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The Equilibrium and Thermodynamics of Methylene Blue Uptake onto Ekowe Clay; Influence of Acid Activation and Calcination

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Abstract— **The equilibrium isotherm study verified that the linear Freundlich model best explained the adsorption data and mechanism. The maximum adsorption capacities, 9.709, 13.889, and 18.868g/g for RS, RCS and ACS respective obtained from the Langmuir isotherm model at 25^{o}C. Verifiable with increased filtration rates, acid activation and calcination improved the clay porosity and the total surface area; RS-22.04, RCS-30.36 m^{2}g^{-1} and ACS-40.92m^{2}g^{-1}. Sample PZCs were less than solution pH indicating cation affinity and enhanced dye adsorption. Dye uptake varied with temperature and adsorption equilibrates around 80min. Langmuir model (ΔG°<-5KJ/mol) and thermodynamics (ΔG°>-18kJ/mol and ΔH) revealed a spontaneous and exothermic physisorption of MB dye onto the raw and modified samples. ΔS^* suggested an associative adsorption mechanism and ΔS^o proposed an induced randomness and changes at the solute/solvent interface.**

Index Terms— **Adsorption, Activation, Calcination, isotherm, thermodynamics**

I. INTRODUCTION

Water is one of the implicit requisites for a healthy human population. Up to 70% of the world's water usage is involved in food production, both natural and industrial. Since we cannot make or produce water it is necessary to manage and conserve the much nature has made available. 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. The ground serves as water reservoir where surface waters drain-into forming underground water, the major source of drinking water for more than one-half of the world's population, both rural and urban communities.

Population explosion, haphazard rapid urbanization, industrial and technological expansion, energy utilization and waste generation from domestic and industrial sources have rendered many waters unwholesome and hazardous to man, living organisms and the environment around them.

Problems in domestic and industrial water quality include presence of inorganic elements and compounds (anions and cations), organic matters, and variety of pathogens. These contaminants are the major causes of various water-borne diseases, food poisoning, and the breakdown of some industrial machinery.

There are little or no stringent laws guiding environmental pollution in many nations: Yasin et al., 2007; Chatterjee et al., 2009; Rahman, et al. 2012; Gulnaz, et al. 2004 and Velmurugan et al., 2011 have reported recent global anthropogenic activities are solely responsible for the introduction of dye into water bodies. In spite the preventive measures in textile and colour allied industries; coloured effluent arises as a direct result of production of the dye, its use and the use of finished products of dye composition.

Dye in wastewater is highly visible and can obstruct light penetration which is highly threatening to aquatic lives (Chang, et al. 2004). Spontaneous photo and thermal remediation measures of dye removal in liquid effluents are non-viable as a result of its high stability to heat and light irradiation.Nasra et al., (2006) have reported dyes to be responsible for low biochemical oxygen demand (BOD) and high chemical oxygen demand (COD). Dye has been cited to be dangerous, mutagenic and carcinogenic in nature (Crini, 2006 and Safa & Bhatti, 2011), can destroy or inhibit metabolism in some microorganisms, has defied biodegradation, and its removal from wastewater has been very stringent due to its complex structure and synthetic origins.

Methylene blue is a basic dye that has gained extensive uses in different fields; biology, chemistry, medicine (microbiology, surgeries, diagnostics) (Rahman et al., 2012) and also in textile industries. It is not significantly metabolized by the liver if ingested; resists stomach acidity; and can quickly be filtered out by the kidneys. Methylene blue has been used particularly for adsorption studies, not only because of its environmental concern but also for the fact that it has been recognized as a model adsorbate for the removal of organics (Hameed et al., as cited in Abechi, et al. 2011). It has been used extensive to study adsorption onto low cost adsorbents: Rice Husk (Safa & Bhatti , 2011, Rahman et al, 2012), palm kernel shell (Abechi, et al., 2011), and Coconut shell (Yasin et al, 2007).

Adsorption over the years has remained a successful technological procedure for colour removal from effluents using natural and modified adsorbents. Adsorption is a process by which atoms, molecules or ions are retained on the surfaces of solids by chemical or physical bonding. The degree of adsorptive uptake of any specie is not only dependent on the adsorption factors but also on the possible potent modifications that could be made on the absorbent. The adsorbate-adsorbent binding energy ascertained the

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nature of adsorption as physisorption, chemisorption or both. Low temperature (below critical temperature), intermolecular forces (Van der Waals forces), low enthalpy ($\Delta H<20$ kj/mol), multilayer adsorption, low activation energy characterize physisorption while high temperatures, strong covalent or ionic bond, high enthalpy ($\Delta H \geq 40$kJ/mol), monolayer adsorption, and high activation energy characterize chemisorption. These could be described in the equilibrium and thermodynamic models that form major unprecedented requisites and aspects of adsorption studies and system design.

