*International Journal of Engineering Science Invention*
*ISSN (Online): 2319 – 6734, ISSN (Print): 2319 – 6726*
*www.ijesi.org ||Volume 4 Issue 9|| September 2015 || PP.32-42*

# Optimal Process Parameters for the Adsorption of Methylene Blue on Thermally Activated Enugu White Clay as A Local Adsorbent

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***ABSTRACT** : In this work, the optimal parameters for the adsorption of MB by Enugu White clay as a local adsorbent was investigated. The clay was obtained from Enugu, South-East province of Nigeria. In the research work, the physicochemical properties, such as moisture content, volatile matter, specific surface area, and oxides of metals, and also the effect of thermal activation on them were analyzed. Standard gravimetric methods were used to characterized the clay. The pH value was determined with a pH meter, while the metal oxides and Silicate, Alumina and oxide of Fe, were determined using EEL flame photometer and Pye-Unican Spectrophotometer respectively. Adsorption kinetics and isotherms were also determined by carrying out experiments using a batch reactor, and the results showed that Psuedo second order kinetic model fits the MB, adsorption best, with rate constant of 0.2279g/mg.min and activation energy of 303.4J/mol.K. Equilibrium results showed that MB adsorption by Enugu while clay can be correlated using both Freundlich and Langmuir adsorption isotherms. Palm Oil was also used to test the bleaching performance of the activated clay, and the results showed the clay to be effective. Response surface methodology (RSM), via Central Composite Design,(CCD), was applied in the determination of the optimal adsorption conditions, as time – 100min, adsorbent dosage – 0.2g, pH – 8 and MB concentration 80mg//lit. The predicted concentration value was 82.83% at 0.967 desirability. The result showed that Enugu white clay has a good adsorptive capacity and can be used as a cheap and effective local adsorbent for the removal of pigments during refining of vegetable oils.*

***KEY WORDS:** Adsorption, Isotherm, Adsorbent, MB, Clay, Palm Oil.*

## 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 adsorption, [1]. Adsorption is present in many physical, biological and chemical systems and is used extensively in industrial processes for the purposes of separation and purification. The high cost of commercial adsorbents, especially activated carbon, restricts their uses and applications, [2]**,** and hence the need to substitute them with the unconventional, locally available, cheaper and environmentally friendly adsorbents. The utilization of locally available materials as a raw material in the production of adsorbents is in line with Nigeria's economic transformation agenda.

A wide range of materials have been researched for that purpose, [3], [4],and [5]. Adsorption kinetic studies are important in predicting the rate of pollutant removal from aqueous systems. [6**]**, provides information for selecting optimum operating conditions, identifying reaction pathways, understanding rate limiting steps and, are also essential for scaling-up of laboratory studies to industrial applications.

Adsorption isotherm or equilibrium data are fundamental requirements for the design of adsorption system. The equilibrium is achieved when the capacity of the adsorbent material is reached, and the rate of adsorption equals the rate of desorption. The theoretical adsorption capacity of an adsorbent can be calculated with an adsorption isotherm. Although, there are many adsorption isotherms, there are two basically well established types of isotherms; the Langmuir and Freundlich isotherms, ][7]. The significance of adsorption isotherm is that it shows how the adsorbate molecules are distributed between the solution and the adsorbent (solid) at equilibrium concentration on the loading capacity at different temperatures. Langmuir adsorption isotherm is often used for the adsorption of a solute from a Liquid solution. It is best known of all isotherms describing adsorption process, [8]**.** The adsorption isotherm may be expressed as;

$$\frac{q_e}{q_o} = \frac{q_e C_e}{1 + k_1 C_e} \quad (1)$$

The above equation can be rearranged to the Linear form;

$$\frac{C_e}{q_e} = \frac{1}{q_o k_l} + \frac{C_e}{q_o} \quad (2)$$

Where, $q_e$ – Amount of adsorbate adsorbed at equilibrium mg/g, $C_e$ – Equilibrium concentration mg/l, $k_L$– Langmuir adsorption constant related to energy of adsorption (L/mg), $q_o$ – Maximum adsorption capacity corresponding to complete monolayer coverage (mg/g).

The Linear form can be used for Linearization of experimental data by plotting $C_e/q_e$ vs $C_e$. The Langmuir constants $q_o$ and $k_L$ can be obtained from the slope and intercept of the Linear plot respectively, [9].

T he Freundlich isotherm is the earliest known relationship describing the adsorption equation, [8]. The work of Freundlich on Liquid - solid adsorption led to the formation of the empirical equation.

$$q_e = k_f C_e^{½} \quad (3)$$

Where, $q_e$ = amount of adsorbate adsorbed at equilibrium mg/g, $C_e$ = equilibrium concentration mg/L, $k_f$ and n are empirical constants depending on several environmental factors and n is greater than one. The Linearized form is obtained by taking logarithm of both sides of equation (3).

$$L_n q_e = L_n k_f + \frac{1}{2} L_n C_e \quad (4)$$

A plot of $L_n q_e$ vs $L_n C_e$ will be a straight Line, if the data follows Freundlieh adsorption isotherm. The constants can be determined from the slope and intercept of the linear plot, [10].

