

Optimizing The Adsorption of Methylene Blue Dye onto Raw and Modified Ekowe Clay using RSM

Daniel C. Emeniru, Okechukwu D. Onukwuli, Pere-ere Douye Wodu, Livinus A. Obasi

Abstract: - This study explicates the optimum condition for effective and efficient uptake of cationic dye onto raw and modified (acid activated and calcined) Ekowe clay. The clay modification spanned 750°C calcination of RS to produced RCS and 0.5M_{H₂SO₄} activation of RS then 750°C calcination to produce ACS. The pH, acidity, CEC, PZC, surface area and filtration rate opened the adsorptive characteristics of the clay samples. Factors' combinations of the RSM-CCRD (Central composite rotatable design of Response Surface Methodology) were applied in the batch adsorption experiments for statistical evaluation and Optimization of the Methylene Blue (MB) uptake. Calcination incurred structural and morphological change enhancing porosity and total surface area of the clay. The RSM showed; the correlation of MB uptake and studied variables fitted quadratic model, showing uptake variation with time, pH, dye concentration, clay amount and temperature. The analysis of variance exposed that all main factors influenced MB uptake. The effective and material economic optimum result: 66.92%, 62.79% and 53.53% MB uptake for ACS, RCS and RS respectively at conditions of 47min, solution pH-3, 20mg/L dye concentration, 0.35gclay and 25°C showed that calcination of raw and activated Ekowe clay enhances its optimum adsorptive capacity for MB dye uptake.

Keywords: Activation, Calcination, Adsorption factors, RSM, Quadratic model, Statistical Analysis, ANOVA, Optimization.

I. INTRODUCTION

As a major component of agriculture and manufacturing, good water management is very essential for good health and comfort, the end purpose to every human endeavour. Since we cannot make or produce water it is necessary to manage and conserve the much nature has made available. Population explosion, haphazard rapid urbanization, industrial and technological expansion, energy utilization and waste generation from domestic and industrial sources have rendered surface and underground waters, the major source of daily used water, unwholesome and hazardous to man, other living organisms and the environment around them. Besides the porous environmental laws and enforcement strategies which have allowed the discharge of untreated domestic and industrial effluent into waterways, the government has over the years being unable to meet the ever increasing water demand hence local and urban inhabitants have had to look for alternative water sources such as streams, shallow wells, boreholes and even ponds which are the likely reservoir for the hazardous effluents.

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This calls for great need for water to be highly safe for both domestic and industrial use. Literature has revealed that the entry of potentially hazardous substances into the ecosystem is increasing exponentially day by day. Contamination of water spans the presence of excess of free elements and compounds, natural organic matters, and variety of pathogens capable of effecting various water-borne diseases, food poisoning, and the breakdown of some industrial machinery. Amongst the numerous water contaminants dyes in wastewater is highly visible and can obstruct light penetration (Chang et al., 2004) which is harmful to aquatic flora and fauna. Literature has revealed that dye in wastewater resulting mainly from coloured allied industrial waste as well household discharge is very stable to light irradiation and heat, and has defied biologically decomposition due to the complex structure making dye removal stringent and typical. Like all other water contaminants, the alleviation of dye in water and wastewater can be achieved by adsorption with an efficient natural or modified adsorbent. Being the most popular processes for dye removal, there is need to enhance the adsorption mechanism and improve the effectiveness via optimizing the dye uptake.

The advent and application of clay, a remarkable phyllosilicate of diverse species with regards the mineral composition and of high proclivity of adsorption, has lessened the constraint of affordability, availability and application friendliness typical of activated carbon and other biosorbents. Studies have proven clay adsorbent can be modified to enhance effectiveness, recyclable (regeneration) and has high dye uptake efficiency relative to activated carbon. It is profoundly popular that virtually all phyllosilicates would adsorb dye however; the extent of adsorption and the best condition for the most considerable adsorption is exceptional in choosing clay adsorbents.

The designing of experiment and standardization of variables affecting a system is very critical in optimization process (Narayana et al., 2011) were Response Surface Methodology (RSM) is called into play. The primary goal of designing experiments has been identified to entail finding the operating conditions that maximizes or minimizes the response of interest. RSM employs experimental design which usually applies before regression analysis is employed to evaluate the accuracy of a process model. It entails mathematical and statistical techniques in the development of adequate functional relationship between the process response of interest, Y and a number of associated control/input variables, x_1, x_2, \dots, x_n (Khuri and Mukhopadhyay, 2010) to proffer valid, reliable and sound conclusions regarding the effectiveness, efficiency and economical authenticity of the process under study. It is commonly portrayed as the processes of identifying and fitting an appropriate response surface model to an

experimental data thereby studying the significance of the effect the factors supposed to have influenced on the studied response. It describes and explains the relationship between one or more responses and a group of variables. Central Composite Design (CCD) makes-up the characteristic pit fall of normal full factorial first and second order designs such that when the models show an evidence of lack of fit, axial points are added to the quadratic terms with more center points. While the center points contain information about the surface curvature, the axial points allow for the experimenter to obtain an efficient estimation of the quadratic terms. Central Composite Rotatable Design (CCRD) is a CCD where the precision of the estimated response surface at some point, x depends only on the distance from x to the origin, not on the direction, and variation on the response, y remains same when the design is rotated about the center implying there is provision of equal precision of estimation of the surface in all directions. Since the reason for using response surface analysis is to locate unknown optimization, rotatable design became more preferred. CCRD, one of the experimental designs applicable in RSM, is easier to handle and preminent when considering the optimization of a process with ≥ 3 factors at a time. The main idea of the CCRD is to use a sequence of designed experiments to obtain an optimal response. RSM comprises of statistical experimental design precisely full factorial and fractional factorial designs; regression modeling techniques and optimization method (Zenganch et al., 2002). Full factorial design is typical of < 3 factors at two levels so as to avert impracticability of high number of experiments. The advent of fractional factorial design lead the consideration of > 3 factors at ≥ 3 levels. RSM, as regards fractional factorial design, aids and enhances practical engineering purposes, where high costs of performing advanced numerical analysis is not desirable and time is of essence. Bradley, (2007) have linked the sole objective of RSM to the optimization of process responses and the understanding of how the response changes in a given direction by adjusting the design variables. Therefore the CCRD factorial design still stands revolutionary in most chemical engineering processes where RSM is applied.

In order to get the most efficient result in the approximation of quadratic models, it is necessary the proper experimental design is applied to collect data after which the ANOVA of the RSM employs the least square method and response surface plots in the data analysis. The regression model, a mathematical model, defines the relationship between the independent variables (factors, x_i) and the response, y . The suitability of quadratic model to RSM is anchored on its flexibility to take on a wide variety of functional forms, works well as approximation to a true response surface problem, ease in the estimation of model coefficients (β s) applying least square method, and capability to augment surface curvature. Though first order model can approximate a true response function, its application does not accommodate surface curvature that is remedied in the second order (quadratic) model as considered in this work. The ANOVA of the choice RSM model reveals factors and interactions of significant effect on the response of interest. Having that response surface plot is not a plane, mainly for > 3 factors designs, it is more complicated to determine the

optimum value using the 3D or contour plots rather the plots can only help characterize the surface shape to aid locating the optimum response approximately. The surface shape could present a minimum, maximum, ridge and/or saddle.

Optimization has gained importance in the field of engineering and manufacturing, typically in chemical engineering research and wastewater treatment processes. Experimental optimization as applied in this study for response surface models is most preferred in that: it finds approximate good models and iteratively (allowing the fitted model of one to be applicable in determining the operating conditions of another experiment) searches for near optimal operating conditions, considered the effect of randomness which is known to affect final results, and necessitates the input of the experimenter. To achieve optimum objective, more efficient material and operating conditions play significant roles in the material economy, performance and effectiveness. In this study, the objective of MB dye uptake and material effectiveness can be ascertained by the optimum conditions (variables): contact time, solution pH, initial MB concentration, clay amount, Temperature and highest uptake.

This is achievable, like in all fields of inquiry, by carrying out experiments which entails making purposeful changes in the input process variables so as to find out what effect these changes would have in the process. Optimizing the uptake of MB dye therefore requires a response surface model that would represent the way that each factor and their interactions partake in determining the studied response. Clay samples from many urban and rural areas in Nigeria have not being considered for studies, presumably, either clay in these places have not caught research interest or there is barrier of remoteness in sourcing the clay. Seemingly, the potency of Nigerian clays in the adsorptive removal of contaminants from waters is not amply verified in the literatures, in spite the abundance of the mineral especially in the southern Nigeria.