These models are typical with fundamentally description of the interactive behavior between adsorbate and adsorbent. The choice of a model is its applicability over the entire range of process conditions. Bearing in mind that models are mainly mechanisms, the model of best fit would show best curves and graphs representing the model equation that elucidate the adsorption system. Note: Model fitness does not imply the model represents what actually happens in the system under study, also difference in fit can be explained entirely in terms of experimental errors which statistically the difference may not be significant. Therefore, it is reasonable that the simplest and easiest-to handle equations of satisfactory fit be considered in a study. It is factual to choose the less complicated of two models that equally fit a data. Notwithstanding, finding the correct model from the Equilibrium, kinetics and thermodynamic data has shown some difficulty even in the most carefully conducted programe of experimentation; owing that the magnitude of the experimental error will very likely mask the differences predicted by the various mechanism. It is therefore hardly ever possible to determine with reasonable confidence which is the correct model. In adsorption study, against all odds, analysis has basically been on these models and amongst the most popular models are: Equilibrium isotherm models (Langmuir, Freundlich, Temkin, Dubinin–Radushkevich isotherm, etc) and thermodynamic model.

Characteristic advantages have been recorded with the use of low cost adsorbents: efficiency, low investment and operational cost, minimum chemical sludge formation and possible regeneration. Though many adsorbents such as activated carbon, peat, chitin, and others have proved quite effective in colour removal, there are flaws of concerns in affordability, availability, application friendliness, etc which has been taken care of with the advent and application of clay. Studies have proven clay adsorbent recyclable (regeneration), abundant (availability), cheap (affordability) and user/application friendly. Clay adsorbent compared with activated carbon and other adsorbents has shown equivalent and in some studies better potency in dye removal from aqueous solutions.

Clays are extremely fine particles exhibiting chemical properties of colloids (Wikipedia: Deer, W. A. 1985). Clay minerals are fine hydrous aluminum silicates with large interlayer space that can hold significant amounts of water and other substances and are encompassed of large surface area that allow swelling and shrinking. Clay minerals typical with the adsorptive removal of water contaminants have been categorized with 1:1 and 2:1 phyllosilicates been most popular and comprising the following groups: Smectite, Kaolinite, Illite, chlorite, etc. Clay types like Montmorillonite, Kaolinite, Bentonit, and Illite are widely preferred and used because of their high specific surface area, chemical and mechanical stability, a variety of surface and structural properties, abundance and low cost (Bailey, et al.1999).

The findings of this study would encourage the use of abundant local clays as competitive alternatives, reduce the risk of local carbon activation, and reduce the use of high sludge generating methods. Numerous abundant locally sourced clays of competitive and substitutive viability to activated carbon have not been considered for study. Though clay and its modified forms have been reported as good adsorbent for dye removal from aqueous solution, the adsorption propensity of Ekowe clay, raw and modified, has not been verified. Ekowe clay is a clay obtained from a hamlet, Ekowe, in Southern Ijaw L G A, Bayelsa state Nigeria. Activation of clay is very common in the literatures however; calcination has not gained wide application as a viable modification technique. Besides the work of Talaat et al (2011) which reported very poor Heavy Metal uptake unto activated calcined Kaolinite, no study has considered the effect of calcination on raw and activated Ekowe clay for Methylene Blue uptake.

This study seeks to apply activation and calcination in an attempt to modify a Nigerian clay into a valuable clay adsorbent for dye removal from aqueous solution and as well strengthen, expand and validate the findings of related studies.

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. The clay was 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 $H_2SO_{4(aq)}$ 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 SO_4^{-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*

All solutions' (stock and experimental concentration) preparation applied the dilution theory using predetermined quantities of solid/granule/liquid chemicals and distilled water.

5g commercial Methylene Blue (MB) ($C_{16}H_{18}N_3SCl.3H_2O$) was dissolved in distilled water to produce 5g/L dye stock solution. The experimental concentrations (20, 25, 30, and 35mg/L) were obtained by dilution.