Ejikeme et al [11], had earlier worked on the optimal bleaching performance of acid activated Ngwulangwu clay, using Central Composite Design (CCD) to optimize the process variables.

In this work,

- The physicochemical properties of Enugu White Clay as well as the test palm oil were determined.
- The kinetic of MB adsorption by Enugu White Clay, which is important in predicting the rate of removal of impurities by the adsorbent was established.
- The activation energy for MB adsorption was also determined.
- Response Surface Method, via CCD, was used to find the most suitable conditions to optimize the process variables
- The interaction between the variables was analyzed by applying the ANOVA method of analysis

## II. MATERIALS AND METHODS

### *2.1 Sample Collection and Characterization*

The material for the research is Enugu White clay collected from Enugu in the South-Eastern province of Nigeria The adsorbent was collected during the peak of dry season (March) 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 was also determined. The Palm oil was also characterized before and after bleaching with the activated clay. Results are shown in table I

### *2.2 Methylene Blue (Stock) Solution Preparation*

A MB stock solution of 100 mg/l was prepared by dissolving 1g of methylene blue in 1000$cm^3$ (Litre) of distilled water. The desired concentrations for adsorption were made by diluting the stock solution.

### *2.3 Acid Activation of Enugu white Clay*

The dry sample of the raw clay was treated with 1.5M $H_2SO_4$ at acid to adsorbent ratio of 1:1. The activation was carried out in a around bottom flask. The slurry was continuously stirred at a temperature of 90$^oC$ for 3 hours. When activation was completed, the slurry was filtered and washed several times with distilled water until neutral pH was obtained. The sample was dried at 105$^oC$ to reduce moisture content. The dry sample was stored in an air tight container.

### *2.4 Thermal Activation of White Clay*

The materials for the experiment were; White clay sample, Crucible, Weigh balance, Furnace, Sieve plates, Piston and mortar. l00g 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, 100, 120,

and 150μm mesh sizes and stored in a dry container to be characterized and for bleaching experiments. The above procedure was repeated for temperatures of 200°C, 350°C, 650°C, and 1000°C, and different calcination times of 1, 2, 3, 4 and 5 hours. 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.

***2.5 Particle Size Distribution of Bleaching Clay.***

In this experiment**,** Laboratory sieve numbers 20, 40, 60, 80, 100, 120 and 150, and prepared Enugu white clay sample were used. The sieves were arranged into a nest of sieves with the coarsest on top and the finest at the bottom. About 150g of the clay sample was placed on the top sieve. To prevent loss of the particles, a lid was used to cover the top sieve and a solid tray at the bottom. The sieve nest was vibrated by gentle shaking of hand for 3 minutes. The nest was dismantled and the materials collected from each sieve weighed.

***2.6 Characterization of Enugu White Clay***

The clay was characterized before and after activation by the methods described in [12],[13],[14],[15], and [16], while the Chemical characterization experiments were also carried out to determine the level of metal oxides in the clay sample before and after activation with a view to knowing how to control the level in order to achieve the desired adsorptive power of the clay after activation. A Pye-unican 500UV, Visible Spectrophotometer, EEL Flame Photometer, and Clay sample. The Pye – Unican Spectrophotometer was used for the analysis of $SiO_2$, $AI_2O_3$, $Fe_2O_3$, while the EEL Flame Photometer was used for the analysis of CaO, MgO, $Na_2O$, $K_2O$ and $SO_3$. and the results are shown in tables I, and II

| **PARAMETER** | **Raw Clay** | **Activated Clay** |
|---|---|---|
| Moisture content % | 8.75 ±0.57 | 65 |
| Volatile matter % | 2.46 ± 0.04 | 0.5 |
| Fixed carbon % | 0.84 ± 0.08 | 0.62 |
| Specific Gravity g/cm$^3$ | 2.57 | 2.5 |
| pH | 5.7 | 7.3 |
| Bulk density g/cm$^3$ | 1.56 | 0.9 |
| Non Clay Residue (%) | 3.55 | 0.86 |
| Titratable Acidity (mg NaOH/g | 0.78 | 0.8 |
| $SiO_2$ | 63.39 | 62 |
| $AI_2O_3$ | 4.42 | 4.75 |
| $Fe_2O_3$ | 0.11 | 0.01 |
| CaO | 1.62 | 0.05 |
| MgO | 2.33 | 0.7 |
| $Na_2O$ | 4.10 | 0.58 |
| $K_2O$ | 3.48 | 1.25 |
| Ignition loss | 11 | 8.4 |

***Table I The physicochemical properties of raw and activated Enugu White Clay..***

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

| **Properties** | **Thermal Activated White clay** | **Fuller's Earth** | **Fulmont AA** |
|---|---|---|---|
| $SiO_2$ | 62 | 52.26 | 61.7 |
| $AI_2O_3$ | 4.75 | 14.33 | 12 |
| $Fe_2O_3$ | 0.01 | 3.04 | 5.7 |
| CaO | 0.05 | 3.02 | 4.1 |
| MgO | 0.7 | - | 2.3 |
| $Na_2O$ | 0.58 | 0.40 | 0.2 |
| $K_2O$ | 1.25 | 0.48 | 0.32 |
| Ignition loss | 8.4 | - | 6.2 |