The Ekowe clay affinity for synthetic dye, a chemical that has defied bio and thermal degradation, is revealing considering the clay has not been documented in the literatures and the weight of colour alliance in most Nigerian products. Though extensive studies have centered on activation modification, calcination and its combination with activation have remained very scanty. This study therefore seeks to modify a Nigerian clay (Ekowe clay) applying calcination (high temperature pyrolysis) into a colour scavenging and affinitive characteristics adsorbent for the optimal removal of MB dye, a prototype textile effluent. This vied to evaluate the efficiency and effectiveness of the raw and modified clay in treatment of coloured effluents such as that being emptied into water sources.

The characterization of the Clay samples with regards to its influence to dye uptake covered PZC, CEC and surface area of the samples. The batch adsorption study spans the consideration and analysis of the adsorption factors: contact time, dye concentration, clay amount, aqueous dye solution pH and process temperature. The optimum conditions and MB uptake was approximated using the RSM for the studied samples: raw (RS), raw calcined (RCS) and 0.5M H_2SO_4 activated-calcined (ACS).

II. MATERIALS AND METHOD

A. Materials

The equipment, apparatus and all the chemicals; analytical grade reagents, solid granules and powders, used were properties of Springboard Laboratory, Udoka Housing Estate, Awka, Anambra state.

B. Adsorbent Preparation

The crude clay, mined from an excavated swampy site at Federal Polytechnic Ekowe, Bayelsa state was first purified by washing in its source water to remove sand and suspended organic matter. Then washed trice with distilled water to remove impurities (dissolved chemicals impurity) relative to the source water. The purified raw clay was allowed to dry at ambient temperature for four (4) days, covered with sieve cloth material to prevent dust and other solid impurities. The purified clay was further dried in an oven at 45°C for about 24hrs and referred as raw clay, RS. The raw Ekowe clay sample (RS) was modified by activation and calcination to suit the requisite samples scoped for this study.

A quantity of RS was mixed with sufficient amount of 0.5M H₂SO_{4(aq)} solution in a beaker and mixture was heated in an electronic thermostatic water tank for 3hrs at 90°C. The heated mixture was allowed to cool, decanted and the activated clay sludge was washed with distilled water until it was free of SO₄⁻² ions by indicating a neutral pH (≈7) with a pH indicator paper. The activated sample was dried in an oven at 40°C for 3hrs and crushed. Raw and activated samples were calcined in a muffle furnace at 750°C for 4hrs to produce raw-calcined sample (RCS) and activated-calcined sample (ACS). The calcined samples were cooled in a desiccator, crushed and sieved with 75µm sieve (200 Mesh ASTM). The RS, RCS and ACS were packaged in polyethylene bags and stored to be used for the adsorption experiment.

C. Solution Preparation

The calculated amounts of the chemicals (solids/granules) were dissolved in corresponding amount of distilled water and the dilution theory applied to prepare the stocks and solutions of required experimental concentration. The experimental concentrations (20, 25, 30, and 35mg/L) of Methylene Blue (MB) (C₁₆H₁₈N₃SCl.3H₂O) were obtained by dilution of 5g/L dye stock solution prepared from 5g of the commercial MB dye.

D. Batch adsorption studies

Following the influence of adsorption factors: pH, contact time, initial adsorbate concentration, adsorbent amount and temperature, being widely considered in studies that investigate experimental factors' effect on target responses, batch mode has been ascertained and frequently used as the best mode that will provide runs on which the factor effects can be checked. Duplication of experimental runs is known to authenticate and ascertain regularity of experimental values for parameters determination and statistical error control. The mass balance equation below gives the adsorbate uptake onto the adsorbent:

$$q_t = \frac{C_0 - C_t}{m} V$$

(1)

q_t is the dye uptake after the experimental time (g/g), C_0 and C_t are the dye concentrations at $t=0$ and $t=t$, m is the amount of clay used and V is the volume of dye solution.

Experiment: Blank runs (without clay) were undertaken using 50mL MB solutions of 25mg/L and 35mg/L at solution pH 7.20 and 40°C for 50min to verify adsorption on glassware. The dye stained the walls after 24hrs of stocking. Therefore, dye solutions were prepared and used daily.

In the actual experimental runs, the uptake factors were varied according to the design matrix of *Table 3* at constant solution volume (0.03L). The use of centrifuge was employed after each time interval to obtain the residual solution and the residual dye concentration was determined from the Absorbance obtained using the APEL PD-3000UV spectrophotometer at a wavelength of 610nm. The absorbance was converted to concentration using the linear calibration graph.

E. Response Surface Methodology

Fazeli et al., (2012) cited the choice of experimental design as being dependent on the type of problem, the number of factors as well as their levels. Factors >4 and level ≥4 for experimental designs in RSM have been applied sparsely in adsorption especially for clay and MB dye studies therefore as applied in this work, higher order (≥3) interaction effects were neglected and fractional factorial design was adopted as manipulations to reduce the number of required runs for the estimation of the 5factors, 5levels effects and the significant factors that affect the MB uptake.

The choice of α determines the ratability of the CCD as defined by $\alpha = 2^{q-k/4}$ for a fractional factorial design. The fractional factorial design ($q=5$ and $k=1$) as adopted have an axial distance $\alpha = \pm 2.00$. The number of design points in the CCRD was based upon a one fraction (1/4) fractional factorial design yielding 16 factorial points (obtained from 2^{q-k} ; number of variables/factors, $q = 5$ and fraction, $k = 1$), 6 central points; and 10 axial points (obtained from $\alpha = 2q$) making the 32 experimental runs in *Table--*. As cited in Montgomery (2000), center point experiments should always be included in factorial designs to minimize the risk of missing non-linear relationships at the middle of the intervals and to aid the determination of confidence intervals. The design runs as adopted in the experimentation were randomized though reported in standard order. Randomness minimizes the effects of the uncontrolled factors and annuls the potency of having different optimal operating conditions resulting from the different fitted response surface models, likely of a repeated experiment.

Though first order polynomial of RSM can approximate a true response function, its application does not accommodate surface curvature that is remedied in the second order polynomial typical of Central Composite Rotatable Design (CCRD). The second order polynomial known to be the best and so applied in this study; five factors were considered and analyzed using design expert version 9. Following the postulate of Mayers and Montgomery (1995), the true response of an adsorption system, Y , depends on n controllable input factors (x_1 ,

x_2, \dots, x_n) which culminates into the condensed functional expression:

$$Y = f(x_1, x_2, \dots, x_n) + \varepsilon \quad (2)$$

Where x_i is input factor, f is the true response function (usually unknown and complicated) and ε representing sources of variability not accounted for in f , often considered as statistical error.

The uptake analyses were based on the response surface model developed as shown below in condensed and actual form:

$$Y = \beta_0 + \sum_{j=1}^q \beta_{1j} x_j + \sum_{j=1}^q \beta_{2j} x_j^2 + \sum_{i < j} \beta_{ij} x_i x_j + \varepsilon \quad (3)$$

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_5 x_5 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{44} x_4^2 + \beta_{55} x_5^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{14} x_1 x_4 + \beta_{15} x_1 x_5 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4 + \beta_{25} x_2 x_5 + \beta_{34} x_3 x_4 + \beta_{35} x_3 x_5 + \beta_{45} x_4 x_5 + \varepsilon \quad (4)$$

Where y is the response, β is the regression coefficient, β_0 is the intercept term, the main effects terms, β_i ; the quadratic effects terms, β_{ii} ; and the interaction effect terms, β_{ij} . The above quadratic model for the uptake being a linear function of β , the linear regression analysis technique is most adequate (Kathleen et al., 2004).

Table 1: Actual and coded factors and levels

Un-coded Factor	Coded Factor	Levels				
		-a	-1	0	1	a
Contact time (min)	X ₁	20	50	80	110	140
pH	X ₂	3	5	7	9	11
Dye Conc. (mg/L)	X ₃	15	20	25	30	35
Clay Amt. (g)	X ₄	0.2	0.3	0.4	0.5	0.6
Temp. (Deg.)	X ₅	20	30	40	50	60

The independent variables, experimental range and levels investigated for the CCRD are reported in Table 1. Formulating the design matrix (Table 3) for the coded factors applied (5) to yield the low and high level code: -1 and +1 respectively.

$$x_i = \frac{x_i - x_{cp}}{\Delta x_i} \quad (5)$$

With coded value of variable (x_i), actual value of variable (x_i), real value of variable at the center point (x_{cp}) and the step change value (Δx_i).