D. *Surface Area*

This work adopted Sears' method as proposed by G. Sears, (1956) for the surface area determination of the clay samples. The method has gained wide application in clay studies; Al-Degs, et al. (2001); Shawabkeh and Tununji, (2003); Khraisheh et al., (2004); Bhattacharyya and Gupta (2006) & (2009); Osmanlioglu, (2007). Applying same procedure for RS, RCS and ACS; 0.2g of sample was mixed with 15mL of distilled water in a flask and acidified with dilute acid (HCl) to pH4. 5g $NaCl_{(s)}$ was added and the volume made up to 25mL with distilled water. The solution was titrated with 0.10M $NaOH_{(aq)}$ observing the pH. The volume (V) required to increase the pH from 4 to 9 was recorded. The volumetric analysis was duplicated for each sample and the average used for surface area calculation (ALzaydien, 2009). The surface area (S) according to Sear's method was estimated as:

$$S\ (m2g\text{-}1) = 32V - 25 \qquad (1)$$

E. *Batch Adsorption Studies*

Batch process has been mostly used in model experiments where the influence of factors like time and temperature are of the essence. Duplication of experimental runs is known to authenticate and ascertain regularity of experimental values for parameters determination. The mass balance equation below gives the adsorbate uptake onto the adsorbent:

$$q_t = \frac{C_o - C_t}{m} V \qquad (2)$$

q_t is the dye uptake after the experimental time (*g/g*), C_o 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 to verify adsorption onto glass wares. Though no adsorption took place, it was noticed, the dye stains the walls of glassware after 24hrs of stocking the solution. Therefore, dye solutions were prepared and used daily.

In the actual runs for equilibrium study, time and dye concentration were varied (20, 50, 80, 110, 140, and 170Min.; and 15, 20, 25, 30 and 35mg/L) at constant solution volume (0.03L), pH (5.5), Clay amount (0.3g), and Temperature (27°C). The thermodynamic experiment was performed at varied temperatures (20, 30, 40, 50 and 60°C) keeping other factors constant as above including time (30min). 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 spectrophotometer absorbances were converted to concentrations using linear calibration graph.

III. RESULTS AND DISCUSSION

A. M*odifi*cation

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, H_2SO_4, 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 (Tab. 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, SO^{2-}.

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.

Table 1: Analytic Characterization

Sample	pH	Acidity (%)	PZC	CEC ($cmolKg^{-1}$)	Surface Area (m^2g^{-1})	Filtration Rate Time (Min.)	Filtration Rate Rate (mL/m^2S)
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

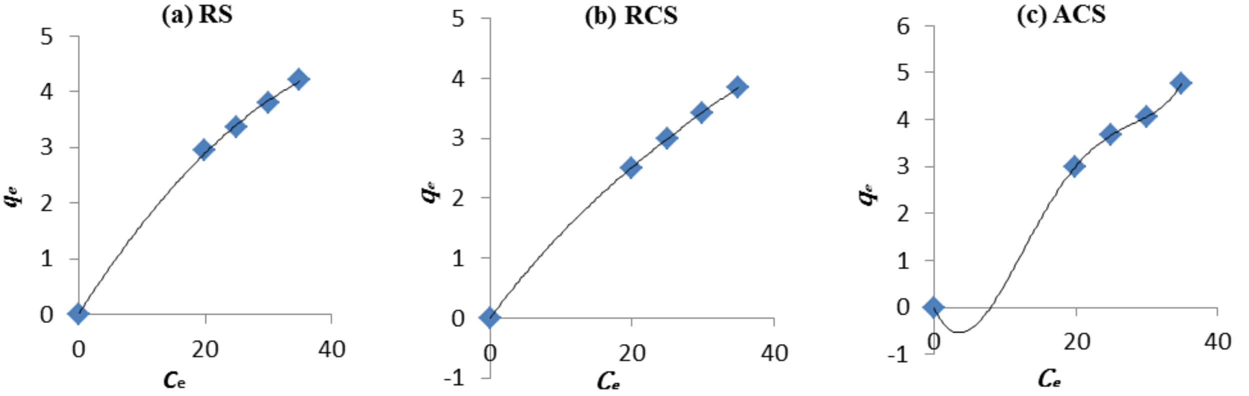

Figure 1: adsorption isotherm of MB onto (a) RS, (b) RCS and (c) ACS

B. *Equilibrium Adsorption Isotherm Models*

Langmuir: The Langmuir isotherm describes adsorption as a monolayer surface phenomenon. It suggested that surface adsorption is a reversible phenomenon with maximum adsorption occurring at equilibrium. The saturated monolayer isotherm model can be represented as

$$\theta = \frac{q_e}{q_{max}} = \frac{KC_e}{1+KC_e} \quad (3)$$

Where θ is the surface coverage, C_e and q_e are the equilibrium dye concentration (mgL^{-1}) and uptake (mgg^{-1}),q_{max} is the monolayer adsorption capacity (mgg^{-1}), and K_L (k_{ads}/k_{des}) is the dynamic equilibrium constant (Lg^{-1}) related to adsorption site energy and sorbate affinity, and as well determines the direction of equilibrium. Equation (1) is linearized as

$$^1/_{q_e} = \frac{1}{K_L q_m}\left(^1/_{C_e}\right) + ^1/_{q_m} \quad (4)$$

The slope and intercept of the plot of $^1/_{q_e}$vs $^1/_{C_e}$gives the Langmuir parameters ($k_L$andq_m) as reported in *Table* 2. The marked increase in q_m for RCS (13.889g/g) relative to RS (9.709g/g) indicated improved uptake due to calcination and the rise in q_m from RCS (13.889g/g) to ACS (18.868g/g) showed that activation then calcination enhanced the uptake of MB onto Ekowe clay. ACS showed 35.85% increase in$q_m$relative to RCS and RCS increased by 43.05% relative to RS. These suggested that activation and calcination enhanced the surface areas generating more adsorption sites.