### *2.7 Methylene Blue Adsorption*

The adsorption was carried out using batch adsorption method of [7]. A fixed amount of adsorbent (2g) was mixed with MB solution with concentrations of 50, 90, 110, and 150 mg/l at 30$^{o}$C. The system was agitated for 2hours, and the resultant solution filtered. The filtrate was analyzed with UV-spectrophotometer for the residual MB. The uptake of MB was calculated from the relationship, as given by, [17].

$$q_e = \frac{V}{m}(C_o - C_e) \quad \text{…….. (5)}$$

Where, $q_e$ - Amount of MB adsorbed at equilibrium mg/g, V -Initial volume of MB (litre), m–Mass of adsorbent (2g), $C_o$–Initial concentration of MB mg/L, Ce–Equilibrium concentration of MB mg/L.The experiment was repeated at 40, 50 and 60$^{o}$C.

### *2.8 Residence Time Distribution*

The effect of contact time on the uptake of MB by Enugu White Clay was investigated at MB concentration of 50mg/l at adsorbent dosage of 2g per 50ml of the MB solution. The experiment was carried out by shaking the adsorbent suspension in the MB solution for 20,40,60,80,100 and 120 minutes. The suspension was filtered and the filtrate analyzed for the residual MB using UV-spectrophotometer at 661nm wave length, a length corresponding to maximum absorbance, and the MB removal efficiency determined by;

$$\%\ \text{MB removal efficiency}\ q_e = \frac{(C_o - C_t)x100}{C} \quad \text{…….(6)}$$

The uptake of MB was calculated from [6], with the relationship given by;

$$q_t = v\,(C_0 - C_t) \quad \text{…….. (7)}$$

Where $q_t$ = MB adsorbed at time t (mg/g), v = Initial volume of MB (Litre), m = Mass of adsorbent used (2g), $C_o$ =Initial concentration of MB mg/L, $C_t$ = Concentration of MB at time t > 0 mg/l.

### *2.9 Bleaching Experiment*

The aim of bleaching is to test for the bleaching efficiency of the activated clay by reducing 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 and presented in tables III

***Table III, Physio-Chemical Properties of the raw and bleached Oils used in testing the performance of the thermally activated Enugu white clay***

| **Properties** | **Raw Palm Oil (RPO)** | **Bleached Palm Oil (BPO)** |
|---|---|---|
| Colour (Physical Appearance) | Deep Orange | Light Orange |
| Odour | ...of Palm Oil | … of palm fruit |
| Taste | ...of Palm Fruit | Bland |
| Specific Gravity | 0.9482 | 0.9242 |
| Melting Point(°C) | 36.5 | 34 |
| Moisture (%) | 1.5 | 0.05 |
| Refractive Index | 1.4516 | 1.4565 |
| Free Fatty Acid (%) | 2.80 | 3.0 |
| Lovibond Red Unit (1" Cell) | 21 | 3.2 |
| Anisidine Value (M.eq/kg) | 7.2 | 4.05 |
| Peroxide Value (M.eq/kg) | 48 | 3.00 |
| Phosphorous (Ppm) | 6.0 | 5.52 |
| Iron (Ppb) | 3.5 | 4.5 |
| Saponification Value | 210 | 215 |
| Iodine Value | 44 | 47 |

### *2.10 Optimization with CCD*

Optimization of the factors for the adsorption of MB by the activated Enugu Clay was carried out using Central Composite Design, a type of Response Surface methodology, RSM. The CCD had two factorial level with 3 numeric factors, which also had 6 axial points and 6 centre points. The factors and levels used for the CCD are shown in Table IV, while the design matrix with the responses is shown in table V.

***Table IV, Factors and levels for the RSM (CCD)***

| Variable | Units | $-\alpha$ | -1 | 0 | +1 | $+\alpha$ |
|---|---|---|---|---|---|---|
| Adsorbent dosage | Mg/g | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 |
| Initial concentration | Mg/l | 10 | 30 | 50 | 70 | 90 |
| pH | | 2 | 4 | 6 | 8 | 10 |