The analysis of variance (ANOVA) fitted the data to the response surface quadratic model hence characterizing the model. It explained the influence of all the experimental variables' main and interaction effects and evaluates R^2 , and the model equations and coefficients in terms of the coded and actual variables. The ANOVA was predicated on the assumptions that: the expected values of the errors are zero, the variances of all errors are equal to each other, the errors are independent and the errors are normally distributed. Main effect does not mean the principal effect of a variable rather it entails the effect of a variable averaged over all values of other variables involved. In a system that is typical of interactive effect, main effect interpretation is a pseudo concept that cannot appropriately describe the system. The interaction effect, which explains the dependence of one variable on the levels of the other variables, supersedes the main effect because most often than not there are more than one factor considered in an experiment. The analysis spanned the main, quadratic and two factor interaction effects. The three factor interactions and higher order interactions are of no interest in an experiment and to an experimenter hence, to ensure simplicity of model was neglected.

Provided the fitted model equations approximate adequately the true (unknown) process responses, the optimum operating conditions of the model will be close to the optimal operating conditions of the experiment (true system). Response surface 3D and contour plots were generated to understand the interaction of different variables. The optimal points for the variables were obtained from which the process was optimized.

Design Expert software version 6.0.6 and 9.0 (STAT-EASE Inc., Minneapolis, USA) was used for the experimental designing, modeling, model fitting, statistical analysis of the experimental data to evaluate its fitness to the model equations developed and to evaluate the statistical significance of the equations and optimization of the process.

Table 2: Analytic Characterization

Sample	pH	Acidity (%)	PZC	CEC (cmolKg ⁻¹)	Surface Area (m ² g ⁻¹)	Filtration Rate	
						Time (Min.)	Rate (mL/m ² S)
RS	5.52	32	2.67	10.54	22.04	29.00	6.050
RCS	5.41	39	2.46	16.11	30.36	25.00	7.018
ACS	5.72	47	2.50	8.11	40.92	23.63	7.423

III. RESULTS AND DISCUSSION

A. Modification

Acid activation of clays limits the possible decomposition of the crystalline structure and increase the specific surface area (Bhattacharyya & Gupta 2009). Higher activation acid concentration is capable of causing adsorbent framework collapse more particularly under severe activation conditions. The activation acid, H₂SO₄, likely has produced a progressive dissolution of the octahedral sheets; the edges of the platelets of the raw clay structure were opened creating micro-porosity between the tetrahedral

silicate sheets that maintained the skeleton of the clay mineral and contained the silanol groups thus, both the specific surface area and the pore diameter increased. Surface area enhancement with activation modification is portrayed in the value difference of RCS and ACS (Table 1) as well as their relative filtration rates could imply structural changes due to activation. The high pH of ACS suggests that activation could have altered the acidic structure of the clay making it prone to forming hydrolyzed basic compounds in solution in lieu of the acidic ion, SO²⁻.

Calcination in clay study has scantily been applied for heavy metal (Aivalioti et al., 2010) mainly on the resolve of its high capacity of improving surface area via porosity

enhancement and mineral transformation. Calcination influences the crystalline structure of adsorbent materials hence improves fineness and porosity; surface area as seen with the relative values of RS and RCS. Calcination as applied in this work is based on its propensity of total surface (area) improvement, enhancement of pore volume distribution, clay minerals transformation to suit its use and the enhancement of the reactive properties of the clay minerals. The low filtration rate for RS could be ascribed to organic matter content which was lost on calcination as explained by the increase in the rate of RCS, recalling that carbonization, calcination phenomenon, is typical pore opening. Calcination time and temperature within 4hour and 750°C respectively have been reported by Aivalioti et al. (2010), Hefne et al. (2008), Talaat et al. (2011), Krishna and Gupta (2006 & 2009). Table 1 illustrates the order of increasing surface areas as RS<RCS<ACS. The increase can also be attributed to the removal of admixtures or hydroxyls through volatilization at high temperature (Aivalioti et al, 2010).

The modifications' surface area and porosity enhancement altered the filtration rates of the modified samples such that their high rate value (Tab. 1) implied high porosity according with the penetration postulate of availing all the sorbent surfaces for sorbate interaction.

B. Effects of the Adsorption Factors

The effect of the experimental and statistical model factors were analyzed on the basis of the influence of the factors with respect to the response under consideration, dye uptake. The analysis as elucidated below is based on the main effect plots of the ANOVA for the MB dye uptake on the various samples. In lieu of the above, the main effects of all the samples were in concordance with respect to the modifications and their expected effect.

Contact time: Generally, contact time enhances adsorption up to a point of dynamic equilibrium or onset of desorption. It is an effective and economic optimization factor. Adsorption is a function of time; Ramamurthi, et al. (2009) and Njoku, et al. (2011) reported adsorption equilibrium time to be adsorbate concentration dependent. In the time effect plot below (Fig.1a), the rapid increase in uptake with time is consistent with all cases in the literature. The fall in uptake with increasing time ($t > 80$ min) can be attributed to desorption probably due to agitation and competition for adsorption site. However, though the time for max uptake is approximately the same for all samples; the uptake at the max. time differ as shown in the plots: ACS \approx 59, RCS \approx 58 and RS \approx 48.

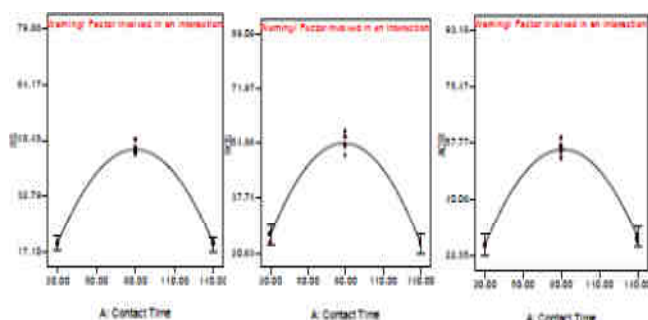


Fig. 1a: Plots for the effect of contact time

pH: At low pH, silica attracts cationic sorbates by coulombic forces while the negative charge density on the surface of the sorbent decreases as the pH increases. Cations are presumed competitive in ion-exchange processes thus, high acidity; though lower than minimum acidity of precipitation, is said to favour cation exchange via hydrolysis (Inglezakis, et al. 2007). The charge sign on clay surface is dependent on the pH of submerging solution. Fig. 1b shows a plot of decreasing uptake with increasing pH up to pH7 around which the lowest uptake was observed for all the samples. However, uptake increased with increasing pH from $7.4 \leq \text{pH} \leq 7.2$ to 11. It is emphatic that surfaces of insoluble hydroxides like clay protonates in acidic medium and deprotonates in alkaline medium. The decrease in uptake with increasing pH may be linked to successive protonation reduction and deprotonation enhancement of the clay resulting in subsequent electrostatic repulsion between increased positively charged sites on the clay and the dye cations. Around the neutral pH (7), like charge repulsion persistence could be responsible for the minimum uptake. In the concept of PZC, clay surface has been revealed to exhibit amphoteric behavior; capable of developing either a positive or negative overall surface electrical charge. As a result, at $\text{pH} > 7$, where the solution assumes the properties of alkalinity, the clay surface act as proton donors (deprotonation) leaving the surface with negatively charged sites that enhanced cation attraction and increased dye uptake. This is in concordance with Narayana et al, (2011); S. Chatterjee et al. (2009). The plots and Table 3 revealed best uptakes at extreme pHs with highest uptake at pH3 for all samples/cases: uptakes at pH3 and 11 showed percentage difference of 4.84% for RS, 7.14% for RCS, 9.34% for ACS.

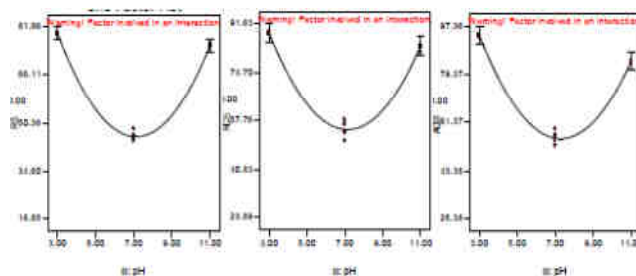


Fig. 1b: Plots for the effect of pH

Adsorbent Dosage and Initial Concentration: Depending on adsorbent quantity and efficiency, uptake is more effective at high adsorbent quantity and low adsorbate concentration, low at low quantity and concentration, and moderate at this interval. This is propped by availability of adsorption sites subject to sorbent quantity and surface area relative to sorbate concentration (Djamila & Zoubida, 2007 and Ramamurthi, et al. 2009). The clay amount effect plot (Fig.-) indicated marked asymptotic lines of increasing uptake with clay amount showing a high probability of equilibration at clay amount > 0.6 g. The clustered uptake points around 0.4g could imply the vicinity of optimum clay amount. In consonance with the literature, increase in clay amount is relative to increased contact surface area and increased number of adsorption site typical of increased uptake. This explains the increasing MB dye uptake with increasing clay amount: increased adsorption site. Plots of

Fig.1c showed steady increase in uptake with increase in dye concentration for all the studied samples.