The essential attributes of Langmuir isotherm can be express by a dimensional constant, R_L called equilibrium parameter (Dalaran, et al 2009) or separation factor (Chatterjee, et al 2009; Safa & Bhatti, 2011) defined as,

$$R_L = \frac{1}{1+KC_o} \quad (5)$$

Where, K_L is the Langmuir constant ($L\ mg^{-1}$) and C_o is the highest initial dye concentration (Dalaran, et al. 2009). R_L value characterizes the fitness of Lagmuir isotherm and specifies the nature of the adsorption mechanism: $0< R_L<1$ indicates favourable adsorption; $R_L>1$, unfavourable; $R_L=1$, linear; and $R_L=0$, irreversible chemisorption. In *Table* 2, $R_L<1$ for both samples indicated adsorption is favourable. *Figure* **1a** depicts isotherm type I showing that monolayer adsorption governs MB uptake onto RS and RCS. *Figure* **1c** depicts isotherm type V which shows that monolayer adsorption is followed by multilayer adsorption. This explains the high dye uptake of ACS relative to RCS and RS. It can be inferred that activation stimulated the onset of multilayer adsorption that is probably responsible for ACS's high uptake.

Freundlich isotherm: The Freundlich Isotherm is purely an empirical expression which gives the constant temperature variation of sorbate adsorption. It is often used where the actual identity of the sorbate is unknown and has been verified best applicable for a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. It is expressed as

$$q_e = ^x/_m = K_F C_e^{1/n} \quad (6)$$

Linearized in exponential logarithmic forms as

$$lnq_e = lnK + (1/n)lnC_e \quad (7)$$

Maximum adsorption capacity, q_m is related to K_F by the expression:

$$K_F = \frac{q_m}{C_o^m} \quad (8)$$

Where x is the mass of adsorbate adsorbed, m is the mass of the adsorbent, K_F is the Freundlich isotherm constants relating the adsorption capacity (q_e),C_o is the initial dye concentration, and n is the adsorption intensity or heterogeneity factor at the given temperature from which the effectiveness parameter, $1/n$ is obtained. $2≤n≤10$ ($0.1≤1/n≤0.5$) implies adsorption is good and governed more by chemisorption, $1≤n≤2$ ($0.5≤1/n≤1$) suggests adsorption is more favoured by physisorption while $n<1$ ($1/n>1$) implies that adsorption is poor (Hamdaoui & Naffrechoux, 2007, and Mourchid et al. 2013). The model parameters; n, K_F and q_m reported in *Table* 2 were obtained from the slop and intercept of the plot of $lnq_e vs lnC_e$. *Table* 2 shows $1<n<2$ ($0.5≤1/n≤1$) for all samples indicating heterogeneity, favourable and effective adsorption; dominantly physisorption probably as a result of the size of MB molecules (Mourchid et al., 2013). Freundlich model q_m (Tab. 2) is low relative to the Langmuir values.

Temkin Isotherm: Temkin isotherm often describes adsorption behavior of heterogeneous surfaces (Wambu et al., 2011). The isotherm postulates an equal distribution of binding energies over the entire exchangeable sites on the adsorbent surface which is also dependent of the functional groups of the adsorbing surface and that the heat of adsorption of all the molecules or ions in the layer decreases linearly with coverage due to adsorbate-adsorbent interactions. The isotherm is expressed as:

$$q_e = A + BlnC_e \qquad (9)$$

$A = BlnK$ is the Temkin adsorption potential (Gulipalli et al., 2011; Safa & Bhatti, 2011); B = Temkin constant relating to heat of adsorption. Low value of B indicates weak interaction between adsorbate and adsorbent, consistent with physical interface between adsorbate and adsorbent surfaces (Wambu et al. 2011).Values of R^2, *A* and*B* were estimated from slope and intercept of the plot q_e vs *ln* C_e. *Table* 2 reports B_T<8kJ/mol suggesting weak interaction between MB ions and the samples' surfaces thus indicating that the adsorption is very likely physisorption.