***Table V , CCD Design Matrix with responses.***

| Std. order | Run order | Factor 1 A: Adsorbent(g) | Factor 2 B: pH | Factor 3 C: Initial Conc.(mg/l) | Response MB Remove (%) |
|---|---|---|---|---|---|
| 4 | 1 | 0.20 | 8.00 | 80.00 | 83.8 |
| 13 | 2 | 0.14 | 6.00 | 50.00 | 72.32 |
| 11 | 3 | 0.14 | 2.00 | 110.00 | 48.22 |
| 15 | 4 | 0.14 | 6.00 | 110.00 | 69.99 |
| 2 | 5 | 0.20 | 4.00 | 80.00 | 59.33 |
| 16 | 6 | 0.14 | 6.00 | 110.00 | 65.32 |
| 3 | 7 | 0.08 | 8.00 | 80.00 | 60.12 |
| 8 | 8 | 020 | 800 | 140.00 | 70.14 |
| 10 | 9 | 0.26 | 6.00 | 110.00 | 76.11 |
| 20 | 10 | 0.14 | 6.00 | 110.00 | 63.12 |
| 6 | 11 | 0.20 | 400 | 140.00 | 52.11 |
| 14 | 12 | 0.14 | 6.00 | 170.00 | 83.13 |
| 7 | 13 | 0.08 | 8.00 | 140.00 | 45.12 |
| 17 | 14 | 0.14 | 6.00 | 110.00 | 60.52 |
| 9 | 15 | 0.02 | 6.00 | 110.00 | 50.01 |
| 12 | 16 | 0.14 | 10.00 | 110.00 | 80.51 |
| 1 | 17 | 0.08 | 4.00 | 80.00 | 56.72 |
| 5 | 18 | 0.08 | 4.00 | 140.00 | 42..31 |
| 18 | 19 | 0.14 | 6.00 | 110.00 | 62.17 |
| 19 | 20 | 0.14 | 6.00 | 110.00 | 58.22 |

## III. DISCUSSION

Tables 1 shows the results of the analyses of raw and activated Enugu white clay samples. It was observed that natural white clay was ideal in terms of non-clay residue, moisture content, ignition loss and titratable acidity, but low in bulk density. [18], noted that physical properties of clay influence their ability to adsorb carotenoids. [19], also showed 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 capacity. [20], in his experiment on natural clays, observed that high level of $SiO_2$ (about 63%), in a clay sample proves it to be montmorillonite. The results satisfy the condition.

### *3.1 Specific Surface Area*

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, [12].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, [21]. 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.

It was observed that $SiO_2$ of activated white clay is very good compared to Fuller's earth and Fulmont AA. $Al_2O_3$ and $Fe_2O_3$ 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, table II. 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 62, showing it to be a standard adsorbent. The removal of more soluble constituents vastly increased the specific surface area of the clay. [22], showed that these factors favour bleachability as the efficiency of the earth sample is proportional to its surface area.. Time of activation (contact time), which gave the best result was 4hours.The results of Table I were analyzed in, [22], [23] to [33].

### *3.11 Optimization of Parameters*

Numerical optimization was used to search the design space using the model created to find the factor setting that met the desired goal of maximal removal efficiency. With 20 solutions founds (table V), the optimal conditions were selected based on the highest desirability. The optimum conditions are: Adsorbent dosage of 0.2g, initial concentration of 80mg/l, pH of 8 with MB removal efficiency of 82.289% at desirability of 0.967. The optimum conditions were validated by repeating the adsorption at the predicated optimum conditions.

### 3.11.1 Analysis of Variance (ANOVA)

Analysis of variance is a method of dividing the variation observed in experimental data into different parts, each attributable to a known source. It shows if the factor or models in the experiments are significant, the result is shown in table X

***Table VI ANOVA Table***

| Source model | Sumof square | df | Mean square | F value | P-vallue prob>F |
|---|---|---|---|---|---|
| model | 2484.23 | 3 | 828.08 | 27.79 | <0.0001 |
| A-Adsrbent dosage | 801.88 | 1 | 801.88 | 26.91 | <0.0001 |
| B-$p^H$ | 801.60 | 1 | 801.60 | 26.90 | <0.0001 |
| C-Initial Conc | 880.75 | 1 | 880.75 | 26.90 | <0.0001 |
| Residual | 476.71 | 16 | 29.79 | 29.56 | |
| Lack of fit | 393.07 | 11 | 35.73 | 2.14 | 0.2076 |
| Pure Error | 83.65 | 5 | 16.73 | | |
| Cor Total | 2960.95 | 19 | 16.73 | | |

The Model F-value of 27.79 implies that the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate that model terms are significant. In this case A, B, C are significant model terms. Values greater than 0.1000 indicate that the model terms are not significant. The "Lack of Fit F-value" of 2.14 implies the Lack of Fit is not significant relative to the pure error. There is a 20.76% chance that a "Lack of Fit F-value" this large could occur due to noise.

R-Squared 0.8390
Adj R-Squared 0.8088
Pred R-Squared 0.7354
Adeq Precision 17.678

The "Pred R-Squared" of 0.7354 is in reasonable agreement with the "Adj R-Squared" of 0.8088. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 17.678 indicates an adequate signal.