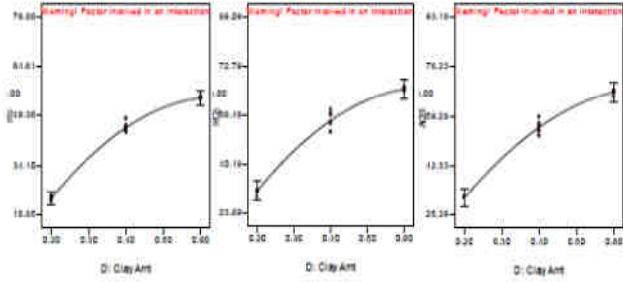


Fig.1c: Clay amount effect plot

It is typical in suspensions, as particle concentration increases; particle movement became more restricted, and the precipitation and settling propensity increases. Therefore, as the MB concentration increase; tied to non-elastic collision of its molecules, restricted motion of the molecules sustained decrease in kinetic energy and enhance the stability of weak molecular adsorptive attractions. Inspection of Fig.1d showed slight asymptotic inclined graph, indicating the tendency of adsorption-desorption equilibrium at dye concentrations $>>35\text{mg/L}$ likely when all adsorption sites have been occupied.

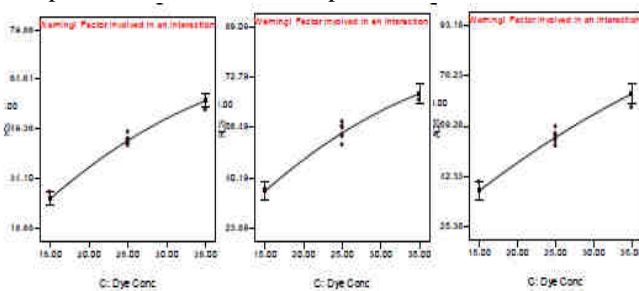


Fig.1d: Dye concentration effect plot

Temperature: Most studies have reported adsorption enhancement with increase in temperature, though, increase to certain degree. The increase in adsorption with temperature can be linked to internal surface exposure due to adsorbent species disintegration and decreased boundary layer thickness/resistance; enhancing site interaction and mass transfer. However, based on kinetic energy-temperature relationship; increasing temperature increases molecular speed and weakens Van der waal force that characterizes physisorption. Increased temperature is preferred in chemisorption predominant systems where increased entropy and activation energy are essential. In all cases, physisorption is stable at low temperatures and adsorption enthalpy and entropy of adsorption are temperature dependence. The plots of Fig.1e generally depicted slight increase in uptake with temperature (20 to 30°C) and a marked fall with further increase in temperature up to 60°C. Increased uptake at low temperature probably verifies the exothermicity of the process while increased temperature probably increases the kinetic energy of the dye molecules, breaking the weak physisorption attraction. The plots showed a brief equilibrium at $27 < \text{Temp} < 35^\circ\text{C}$ with average temperature for maximum uptake at 27°C . The MB dye uptake showed $\approx 22\%$ average decrease with increasing temperature.

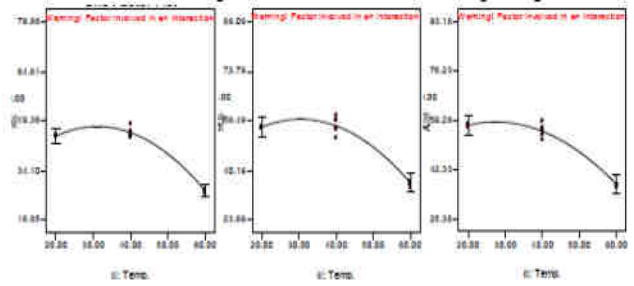


Fig.1e: Plots for the effect of Temperature

C. Response surface method (RSM)

The one fraction (1/4) fractional factorial CCRD applied yielded the matrix and %uptakes as reported in Table 3. The rotatability of the design defined by the axial factor, $\pm\alpha$ ($\alpha = \pm 2$) implied that all the points in the design area are at equal distance from the centre leading to equal distribution of errors. The design has 15 degree of freedom ($df = 15$) ascertained by 5df from the 2-level main factor and 10df from the two-factor interaction terms. This justified the 16 factorial points as used in the design. The statistically predicted dye uptakes derived from the quadratic model and reported in Table 3 showed very high agreement with the observed values. The Table reports average uptake values of the replicated experimental runs. The quadratic models of the uptakes for the coded and actual variable are represented in (6-8) below.

D. Statistical analysis

Model fit: The model fit for the experimental data analysis verified the highest order polynomial where the additional terms are significant, the model is not aliased, the model have insignificant lack-of-fit and the model that maximizes the "Adjusted R-Squared" and the "Predicted R-Squared".

The sequential model and lack of fit sum of squares, Table 5, ascertain the selection of quadratic model based on highest order polynomial that is not aliased. Lack of fit test compares the "Residual error" to the "Pure error" from replicated design points. The lack of fit Prob-F >0.05 and Prob-F <0.05 for the sum of sqaure indicated insignificant lack of fit and verified quadratic model as fit for use as the response predictor for the samples. The cubic model showed insignificant Lack of fit yet, was not considered as choice model because it is aliased. By this choice, adding the quadratic terms to the model's inherent terms is justified. The standard deviation ("Std. Dev."), R^2 , Adj R^2 , Pred. R^2 , and PRESS (Table 4) of the quadratic model for all the samples indicated the model is adequate to correlate and verify the accuracy of the predicted and experimental dye uptakes.

Analysis of Variance(ANOVA): Section 4.5 above elucidates the main effect plots of the ANOVA. The response surface graphical analysis (surface plots) relates the MB uptakes to the process variables. The Mean 'F-Values' of 152.59, 77.00 and 72.90 for RS, RCS and ACS respective and the "Prob-F" value <0.0001 implied adequacy of the choice model. There is only a 0.01% chance that the Models Mean 'F-Value' could have occurred due to noise. The F values of the main, quadratic and interaction effects (Table 6), showed the terms of significant effect: degree of significance is

relative to magnitude of F value. This analysis corresponds with Tan et al. (2008) and Narayana et al. (2011). As reported in Table 6: terms of "Prob-F" value <0.05 are significant, the models' Lack of fit in predicting the samples' MB uptake are insignificant typical of "Prob-F" >0.05 and the percentile "Prob-F"(RS-25.51%, RCS-59.21% and ACS-23.31%) open the proclivity of insignificant lack of fit is due to noise. This indicated that the RCS model insignificant Lack of fit is more likely due to noise.

As shown in Table 7, the low "Std. Dev." and high "PRESS" values explicate the accuracy and correlation of the predicted and experimental MB dye uptakes. How well the estimated model fits the data has been highly reported to be characteristics of the value of R^2 which is best to be very

close to unity. If a statistically insignificant variable is added in a model, it increases R^2 while decreasing Adj. R^2 . Therefore, as reported in Table 7, Adj R^2 and Pred. R^2 which must be close, authenticated R^2 indicating 99.64%, 99.29% and 99.25% agreement between the experimentally observed and the predicted MB uptake of Table 3. The percentile values of R^2 also measured the percentage variation of the uptake around the uptake value that is described by the regression equation. R^2 ascertains the existence of correlation between the uptake and the variables. "Adeq Precision", a measure of signal to noise ratio, showed values far greater than 4 indicating adequate signal that the model fitness to navigate the design space is highly precise. The observed and predicted MB uptakes as obtained from the ANOVA quadratic model are reported in Table 3.