Table 2: Parameters of the Adsorption Equilibrium isotherm models

Langmuir Isotherm Model

					Error Analysis		
sorbent	a_L (L/mol)	k_L (L/g)	k_L/a_L $(q_m)(g/g)$	R_L	R^2	**R**	χ^2
RS	7.0367	0.210	9.709	0.120	0.997	0.998	18.764
RCS	3.5184	0.153	13.889	0.157	0.997	0.998	32.991
ACS	3.1985	0.179	18.868	0.138	0.983	0.991	47.762

Freundlich Isotherm Model

					Error Analysis		
	k_F (L/g)	$q_m(g/g)$	**1/*n***	n	R^2	R	χ^2
RS	0.425	10.625	0.644	1.553	0.999	0.999	15.563
RCS	0.256	6.400	0.763	1.311	0.999	0.999	6.565
ACS1	0.281	7.025	0.793	1.261	0.989	0.995	5.891

Temkin Isotherm Model

	$K(L/g)$	A	$B_T(\frac{kJ}{mol})$	R^2	R
RS	0.180	-3.896	2.272	0.994	0.997
RCS	0.142	-4.653	2.385	0.996	0.998
ACS1	0.135	-6.036	3.010	0.980	0.990

Dubinin-Kaganer-Radushkevich (D-K-R)Model

				Error Analysis		
	$q_{max}(g/g)$	**β(mol^{2}J^{-2})**	***E*(Jmol^{-1})**	R^2	R	χ^2
RS	4.879	4 x 10^{-5}	1.118 x 10^2	0.969	0.984	1.566
RCS	4.618	-`4 x 10^{-5}	1.118 x 10^2	0.980	0.990	1.963
ACS1	5.663	4 x 10^{-5}	1.118 x 10^2	0.964	0.982	2.551

Dubinin-Kaganer-Radushkevich (D-K-R) isotherm related the porous structure of the sorbent and mean free energy of sorption per mole sorbate as it is transferred to the surface of the solid from an infinite distance in the solution. The estimated characteristic porosity of the adsorbent and the apparent energy of adsorption are obtained by fitting the adsorption equilibrium data into the D-K-R isotherm:

$$q_e = q_m \exp\left(-\beta\left[RTln\left(1+\frac{1}{C_e}\right)\right]^2\right) \qquad (10)$$

Linearized as

$$lnq_e = lnq_m - \beta\varepsilon^2 \qquad (11)$$

With$\varepsilon = \left[RTln\left(1+\frac{1}{C_e}\right)\right]$ (12)

Where β is mean adsorption energy (mol^2/kJ^2), ε is the Polanyi potential, which givesthe amount of energy required to pull an adsorbed molecule from its adsorption space to infinity; R is gas constant (kJ/molK) and T is the equilibrium temperature (K). Polanyi sorption theory assumed that sorption potential exists over a fixed volume of sorption space close to the sorbent surface (Akhtar, et al. 2006). This potential is related to an excess of sorption energy over the condensation energy and is independent of temperature. The relationship between β and the mean molar sorption energy of the sorbate particles (£) can be given as (Kumar et al., 2010 and Ali et al. 2011):

$$£ = 1/\sqrt{(2\beta)} \qquad (13)$$

£<8kJ/mol characterizes physisorption whereas £>8kJ/mol indicates ion-exchange and likely dominance of chemisorption (Riaz et al. 2006)**.**The values of *E*, *β*, and$q_m$estimated from the plots of $lnq_e = lnq_m - \beta\varepsilon^2$ are reported in *Table* 2. The ACS gave the highest value for q_m while RS and RCS have closely equal values. In *Table* 2, E<8kJ/mol for all the samples therefore, ascribing physisorption as the operating phenomenon.

C. *Statistical Analysis – Coefficients, Error and Deviation*

The correlation coefficient, R measures the direction of the linear relationship between two variables. R≤1 implies the dependent and independent variables have strong relationship such that as the independent variable increases, the independent variable also increases. R>0.8 is generally described as strong while R<0.5 is weak. Coefficient of Determination, R^2 exposes the degree of variation in variable prediction. It gives the ratio of the explained variable to the total variable. It determines the proportion of experimental data that is on/closest to the line of best fit. An error is required to evaluate the fitness of an isotherm equation to the experimental equilibrium data obtained (Chatterjee, et al. 2009). In this study, Regression coefficients (R^2) and a nonlinear Chi-square test were performed for all the isotherm models. The Chi-square test statistic can be represented mathematically as:

$$\chi^2 = \sum\left(\frac{(q_e - q_m)^2}{q_m}\right) \qquad (14)$$

Where q_m is the model equilibrium capacity (mg/g) and q_e is the experimental equilibrium capacity (mg/g). The χ^2 value is small for $q_m \approx q_e$, and χ^2 value increases as $q_m > q_e$. Thus, it is necessary to analyze the data and confirm the best fit isotherm for this adsorption system using the non-linear Chi-square test. The R, R^2, X^2 and Δq were determined using the Microsoft's spreadsheet, Microsoft Excel and shown in *Tables* 2.