### 3.11.2 Model Equations

(a) **Final Equation in Terms of Coded Factors:**

$$\text{MB Removal Efficiency (\%)} = 60.71 + 7.08 \times A + 7.08 \times B - 7.42 \times C \quad \text{.....(8)}$$

**(b) Final Equation in Terms of Actual Factors:**

MB Removal Efficiency (%)
= 50.16396 + 117.98958 x Adsorbent dosage +3.53906 x pH - 0.24731 x Initial Concentration…….(9)

***Table VII: Predicted Values, Actual Values, and Residuals***

| Standard Order | Actual Value | Predicted Value | Residual |
|---|---|---|---|
| 1 | 56.72 | 53.97 | 2.75 |
| 2 | 59.33 | 68.13 | -8.80 |
| 3 | 60.12 | 68.13 | -8.01 |
| 4 | 83.80 | 82.29 | 1.51 |
| 5 | 42.31 | 39.14 | 3.17 |
| 6 | 52.11 | 53.29 | -1.18 |
| 7 | 45.12 | 53.29 | -8.17 |
| 8 | 70.10 | 67.45 | 2.65 |
| 9 | 50.01 | 46.55 | 3.46 |
| 10 | 76.11 | 74.87 | 1.24 |
| 11 | 48.22 | 46.56 | 1.66 |
| 12 | 80.51 | 74.87 | 5.64 |
| 13 | 72.32 | 75.55 | -3.23 |
| 14 | 38.13 | 45.87 | -7.74 |
| 15 | 69.99 | 60.71 | 9.28 |
| 16 | 65.32 | 60.71 | 4.61 |
| 17 | 60.52 | 60.71 | -0.19 |
| 18 | 62.17 | 60.71 | 1.46 |
| 19 | 58.22 | 60.71 | -2.49 |
| 20 | 63.12 | 60.71 | 2.41 |

### 3.11.3 Validation of Model

To validate the model equations obtained for adequacy in predicting response, residual plots were used. ANOVA assumed that residuals were independent of each other and are distributed according to a normal distribution with constant variance. This is shown in table X, where the predicted , actual and Residual values were given according their standard order

### 3.11.4) Normal Plot of Residuals

The normal probability plot indicates whether the residuals follow a normal distribution, in which case the points will follow a straight line. Some moderate scatter, even with normal data were observed. Definite patterns like an "S-shaped" curve, which indicates a transformation of the response may provide a better analysis. This is shown in Fig. 1

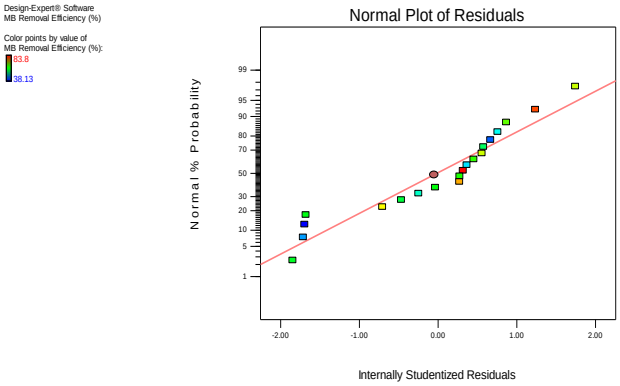



***Fig. 1 Normal Plot vs Residuals***

### 3.11.5 Residuals vs Predicted Plot

This is a plot of the residuals versus the ascending predicted response values. It tests the assumption of constant variance. The plot should be a random scatter (constant range of residuals across the graph.) Expanding variance ("megaphone pattern <"), in this plot indicates the need for a transformation, Fig. 2.

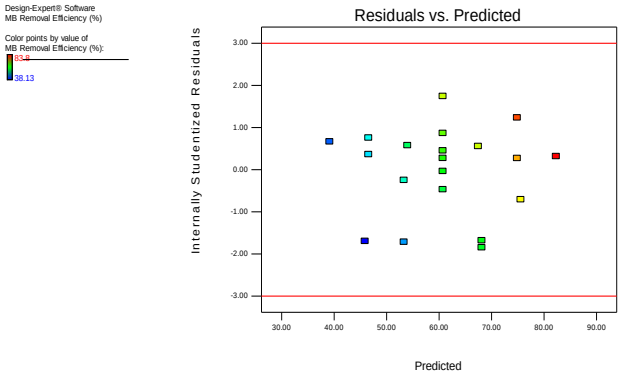



***Fig 2: Residuals vs Predicted Plot***

### 3.11.6 Residuals vs Run

This is a plot of the residuals versus the experimental run order. It allows you to check for lurking variables that may have influenced the response during the experiment. The plot showed a random scatter. Trends indicate a time-related variable lurking in the background. Blocking and randomization provide insurance against trends ruining the analysis. This is shown in Fig.3.

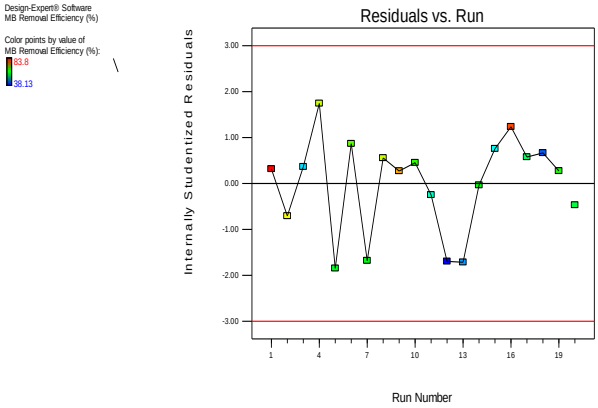



***Fig. 3: Residuals vs Run***

### 3.11.7 Predicted vs Actual

Figure 4 is the graph of the actual response values versus the predicted response values helps to detect a value, or group of values, that are not easily predicted by the model. The data points should be split evenly by the 45 degree line