Table 3: Experimental Design matrix showing observed and model predicted responses

Std Run	Experimental Factors					MB Uptake (%)					
	x_1	x_2	x_3	x_4	x_5	Y_1		Y_2		Y_3	
						Observed	Predicted	Observed	Predicted	Observed	Predicted
1	-1	-1	-1	-1	1	20.25	20.37	26.75	25.99	28.88	29.77
2	1	-1	-1	-1	-1	22.39	23.02	28.89	29.46	30.98	31.56
3	-1	1	-1	-1	-1	25.45	25.69	34.96	34.04	36.05	36.98
4	1	1	-1	-1	1	21.04	21.06	27.54	26.92	29.33	29.96
5	-1	-1	1	-1	-1	57.38	56.68	66.93	66.10	66.02	65.03
6	1	-1	1	-1	1	21.40	20.48	27.90	27.37	30.19	28.90
7	-1	1	1	-1	1	51.50	51.19	61.09	59.07	61.18	60.24
8	1	1	1	-1	-1	62.25	61.45	68.56	67.87	69.67	68.42
9	-1	-1	-1	1	-1	42.11	42.87	52.62	52.99	53.71	54.12
10	1	-1	-1	1	1	62.45	62.99	70.94	71.62	73.03	73.13
11	-1	1	-1	1	1	27.67	27.83	37.58	36.76	39.67	40.13
12	1	1	-1	1	-1	56.00	56.66	63.10	63.62	62.19	62.33
13	-1	-1	1	1	1	66.85	66.06	74.65	73.92	74.74	73.28
14	1	-1	1	1	-1	56.21	55.93	64.99	65.60	88.08	86.30
15	-1	1	1	1	-1	52.35	51.68	61.54	60.65	59.99	58.57
16	1	1	1	1	1	39.25	38.36	46.96	46.38	49.05	47.32
17	-2	0	0	0	0	18.85	19.54	23.89	26.36	25.38	25.60
18	2	0	0	0	0	19.07	19.19	24.50	23.69	26.59	28.05
19	0	-2	0	0	0	79.86	79.78	89.09	88.57	93.18	94.12
20	0	2	0	0	0	75.02	75.91	81.95	84.13	83.84	84.59
21	0	0	-2	0	0	29.93	27.95	36.38	36.03	40.47	37.56
22	0	0	2	0	0	55.25	58.03	65.41	67.42	65.50	70.09
23	0	0	0	-2	0	23.05	24.01	29.50	31.57	31.59	31.47
24	0	0	0	2	0	55.03	54.88	65.66	65.25	65.75	67.55
25	0	0	0	0	-2	45.16	44.84	54.61	54.41	56.70	57.55
26	0	0	0	0	2	27.05	28.18	34.48	36.34	36.57	37.40
27	0	0	0	0	0	44.36	45.82	54.15	54.79	56.24	55.48
28	0	0	0	0	0	46.20	45.82	58.27	54.79	54.36	55.48
29	0	0	0	0	0	46.23	45.82	53.65	54.79	56.74	55.48
30	0	0	0	0	0	45.57	45.82	56.51	54.79	52.60	55.48
31	0	0	0	0	0	48.46	45.82	56.90	54.79	58.99	55.48
32	0	0	0	0	0	44.91	45.82	50.93	54.79	55.62	55.48

Table 4: Quadratic model Summary Statistics

Sample	Std. Dev.	R^2	Adj. R^2	Pred. R^2	PRESS
RS	1.73	0.9964	0.9899	0.9329	617.47
RCS	2.54	0.9929	0.9800	0.9040	964.79
ACS	2.16	0.9950	0.9860	0.9244	780.73

Equation (6-8) coded and actual, illustrate the model and its regression coefficients. Positive sign in front of the terms

indicates synergistic effect, whereas negative sign indicates antagonistic effect (Tan et al. 2008).

Raw sample (RS)

Optimizing The Adsorption of Methylene Blue Dye onto Raw and Modified Ekowe Clay using RSM

Coded: $Y_1 = +45.82 - 0.18x_1 - 1.93x_2 + 15.04x_3 + 15.43x_4 - 8.33x_5 + 3.24x_5 - 7.35 \times 10^{-3}x_{11}^2 + 2.00x_{22}^2 - 0.03x_{33}^2 - 159.43x_{44}^2 - 26.46x_{11}^2 + 10.71x_4x_5 + 32.02x_{22}^2 - 2.83x_{33}^2 - 6.38x_{44}^2 - 9.31x_{55}^2 - 0.023x_{55}^2 + 0.05x_1x_2 - 0.04x_1x_3 + 1.09x_1x_4 - 8.69 \times 10^{-3}x_1x_5 + 0.13x_2x_3 - 28.49x_2x_4 - 0.15x_3x_4 - 9.62x_2x_5 - 0.04x_3x_5 + 2.69x_4x_5 + \varepsilon$ (6)

Actual: $Y_1 = -274.67 + 1.74x_1 - 17.95x_2 + 10.78x_3 + 450.22x_4$

Table 5: Sequential Model and Lack of fit Sum of Squares

	Models Source	Sum of Squares		Lack of fit		Remark
		F Value	Prob > F	F Value	Prob > F	
RS	Linear	2.81	0.0371	139.23	< 0.0001	
	2FI	0.96	0.5109	166.01	< 0.0001	
	<u>Quadratic</u>	<u>246.48</u>	<u>< 0.0001</u>	<u>1.87</u>	<u>0.2551</u>	<u>Suggested</u>
	Cubic	1.95	0.2198	1.17	0.3288	Aliased
RCS	Linear	3.04	0.0271	42.06	0.0003	
	2FI	0.89	0.5639	51.50	0.0002	
	<u>Quadratic</u>	<u>123.67</u>	<u>< 0.0001</u>	<u>0.83</u>	<u>0.5921</u>	<u>Suggested</u>
	Cubic	0.67	0.6624	1.41	0.2876	Aliased
ACS	Linear	2.89	0.0334	66.79	< 0.0001	
	2FI	0.73	0.6899	87.51	< 0.0001	
	<u>Quadratic</u>	<u>192.92</u>	<u>< 0.0001</u>	<u>0.98</u>	<u>0.5173</u>	<u>Suggested</u>
	Cubic	1.41	0.3420	0.025	0.8795	Aliased

Table 6: ANOVA for the Response Surface Quadratic Model

Source		F Value	Prob > F		F Value	Prob > F		F Value	Prob > F	
Mean		152.59	< 0.0001		77.00	< 0.0001		72.90	< 0.0001	significant
A		0.063	0.8065		1.65	0.2252		1.24	0.2896	
B		7.48	0.0194		4.56	0.0561		18.73	0.0012	
C		451.93	< 0.0001		228.10	< 0.0001		218.15	< 0.0001	
D		475.88	< 0.0001		262.70	< 0.0001		268.47	< 0.0001	
E		138.62	< 0.0001		75.65	< 0.0001		83.71	< 0.0001	
A ²		427.37	< 0.0001		250.81	< 0.0001		206.94	< 0.0001	
B ²		626.08	< 0.0001		281.89	0.0001		289.20	< 0.0001	
C ²		4.88	0.0493		2.66	0.1310		0.69	0.4243	
D ²		24.83	0.0004		11.53	0.0060		8.98	0.0122	
E ²		52.95	< 0.0001		25.10	0.0004		16.14	0.0020	
AB	RS	43.49	< 0.0001	RCS	14.84	0.0027	ACS	1.79	0.2083	
AC		189.31	< 0.0001		85.92	< 0.0001		33.20	0.0001	
AD		57.22	< 0.0001		30.74	0.0002		49.89	< 0.0001	
AE		36.18	< 0.0001		12.66	0.0045		28.93	0.0002	
BC		8.79	0.0129		3.74	0.0791		0.00042	0.9841	
BD		173.00	< 0.0001		88.38	< 0.0001		121.32	< 0.0001	
BE		50.90	< 0.0001		16.86	0.0017		2.40	0.1494	
CD		123.31	< 0.0001		65.58	< 0.0001		29.47	0.0002	
CE		24.99	0.0004		11.59	0.0059		27.51	0.0003	
DE		38.18	< 0.0001		18.63	0.0012		5.66	0.0366	
Lack of Fit		1.87	0.2551		0.83	0.5921		1.99	0.2331	insignificant

Table 7: Quadratic Model ANOVA parameters

Sample	Mean	Std. Dev.	C.V.	PRESS	Adeq. Precision	R ²	Adj R ²	Pred R ²
RS	43.39	1.73	3.99	617.47	43.163	0.9964	0.9899	0.9329
RCS	51.59	2.54	4.93	964.79	31.469	0.9929	0.9800	0.9040
ACS	53.53	2.70	5.04	1505.55	31.361	0.9925	0.9789	0.8591

Raw calcined sample (RCS)

Coded: $Y_2 = +54.79 - 1.34x_1 - 2.22x_2 + 15.69x_3 + 16.84x_4 - 9.04x_5$

$-29.77x_{11}^2 + 31.56x_{22}^2 - 3.07x_{33}^2 - 6.38x_{44}^2 - 9.42x_{55}^2 + 9.81x_1x_2$