The results of the coefficient and error analyses of all the isotherm models are shown in *Table* 2. The Freundlich isotherm gave the highest R (0.999, 0.999, 0.995) and R^2 (0.999, 0.999 and 0.989) showing that equilibrium data correlated best with the model for the three samples. However, as reported in the table, the other isotherms showed strong correlation. The R^2 values for all the samples showed that over 96% of the total variation in MB uptake can be explained by the linear relationship between the equilibrium concentration and uptake.

The D-K-R gave the lowest Chi-square ($\mathcal{X}^2$) values of 1.566, 1.963 and 2.551 for RS, RCS and ACS, followed by Freundlich isotherm with values of 15.563,6.565 and 5.891. Though the Freundlich isotherm has the highest R and R^2 values and D-K-R has the lowest, the lowest Chi-square value for the D-K-R implied that the adsorption is not solely a multilayer with heterogeneity as is typical of Freundlich isotherm. Generally, R>0.98 and R^2>0.95 for all the models indicating the models' correlations are invaluable and significant. This and the adsorption isotherm validate that sorption of MB onto the samples is not strictly monolayer or multilayer. The adsorption isotherms (Fig. 1) for RS and RCS showed monolayer adsorption typical of Langmuir model while ACS showed that monolayer preceded multilayer adsorption. It is noteworthy, multilayer adsorption has been reported to be more typical of dye adsorption.

D. *Thermodynamic studies*

In the design of adsorption systems, thermodynamic properties are critical design variables applied in estimating the performance and predicting the mechanism of adsorption processes.

Activation energy in thermodynamic studies exposes the temperature dependence of the reaction rate. Conventionally, reaction rate would increases with temperature; however, in adsorption is not always so as it could go both ways depending on physisorption or chemisorption. It describes the minimum energy needed/must be overcome for sorbate/sorbent surface interaction, even though the process may already be thermodynamically possible. Processes that exhibit negative E_a are exothermic in nature and proceed at lower temperatures. Most often increased temperature increases sorbate solubility and kinetic energy making sorbate/solvent contact stronger resulting in difficulty in sorbate uptake. Thermodynamics activation energy, E_a ($kJmol^{-1}$) and the frequency factor, A were determined at varied temperatures from slope and intercept of Arrhenius equation plot, *lnk* vs *1/T* and reported in *Table* **4**:

$$lnk = lnA - \frac{E_a}{RT} \qquad (15)$$

Where: k = adsorption rate constant, R = gas constant (8.314 J.mol-1K-1) and T = temperature (K).

The negative values of E_a increased with temperature implying exothermicity. At low temperature, adsorbate kinetic energy is low and physical attraction (physisorption) is more stable suggesting increased adsorbate affinity and ease in adsorption. However, with increased temperature even at negative activation energy, the kinetic energy and solubility of adsorbate species increases resulting in difficulty in adsorption (especially for exothermic process).

Thermodynamic activation parameters (ΔH^*, ΔS^* and, ΔG^*) give insight whether an adsorption followed an activated complex using Eyring equation:

$$lnk/_T = {lnk_B}/_h + (\Delta S^o/R) - (\Delta H^o/RT) \qquad (16)$$

With k = adsorption rate constant, k_B is the Boltzman constant (1.3807×10^{-23}J/K), h = Plank constant (6.6261×10^{-34}Js).

$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad (17)$$

ΔG*, ΔH*and ΔS* obtained from slope and intercept of the plot, *lnk/T* vs *1/T* as reported in *Table* **4**. In adsorption it is not always true that external energy (increased temperature) is require for adsorption considering spontaneity, exothermicity and physisorption. Negative ΔG* imply there was spontaneous solvation of the clay mineral forming a complex and the energy released (free energy of solvation) was equal the MB/water free energy of solvation, enough to break the MB/water solvation bond. The energy released in MB/water bond breaking break the clay-water solvation bond hence, MB molecules can be attracted to the adsorption site. Exothermicity as indicated by the negative ΔH* collaborates the assertion about ΔG*. This shows that the free energy of solvation of the clay mineral is greater than the free energy of solvation of MB dye. Positive ΔS* implies dissociative mechanism while negative ΔS* suggests an associative mechanism where adsorption leads to rate order through the formation of sorbate/sorbent activated complexes and it reflects that no significant change occurs in the internal structures of the adsorbent during the process. Negative ΔS* reported in *Table 4* reflected that the molecular mobility depends on the internal energy induced enthalpy and that the adsorption involves an associative mechanism typical of leaving no structural change in the clay adsorbent. These assertion elucidated that adsorption is driven by intermolecular interactions (physisorption) and leads on through the formation of clay and MB dye complexes.