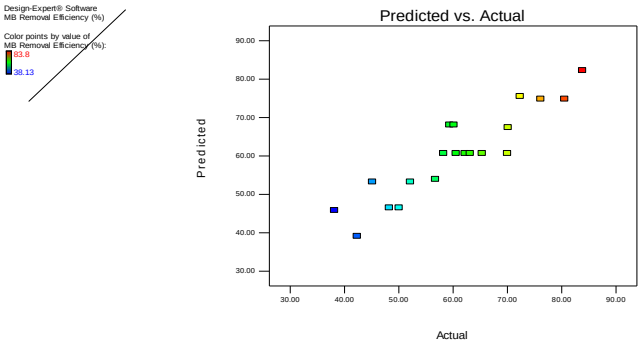
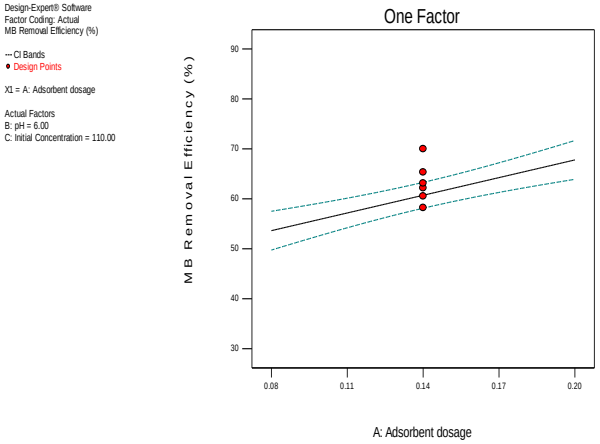


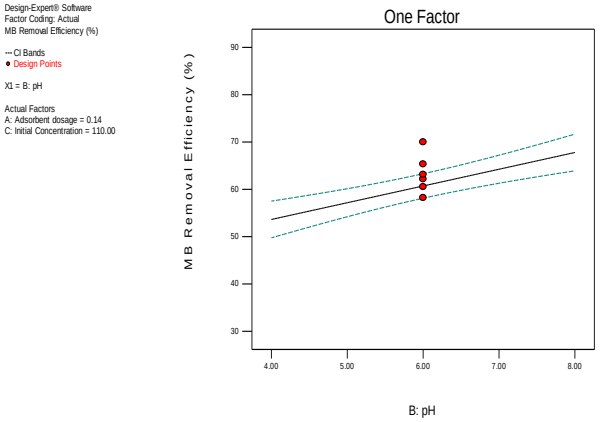

***Fig.4: Predicted vs Actual***

### 3.11.8 One Factor Plot (Bleaching Efficiency)

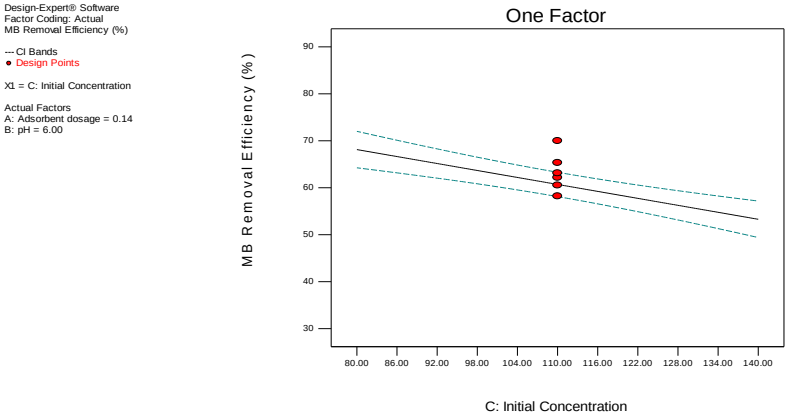
One factor plots are shown in Figs 5(a) to (c)




***(a) MB removal efficiency(%) Vs Adsorbent dosage***




***(b) MB removal efficiency(%) Vs pH***




***(c) MB removal efficiency(%) Vs Initial concentration***

***Figs 5, One factor plot of adsorbent dosage, pH and Concentration effects***

Fig. 5, shows the effects of the process variables on the removal efficiency of the activated Enugu white clay. It can be seen that the three factors of clay dosage, pH, MB Concentration had positive effects on the removal efficiency of Activated Enugu White clay. It therefore mearnt that as the factors increased, the removal efficiency increased. Fig. 5 (a), shows that the removal efficiency continues to increase as the clay dosage is increased. This could be attribited to the high surface area available foe adsorption. There tend to be no limit to clay dosage, but sound jugement is to stop clay increase at the optimum point when any additional clay dose did not result to a corresponding removal of MB. In Fig 5 (b), MB adsorption also increased with pH, as noted by [27]. This is because, according to [2], the degree of ionization is affected by the pH, which in turn affects adsorption. The effect of Concentration of Mb is shown in Fig.5 (c). As shown, the removal efficiency reduces with increase in concentration. It follows that the higher the intial conncentration of Mb, the lower the removal efficiency.