$-23.59x_3x_4 + 14.11x_1x_4 - 9.06x_1x_5 + 4.93x_2x_3 - 23.92x_2x_4 - 10.45x_2x_5 - 20.61x_3x_4 - 8.67x_3x_5 + 10.98x_4x_5 + \varepsilon$

Actual: $Y_2 = -276.50 + 1.83x_1 - 17.33x_2 + 11.24x_3 + 474.90x_4 - 2.93x_5 - 8.27 \times 10^{-3}x_{11}^2 + 1.97x_{22}^2 - 0.031x_{33}^2 - 159.56x_{44}^2$

$$0.024x_{55}^2 + 0.041x_1x_2 - 0.039x_1x_3 + 1.18x_1x_4 - 7.55 \times 10^{-3}x_1x_5 + 0.123x_2x_3 - 29.91x_2x_4 - 0.13x_2x_5 - 10.31x_3x_4 - 0.043x_3x_5 + 2.75x_4x_5 + \epsilon \quad (7)$$

0.5MH₂SO₄ Activated-Calcined Sample (ACS)

Coded:

$$Y_3 = +55.48 + 1.23x_1 - 4.76x_2 + 16.26x_3 + 18.04x_4 - 10.07x_5$$

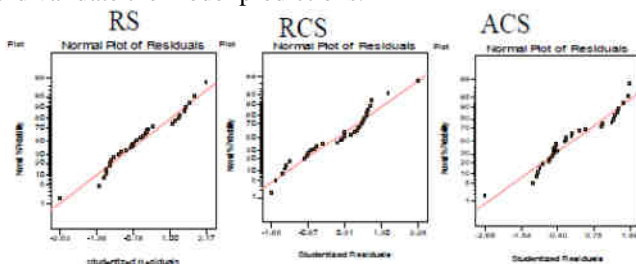
$$-28.65x_{11}^2 + 33.87x_{22}^2 - 1.65x_{33}^2 - 5.97x_{44}^2 - 8.00x_{55}^2 + 3.60x_1x_2$$

$$-15.54x_1x_3 + 19.05x_1x_4 - 14.51x_1x_5 + 0.055x_2x_3 - 29.71x_2x_4 - 4.18x_2x_5 - 14.64x_3x_4 - 14.14x_3x_5 + 6.41x_4x_5 + \epsilon$$

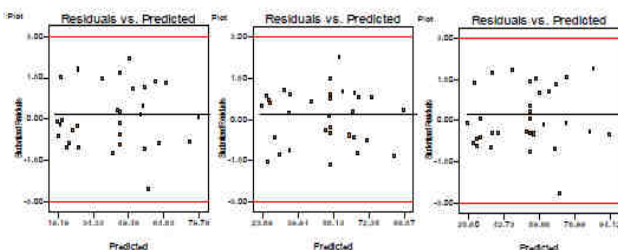
$$\text{Actual: } Y_3 = -275.71 + 1.69x_1 - 15.12x_2 + 10.27x_3 + 461.32x_4 + 3.56x_5 - 7.96 \times 10^{-3}x_{11}^2 + 2.12x_{22}^2 - 0.017x_{33}^2 - 149.19x_{44}^2 - 0.02x_{55}^2 + 0.015x_1x_2 - 0.026x_1x_3 + 1.59x_1x_4 - 0.012x_1x_5$$

$$+ 1.38 \times 10^{-3}x_2x_3 - 37.13x_2x_4 - 0.052x_2x_5 - 7.32x_3x_4 - 0.071x_3x_5 + 1.60x_4x_5 + \epsilon \quad (8)$$

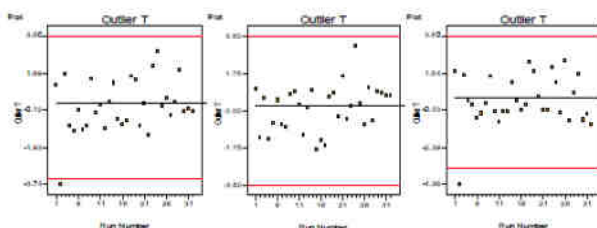
Diagnostic Model Plots of the ANOVA: The diagnostic model plots were and can best be analyzed by inspection. Figs.2a illustrates the normal probability plot of the studentized residuals showing that the standardized residuals for the samples are normally distributed. Observing the illustration of Figs.2b, the spread of the studentized residuals is approximately the same across all levels of the predicted values and covered the design space. Figs.2c showed influential uptakes (outlier) for RS and ACS given as 55.25% and 65.50% respectively. All the plots are OK and validate the model predictions.



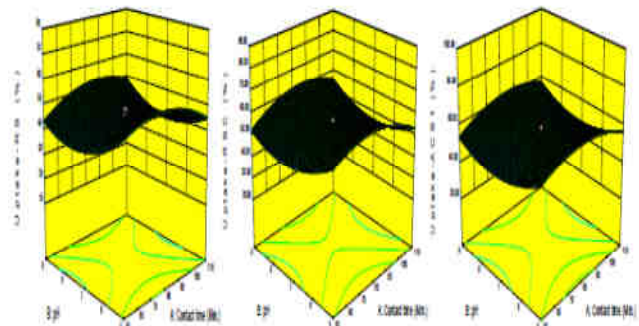
Figs.2a: Normal probability plot of studentized residuals.



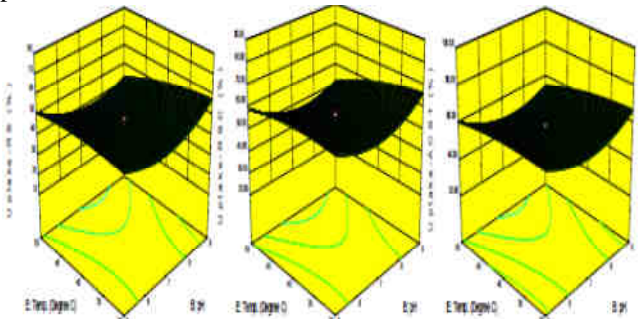
Figs.2b: Studentized Residuals vs Predicted values plot.



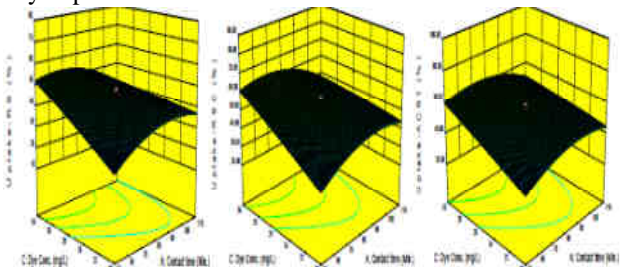
Figs. 2c: Outlier T plots.



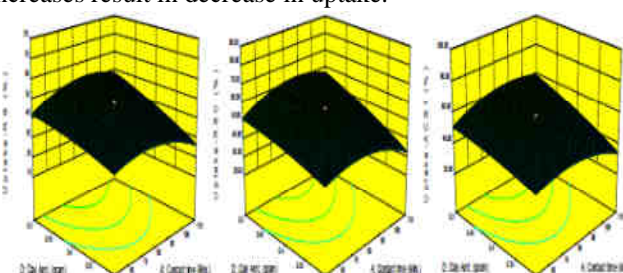
Figs.3a: Saddle shaped surface of Time/pH effect 3D surface plots: Figs.3 shows the factors' interaction effects 3D surface plots for MB uptake. The saddle shape of the RS surface plots is more prominent, followed by RCS and then ACS (Figs.3a). A saddle surface does not have a unique optimum and the saddle point does not correspond to an extreme implying likely no optimum setting exists around experimental data points. The saddle illustrated that increase in Time with increase in pH would lead to decrease in dye uptake; and vice versa.



Figs.3b: Saddle shaped surface of pH/Temperature effects The plots of Figs.3b showed feeble saddle shapes exposed by the contour of the surface plot and as well no extreme or unique optimum exists. In the direction of rising of the contour, increase in pH with Temperature results in decrease in dye uptake.

