reduced to about 10 Red units. AV drops from about 7.8 to below 6.4 but continues with time. FFA is marginally reduced, while PV is reduced from 3.8 in about 45min and then starts to rise sharply as a result of colour fixation at long exposure under atmospheric conditions.

#### IV. CONCLUSION

The results obtained from the physicochemical properties of the local adsorbent (white clay) showed that it met the standard for use as an adsorbent with regard to its moisture content, volatile matter, and fixed carbon content, specific gravity, pH value and the specific surface area. Equally, the thermal activation showed high correlation of the specific surface area and Methylene Blue Adsorbent value with temperature.

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