### 3.11.9 Two Factors Plot(interacting effect)

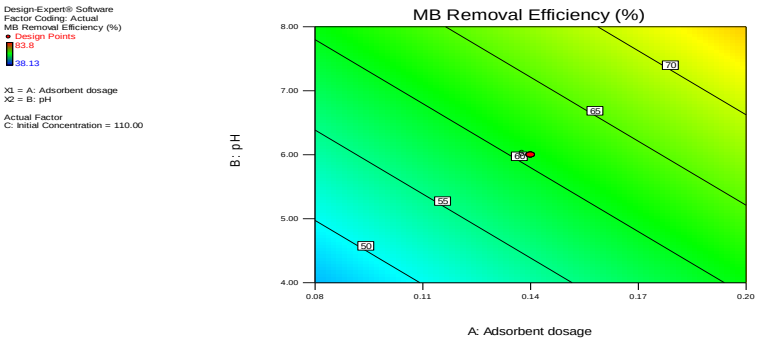



***Fig6 MB removal efficiency(%) of Adsorbent dosage and pH.***

Fig. 6 gives the interacting effect of the factors on the removal efficiency of Enugu White Clay. It is observed that as clay dosage is increased at both low and high pH values, the removal efficiency is increased.

### 3-D Surface plot of pH Adsorbent Interaction

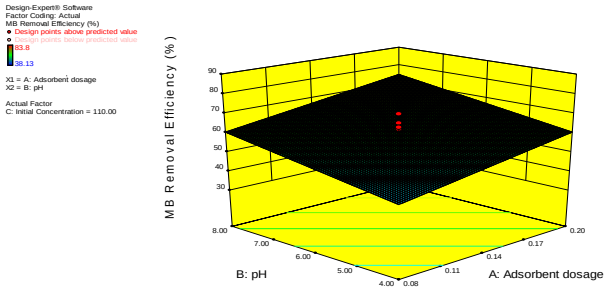



***Fig. 7 MB removal efficiency(%) of Adsorbent dosage and pH interaction***

The 3D plot of the interactive effect of pH and clay dosage is shown in Fig. 7. the result is a flat surface confirming that the model is linear. The surface is sloppy showing that the removal efficiency was reduced as the pH and clay dosage reduced, and the maximum efficiency was obtained aat high clay dosage, and high pH.

## IV. CONCLUSION.

The optimal process parameters on the adsorption efficiency of activated Enugu White Clay and on the bleaching performance of palm Oil, has been investigated. Response Surface Methodology, a type of Central Composite Design, was successfully applied in the experimental design in order to study the effect of the key parameters of pH, Time and Clay Dosage on the adsorption efficiency of MB on the activated clay, and the conditions for the optimal adsorption efficiency were found to be, pH, time and clay dosage of 8, 100min. and 0.2g respectively, at MB concentration of 80mg/lit. The predicted concentration of 82.83% has a good correlation with the actual value of 80%. Validation was done by repeating the experiments at the predicted optimum conditions as shown in table XI. The results obtained from the optimization of the adsorbed MB parameters showed that the adsorption efficiency is linearly affected by pH, and contact time, and quadratic dependent on adsorbent clay dosage, as these can be interpreted from graph and chart shown above. pH, and

clay dosage invariably increase the degree of adsorption of MB. The good correlation between the predicted and experimental values shows that the method adopted is good enough for the process and that all the process variables of pH, contact time, and clay dosage were significant.

## REFERENCES


[1] L.M. Warren., C.S Julian., and H Peter., Unit Operation of Chemical Engineering, 6th edition. (McGraw – Hill Book Co-Singapore. 2001).

[2] R. Malik., D.S. Ramteke, and S.R. Wate., Physicochemical and Surface Characterization of Adsorbent prepared from Groundnut Shell by $ZnCl_2$ activation and its ability to Adsorb Colour. Indian Journal of Chemical Technology, vol. 13, 2006, pp. 319 – 328.

[3] B.J. Nde – Age., R. Kamga, and D. Nguetnkam, J.P. Adsorption of palm oil Carotene and free fatty Acids onto Acid Activated Cameroonian Clays. Journal of Applied Sciences 7 (17), 2007. 2462 – 2467.

[4] A.U. Itodo, F.W, Abdulrahman, L.G., Hassan, S.A, Maigandi, H.U Itodo., Physicochemical Parameters of Adsorbent from Locally Sorted $H_3PO_4$ and $ZnCl_2$ Modified Agricultural wastes. New York Science Journal Vol. 5, 2010. PP.17 -24

[5] J. Kyziol., Effect of physical properties and cation Exchange capacity of sorption of Heavy metals onto Peat. Polish Journals of Environmental studies Vol. 11, 2002. pp 713-718

[6] H. J. Michael, and L.V. Jose., Kinetic Study of Liquid-Phase Adsorptive Removal of Heavy Metal Ions by Almond Tree Leaves Waste. Bulletin of Chemical Society of Ethiopia, 2007. PP. 349 -362

[7] A.A., Mohammed, Thermodynamic Approach in Adsorption of Heavy Metals.Mutah University Jordan.pp737-764 2012. (www.itechope.com)

[8] A.A. Nagham, The Use of Local Sawdust as an Adsorbent for the Removal of Copper Iron from Wastewater Using Fixed Bed Adsorption. Engineering and Technology Journal, Vol. 28, 2010., PP. 224 – 235.