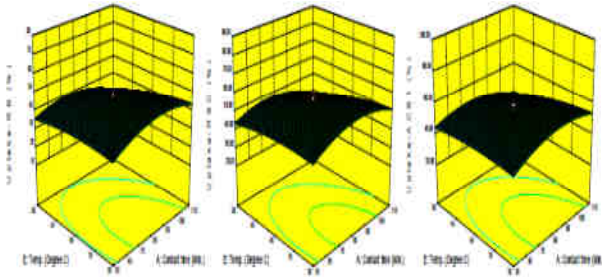


Figs.3c: Ridge surface of Time/Concentration effect Figs.3c and d showed rising ridge surfaces a surface that could be characterized by mainly factor settings. RS of Figs.3c showed a fairer ridge maximum. The plots elucidate increase in MB uptake with increasing Time and dye concentration up to about 80min and 25mg/L when further increases result in decrease in uptake.

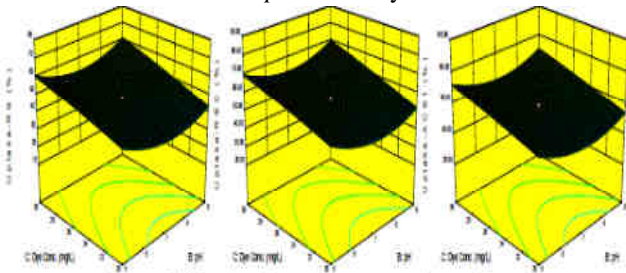


Figs.3d: Ridge (rising) of Time/Clay Amount effect

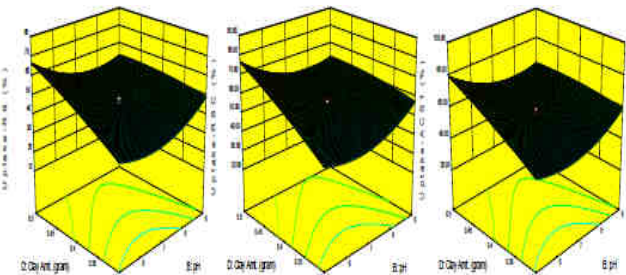
Continues increase in clay amount with increase in Time to about 80min. characterizes the lighter portion of the *Time/Clay Amount* surface plots of Figs.3d showing increase in dye uptake. It showed that the increased uptake is most influence by the increasing clay amount which defined the direction of the rising ridge.



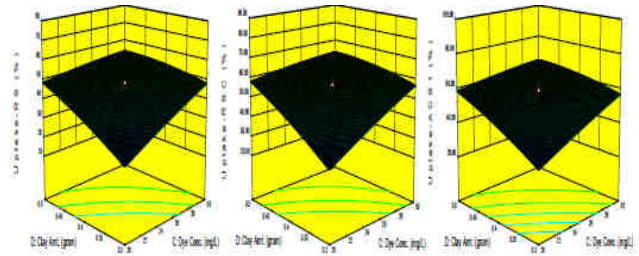
Figs.3e: Ridge of Time/Temperature effect Figs.3e showed rising ridges that tend towards simple maximum characterized by the semi-circular contour centre. Dye uptake increased sharply with increase in *Time* and *Temperature* and experienced a pronounced decrease with increase in *Time* and *Temperature* beyond 80min and 40°C.



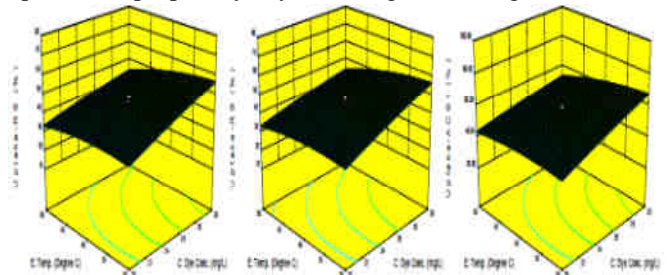
Figs.3f: Ridge (falling) of pH/Concentration effect Figs.3f illustrates falling ridge which portray decrease in dye uptake with increase in pH and Concentration. Beyond pH 7, the surface showed increasing uptake with continued increase in dye concentration. Concentration defined the ridge direction therefore dye uptake is more dependent on the dye concentration.



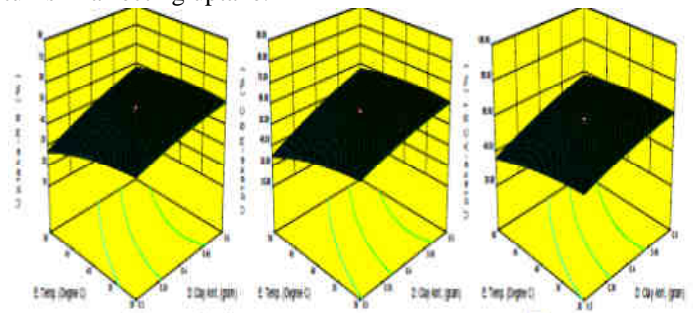
Figs.3g: Ridge (falling) of pH/Clay Amount effect The falling ridge (Figs.3g) typifies a fall in dye uptake with increase in pH and Clay Amount. The surface also showed increase in uptake with further increase in pH beyond pH7 at constant increase in clay amount, even so, the surface portrayed highest uptake at lowest pH. Clay amount defined the ridge direction and hence being the determinant for dye uptake.



Figs.3h: Rising ridge of Concentration/Clay Amount The 3D surface of Figs.3h showed rapid continuous increase in dye uptake with increase in dye concentration and clay amount. This implied as the clay amount increases, the adsorption sites also increase to accommodate relative increase in dye concentration. The surfaces illustrate equilibrium propensity beyond 35mg/L and 0.6g.



Figs.3i: Rising ridge of Concentration/Temperature effect Figs.3i exhibits increase in uptake with continues increase in dye concentration to about 25mg/L beyond which uptake falls, mainly with rising temperature. The origin and direction of the ridge contour showed that both factors took turns in affecting uptake.



Figs.3j: Ridge of Clay Amount/Temperature effect Figs.3j showed rising ridges demonstrating increasing clay amount and temperature with increase in dye uptake. Beyond 40°C at any clay amount, the surface illustrates dye uptake decrease. However, the contour lines suggested the clay amount have greater effect on the dye uptake. It followed generally that increased temperature and contact time have unfavourable influence on uptake while clay amount and dye concentration showed uptake enhancing effects. In all interactions, pH showed sensitivity to extremum and decreased dye uptake at neutral pH.

Table 8: Design matrix showing Optimal Condition and Responses

Runs	Experimental Factors					Optimal Uptakes		
	X ₁	X ₂	X ₃	X ₄	X ₅	RS (Y ₁)	RCS (Y ₂)	ACS (Y ₃)
1	47	3.00	20	0.35	25	53.53	62.79	66.92
2	48	3.00	30	0.40	40	70.98	79.76	83.17
3	60	4.50	20	0.50	30	60.75	73.12	71.98
4	80	4.00	25	0.40	40	61.23	69.37	73.87

E. Process Optimization

The economic optimization based on material and energy conservation expects high dye uptake at relatively low time, clay amount and temperature. Optimizing for efficiency and effectiveness could entail low clay amount capable of high uptake of dye. These conditions are sought for in the various samples in view of the sample with efficient, effective and highest uptake at lowest economic optimum conditions. Therefore, in order to compromise between the uptakes, the function of constraint and desirability were applied using Design-Expert9 (STAT-EASE Inc., Minneapolis, USA).

The four constraints considered include: keeping all factors in range, low level of all factors, centre points of all factors and centre points of other factors at pH4; keeping uptakes in range with constant lower limit of 51% and upper limits of 79.86, 89.09 and 93.18 respectively.

The efficient, effective and economic optimum conditions of Table 8 that gave significant uptake were chosen from the optimal solutions, estimated by the software from the four constraints at high desirability, thus considered for the optimum confirmatory run. The experimental optimum run on the approximated optimum conditions yielded the optimum uptakes as reported in Table 8. The considered optimum conditions; 47min, 20mg/L, 0.35g and 25°C gave 53.53%, 62.79% and 66.92% uptakes for RS, RCS and ACS respectively.