Thermodynamic considerations are necessary to conclude on the nature of the adsorption process. The standard Gibb's free energy change (ΔG^o) is an indication of process spontaneity. The classical Van't Hoff equation below shows the relationship between ΔG^o and K_a (Wambu et al., 2011):

$$\Delta G^o = -RT\ln K_a \quad \Rightarrow \quad \Delta G^o = -RT\ln K_c \qquad (18)$$

K_a = equilibrium constant from Langmuir isotherm and K_c = single point or linear adsorption distribution coefficient (also apparent distribution coefficient). **Note**; at infinite dilution, the adsorption partition/distribution coefficient, K_C becomes the standard equilibrium rate constant, K_a (*l*/g).

$$K_c = q_e/C_e = {}^{F_r}/_{1 - F_r} \qquad (19)$$

Where, F_r = inverse of % uptake at equilibrium.

On integration of $\frac{d\ln K_c}{dT} = \frac{\Delta H^o}{RT^2}$ and re-arranging, we have

$$\ln K_c = (-\Delta H^o/RT) - (\Delta S^o/R) \qquad (20)$$

Therefore,

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (21)$$

The thermodynamic Parameters (ΔG^o, ΔH^o and ΔS^o) estimated from the plot $\ln K_C$ vs 1/T of Van't Hoff's equation and reported in *Table* **4** explain the nature of the process relative to its temperature. The free energy (ΔG^o) as estimated from the Langmuir constant, a_L (Tab. 3) and the Van't Hoff equation plot resulted in negative values. Aydin and Aksoy, (2009), have postulated feasible and spontaneous adsorption of Cr(VI) onto chitosan at temperatures below 313.15K and negative ΔG^o. It is conventional that decrease in the negative ΔG^o with increase in temperature would indicate favourable reaction as bond breaking and molecular mobility in solution increase with temperature thus increasing rate of molecular transfer to reaction site. This is not feasible in physisorption process typical of weak attraction force where increase molecular mobility at increased temperature excites sorbate molecule beyond the surface site attraction force hence preventing adsorption. However, increased negative ΔG^o with temperature implies lower temperature would ease adsorption; that is, physisorption. In *Table* **4**, negative ΔG^o is indicative of a spontaneous and significant adsorption (Akhtar et al, 2006 and Hong et al. 2009**).** It has been reported, $\Delta G^\circ \leq$-20kJ/mol is consistent with sorbate/sorbent electrostatic interaction implying predominant physisorption while $\Delta G^\circ \geq$-40kJ/mol entails a typical and particular involvement of charge sharing and transfer characteristic of chemisorption process. Physico-chemical mechanism is typical of -18kJ/mol$\leq \Delta G^\circ <$-45kJ/mol. Increasing negative ΔG^o with temperature as reported in *Tables* **3** and **4** pointed that lower temperature favoured MB uptake and that the adsorption followed physicochemical mechanism chiefly physisorption.

Unlike endothermicity of positive ΔH^o, exothermic process; characterized by negative ΔH^o involve more bond-making than bond-breaking resulting in the release of extra energy in the form of heat. The heat evolved during physical adsorption is of the same order of magnitude as the heat of condensation (2.1-20.9kJ/mol), while heat of chemisorption generally falls within 80-200 kJ/mol. Cation (metals and dyes) uptake by low cost adsorbents can be attributed to physico-chemical process rather than pure physical or chemical adsorption (Saha & Chowdhury, n.d). The negative ΔH^o as shown in *Table* **4**, characterized the exothermicity of the dye/clay system, implying the total energy absorbed in dye/water solvation bond breaking is less than the total energy released in clay/water solvation bond making, releasing the extra energy in the form of heat. Therefore, in accordance with the above declaration and with Aydin and Aksoy (2009) and Hong et al. (2009), it seems physical (intermolecular) attraction onto sorption sites and solvation describe the mechanism of MB uptake as physicochemical though chiefly physisorption. Positive ΔS^o reflects the sorbent/sorbate affinity and suggests increased randomness at the sorbent/solution interface with some structural changes. The initial adsorbed solvent molecules being displaced by the sorbate species, gain more translational entropy may be due to the molecular weight, thus allowing for prevalence of disorderliness in the sorbate/solvent interaction and increased degree of freedom of the adsorbate species. Negative ΔS^o suggests an enthalpy driven adsorption typical of stable sorbate systems of very low molecular mobility and requiring external influence to increase adsorbate freedom and available for adsorption; chemisorption. The positive ΔS^o reported in *Table* **4** reflected the samples' affinity for the MB dye and suggested increased instability in the dye/water interaction resulting from the excess heat of exothermicity. The water molecule of the broken MB/water complex gain more translational entropy (positive ΔS^o) induced by the excess energy of the clay/water solvation allowing the prevalence of randomness and therefore freeing more MB molecule for attraction on the cay surface. The dye/water instability elucidates the increased degree of freedom of the adsorbed species. These assertions strongly revealed that the MB dye adsorption onto the samples is not enthalpy driven as the adsorption is between the clay and MB dye.