[9] A. Esmaeli, S. Ghasemi, and A. Rustaiyan., Evaluation of the Activated Carbon Prepared from Algae Gracilaria for Biosorption of Cu(II) for aqueous Solution. African Journal of Biotechnology Vol. 7 (12). 2008

[10] E. Erdem, N. Karapinar, and R. Donat., The Removal of Heavy Metal Cations by National Zeolites. Journal of Colloid and Interface Science 280, 2004. pp. 309 – 314.

11] M. Abubakar., A.A Alechenu., A. Manase, and J. Mohammad, Comparative Analysis and characterization of Animal Bones as Adsorbent. Advance in Applied Science Research Vol. 3 (5), 2012.,PP. 3089 -3096.

[12] C.U., Echeji, Kinetics of the Adsorption of Carotene from Palm Oil on Activated Carbon from Enugu Coal. PhD Thesis, Enugu State University of Science and Technology, 2012.

[13] S., Yoshiyuki, and K. Yutaka., Pyrolysis of plant, animal and human waste. Physical and chemical characteristics of the pyrolytic product. Bioresources technology, Vol. 90 9(3), pp. 241-247, 2003.

[14] D.A. Salwa, and E. Essan., Characterization of Egyptian Smectitic Clay Deposits by Methylene Blue Adsorption. American Journal of Applied Science, Vol. 8, 2011, PP. 1282 – 1286

[15] G.Kahr, and F.T. Madsen., Determination of the Cation Exchange Capacity and the Surface Area of Bentonite, Illite and Kaoline by Methylene Blue Adsorption. Applied Clay Science Vol. 9, 1995, PP. 327-336.

[16] Y. Yukselen, and A. Kaya., Suitability of the Methylene Blue Test for Surface Area, Cation Exchange Capacity and Swell Potential Determination of Clayey Soils. Journal of Engineering Geology, Vol. 102, 2008, PP. 38 –45.

[17] B. Volesky, Bisorption and Biosorbents in Biosorption of Heavy Metals. CRC Press: Boca Ration, pp. 3-5, 1990.

[18] P.G.Nutting., Adsorbent Clay , USA eologycal Survey Bulletin, 928, Pp127, 1945.

[19] L.L Richardson,. Use of bleaching Clays in Processing Edible Fats and Oils. J.AOCS.Pp55,777-780, 1988.

[20] T.C. Soon.,and P.B. Shaw., Factors affecting the stability of oil during physical refining of palm oil, Laporte, Malaysia. 1993.

[21] B.C. Amy., Influence of specific surface area on geotechnical characteristics of fine grained soils. Master of science thesis university of masschusetts, 2001.

[22] S.J. Gregg, and K.S.W.Sing., Adsorption Surface area and Porosity, 2nd ed., Academic Press, London,1982.

[23] Ethre-Snell, Clay and Clay Minerals, Interscience Publishers, New York. 1970.

[24] M.J. Suess., Surface Area Measurement and Adsorption of soil. Journal of Irrigation and Drainage Proceeding of the American Society of Civil Engineers, 1964. pp. 87-108.

[25] C.R.De Kimpe., M.R. Laverdiere., and Y.A. Martel., Surface Area and Exchange Capacity of Clay in Relation to the Mineralogical Composition of Gleysolic Soils. Canadian Journal of Soil Science, Vol. 59, No.4 1979.

[26] M.L., Thompson, H. Zhang., M.Kazemi, and J.A.Sando., Contribution of Organic Matter to Cation Exchange Capacity and Specific Surface Area of Fractionated Soil Materials Soil Science. Vol. 148. No 4. 1989, Pp. 250-257.341–347.

[27] G.M., Walter., J.A. Hanna.,and S.J Alen., Treatment of Hazardous Shipyard Wastewater Using Dolomitic Adsorbent. Wat Resources 39, PP. 242 - 248, 2005.

[28] C.H. Lai., and C.Y. Chan., Remoral of metal ions and Humic Acid from water by Iron-coated filter media. Chemospher, 44, PP. 1177-1184, 2001.

[29] J. Bea., S Bhetia., P.Massaratto., Conference proceeding. The 3rd Assia – Pacific coal bed Methane symposium, Brisbana Australia, 2012.

[30] J A. Ibemesi., E. C. Achife., Use of Local clay as decolourizing agent for vegetable oils, Journal of Mining and Geology, Vol. 26, 1,1990.

[31] U.I. Bumberg., Kinetics of bleaching of Vegetable,1988.

[32] D.B. Belaw., G.K. Tribe., The activated earth in Palm Oil refining, and its effects on trace metal contaminants, 1972.

[33] W.J. Weber Jr., and F. O. Digino., Process dynamics in environmental system; Environmental;*scienc and Technology series*, *John Wiley and sons*: New York, 2006, PP 80 -94