IV. CONCLUSION

The adsorption experiments showed improved dye uptake in order of ACS>RCS>RS. The modifications enhanced MB removal from the aqueous dye solution showing enhancement on uptakes as: RCS>RS (calcination), ACS>RCS (activation). The driving force for the improved dye uptake was dependent, internally: on the charges at the edges and exposed hydroxyls surfaces, and the permanent, pH dependent negative charges introduced by substitutions within the lattice structure of the samples; and externally: on the charged sites created at the edges, entrance channels and cavities of flocs formed due to PZC. The RSM suggested quadratic model as the response predictor for the dye uptake. The model ANOVA affirmed the significant influence of the studied factors on the uptake. High temperature and contact time in all interactions as bared by the surface plots have unfavourable influence on dye uptake while clay amount and dye concentration showed adsorption enhancing effect. MB dye solution pH showed sensitivity to extremum with characteristic decreased uptake at pH7 in all cases. CCRD was very suitable in response surface optimization of the MB uptake giving the effective and economic optimum conditions; 47min, pH3, 20mg/L, 0.35g and 25°C with 53.53%, 62.79% and 66.92% uptakes for RS, RCS and ACS respectively. The performances of the modified clay samples relative to the raw sample at the optimum conditions were reasonable with ACS showing the highest uptake. The plausible optimum MB uptakes for a considerably low dye concentration within a short period (<50min.), realized using below-average clay amount at room temperature reflect that Ekowe clay and its modified forms could be considered effective and economically

feasible adsorbents for textile effluent treatment. This study however, revealed that calcination of H₂SO_{4(aq)} activated Ekowe clay (ACS) is a better modification to effect operative and economic optimum MB dye uptake from aqueous solutions.

REFERENCE

1. Aivalioti, M., Vamvakakis, I. &Gidakos, E. (2010).BTEX and MTBE adsorption onto raw and thermally modified diatomite.*Journal of Hazardous Materials*, 178, 136–143.
2. Al-Degs, Y., Khraisheh, M. A. M. &Tutunji, M. F. (2001). Sorption of lead ions on diatomite and manganese oxides modified diatomite. *Water Resources*, 35(15), 3724–3728.
3. Amit Choudhury (2009, June 6). ANOVA. Retrieved Dec 04, 2013 from Explorable.com: <http://explorable.com/anova>. <http://explorable.com/statistical-variance>.
4. ALzaydien, A. S. (2009). Adsorption of Methylene Blue from Aqueous Solution onto a Low-Cost Natural Jordanian Tripoli. *American Journal of Environmental Sciences*, 5(3), 197-208. ISSN 1553-345X
5. Bhattacharyya, K. G., & Gupta, S. S. (2006). Adsorption of Chromium (VI) from Water by Clays. *Industrial Engineering Chemistry Research*, 45, 7232-7240. DOI: 10.1021/ie060586j CCC
6. Bhattacharyya, K. G., & Gupta, S. S. (2009). Adsorptive Accumulation of Cd(II), Co(II), Cu(II), Pb(II) and Ni(II) ions from water onto Kaolinite: Influence of acid activation. *Adsorption Science & Technology*, 27(1), 47-68.
7. Chatterjee, S., Lee, D. S., Lee, M. W., & Woo, S. H. (2009). Enhanced adsorption of congo red from aqueous solutions by chitosan hydrogel beads impregnated with cetyltrimethylammonium bromide. *Bioresource Technology*, 100, 2803 – 2809. doi:10.1016/j.biortech.2008.12.035. Accessible: www.elsevier.com/locate/
8. Carley, K. M., Kamneva, N. Y., & Reminga, J. (2004). CASOS Technical Report on Response Surface Methodology: prepared for CASOS - Center for Computational Analysis of Social and Organizational Systems, ISRI - Institute for Software Research International, School of Computer Science, Carnegie Mellon University.
9. Chang, H., Su, C., Lo, C. H., Chen, L. C., Tsung, T. T., &Jwo, C. S. (2004).Photodecomposition and Surface Adsorption of Methylene Blue on TiO₂Nanofluid Prepared by ASNSS. *Materials Transactions*, 45(12), 3334 – 3337.
10. Design Expert, (2000). Stat-Ease, Design Expert (version 6.0.5) (PC application software).User’s Manual and Software. Stat-Ease Inc. Minneapolis, MN.
11. Djamilia, H. & Zoubida, B. (2007). Lead (II) adsorption on bentonite. *Récents Progrés en Génie des Procédés*, 1-11.94 G P E. ISBN 2-910239-68-3, Ed. SFGP, Paris, France.
12. Fazeli, F., Tavanai, H., Hamadani, A. Z. (2012). Application of Taguchi and full factorial experimental design to model the color yield of cotton fabric dyed with six selected direct dyes. *Journal of Engineered fibers and fabrics*, 7(3), 34-42. www.jeffjournal.org.
13. Hefne, J. A., Mekheimer, W. K., Alandis, N.M., Aldaye, O.A. & Aljvay, T. (2008). Kinetic and thermodynamic study of the adsorption of Pb (II) from aqueous solution to the natural and treated bentonite. *International Journal of Physical Science*, 3(11), 281-288 <http://mineral.galleries.com/minerals/silicate/clays.htm>
14. Inglezakis V. J., Marinos A., Stylianou, D. G., &Loizidou, M. D. (2007). Removal of Pb(II) from aqueous solutions by using clinoptilolite and bentonite as adsorbents. *Desalination*, 210, 248-256.
15. Khuri, A. I., &Mukhopadhyay, S. (2010). Response surface methodology. *Advanced Review: WIREs Computational Statistics*, Vol. 2 (pp. 128 – 149). John Wiley & Sons, Inc.
16. Khraisheh, M. A. M., Al-degs, Y. S. & Mcminn, W. A. M. (2004).Remediation of wastewater containing heavy metals using raw and modified diatomite. *Chemical Engineering Journal*, 99, 177 – 184. doi:10.1016/j.cej.2003.11.029
17. Ma, C. &Eggleton, R. A. (1999).Cation Exchange Capacity of Kaolinite. *Clays and Clay Minerals*, 47(2), 174 - 180.
18. Montgomery, D. C. (2000). Chapter 3: Response surface methodology. In: *Design and analysis of experiments* (pp. 15 – 29). New Jersey: John Wiley & Sons Inc.
19. Montgomery, D. C. (2002). *Teaching Experimental Design to Engineers: Some experiences and advice*. USA: ICOTS6, Arizona State University.

20. Njoku, V. O., Oguzie, E. E., Obi, C., Bello, O. S. & Ayuk, A. A. (2011). Adsorption of Cu(II) and Pb(II) from Aqueous solutions onto a Nigerian natural Clay. *Australian Journal of Basic and Applied Sciences*, 5 (5), 346-353.
21. Narayana S. K. V, King, P., Gopinadh, R., & Sreelakshmi, V. (2011). Response surface optimization of dye removal by using waste prawn shells. *International Journal of Chemical Sciences and Applications*, 2(3), 186-193. ISSN 0976-2590. <http://www.bipublication.com>
22. Osmanlioglu, A. E., (2007). Natural diatomite process for removal of radioactivity from liquid waste, *Applied Radiation Isotopes*, 65, 17–20.
23. Ramamurthi, V., Priya, P. G., Saranya, S. & Basha, C. A. (2009). Recovery of Nickel (II) Ions from Electroplating Rinse Water using Hectorite Clay. *Modern Applied Science*, 3(9), 37-51. Accessible at www.ccsenet.org/journal.html
24. Response surface methodology.n.d. In Wikipedia. Retrieved 26 February, 2014 by 7:11pm.
25. Shawabkeh, R. A. & Tununji, M. F. (2003). Experimental study and modeling of basic dye sorption by diatomaceous clay. *Applied Clay Science*, 24, 111–120.
26. Tschapek, M., Tcheichvilit, L., & Wasowski, C. (1974). The Point of Zero Charge (PZC) of Kaolinite and 8io2+a1203 mixtures. *Clay Minerals*, 10, 219 -229.
27. Tan, I. A. W., Ahmad, A. L., & Hameed, B. H. (2008). Preparation of activated carbon from coconut husk: Optimization study on removal of 2,4,6-trichlorophenol using response surface methodology. *Journal of Hazardous Materials* 153, 709 –717.
28. Talaat, H. A., El Defrawy, N. M., Abulnour, A. G., Hani, H. A. & Tawfik, A. (2011). Evaluation of Heavy Metals removal using some Egyptian clays. *International Conference of Environmental Science and Technology*, Vol.6, 2.
29. WHO, 2007. Water for Pharmaceutical Use. In: *Quality Assurance of Pharmaceuticals: A Compendium of Guidelines and Related Materials*. 2nd Updated Edn. World Health Organisation, Geneva, 2: 170-187.
30. World Health Organization, Geneva. (2005). *Environmental Health Criteria 231: Bentonite, Kaolin, and Selected Clay Minerals*. Prepared by Z. Adamis, J. Fodor & R. B. Williams. ISBN 92 4 1572310 LC/NLM classification: QV 65)
31. Zangench, N., Azizian, A., Lye, L. & Popescu, R. (2002). Application of response surface methodology in numerical geotechnical analysis. 55th Canadian Society for Geotechnical Conference, Hamilton, Ontario.