Table 3: **ΔG^o** obtained from Langmuir constant

Adsorbent	*ΔG^o using k_L from Langmuir Isotherm (T =300K, R =8.3134J/molK)*	
	$a_L(L/mol)$	ΔG^o
RS	7.0367	-4.866
RCS	3.1584	-2.868
ACS	3.1985	-2.900

Table 4: Varied temperature thermodynamics

Sorbent	**RS**			**RCS**			**ACS**		
T (K)	293	313	333	293	313	333	293	313	333

Activation energy									
E_a(kJ/mol)	-5.11E3	-5.45E3	-5.80E3	-5.04E3	-5.38E3	-5.72E3	-5.00E3	-5.34E3	-5.68E3
A		0.2536			0.4119			0.4644	
Activation parameters									
ΔG^*(kJ/mol)	-29.787	-31.821	-33.854	-29.792	-31.826	-33.860	-29.792	-31.826	-33.860
ΔH^*(kJ/mol)	-29.841	-31.878	-33.915	-29.841	-31.878	-33.915	-29.841	-31.878	-33.915
ΔS^*(kJ/mol)		-1.829×10^{-4}			-1.663×10^{-4}			-1.663×10^{-4}	
Thermodynamic Parameters									
ΔG^o(kJ/mol)	-18.814	-18.908	-19.002	-19.048	-19.176	-19.303	-19.211	-19.358	-19.506
ΔH^o(kJ/mol)		-17.43			-17.18			-17.05	
ΔS^o(kJ/mol)		4.722×10^{-3}			6.376×10^{-3}			7.374×10^{-3}	

IV. CONCLUSION

The main purpose of this work is to investigate the constant and varied temperature mechanism of MB dye uptake onto raw (RS), calcined (RCS) and activated-calcined (ACS) Ekowe clay. From the results obtained, it follows that Calcination enhanced the surface area and filtration capacity of the raw and activated clay. The raw and modified samples showed characteristic adsorption-enhancing PZCs that were below the experimental pH. Generally, modification of Ekowe clay improves its affinity and uptake of MB dye.

The type I Langmuir isotherm describes the constant temperature capacity of RS and RCS while type V adsorption isotherm explains the capacity of ACS. The Langmuir isotherm predicted highest MB uptake for ACS attributed to multilayer adsorption. The correlation coefficient, R validated the linearity of increase in dye uptake to decrease in equilibrium concentration and the coefficient of determination, R^2 exposes that a very high proportion of the experimental equilibrium data are very close to the expected data as predicted by the Freundlich isotherm. The R, R^2 and χ^2 of the equilibrium isotherm models implied that the MB dye adsorption onto the clay samples is not solely a heterogeneous surface adsorption typical of Freundlich isotherm rather uptake is governed by monolayer adsorption proceeded by multilayer adsorption. The Freundlich, Temkin and D-K-R isotherm inferred physisorption as the operational adsorption phenomenon.

The negative increase in activation energy (E_a) with temperature indicated exothermicity and implied that low temperature would enhance easy BM dye adsorption (physisorption) and stability. The thermodynamic activation Parameters (ΔG^*, ΔH^* and ΔS^*) indicated that the energy of spontaneous formation and breaking of activation complexes is derived from free energy of solvation and the dye uptake leave no structural change in the clay adsorbent.

The ΔG^o can be estimated from the Langmuir constant, a_L. The ΔG^o, ΔH^o and ΔS^o can also be obtained from the plot of Van't Hoff's equation and the ΔG^o-temperature relationship. The thermodynamic of the adsorption system holds that low temperature favoured MB dye uptake and that the adsorption followed physicochemical mechanism primely physisorption. Negative ΔH^o and ΔG^o indicated significant MB adsorption as well as an exothermic and spontaneous physisorption. The positive value of ΔS^o revealing the clay samples' affinity for the MB dye showed increased instability and randomness in the dye/water interaction interface resulting from the excess heat of exothermicity. The adsorption thermodynamics shows that the uptake of MB dye onto the Ekowe clay samples is not enthalpy driven.

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