

# Environmental Science

*An Indian Journal*

*Current Research Paper*

ESAIJ, 10(12), 2015 [451-461]

## Equilibrium isotherm analyses and thermodynamic studies of the removal of basic dye from solution using castor seed shell

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### ABSTRACT

The equilibrium isotherm analysis and the thermodynamics of the sorption of basic dye by Castor Seed Shell (CSS) was investigated. Isotherm experiments were conducted and the data obtained were fitted into different equilibrium isotherm equation viz: Langmuir I and II; Freundlich; Dubinin-Radushkevich (D-R); Temkin; Harkins –Jura and Halsey isotherm equation. Freundlich, Langmuir (I and II). The Halsey isotherm equations gave the best correlations ( $r^2$ ) than the other isotherm equations fitted with the experimental data. The relationship between the dimensionless parameter,  $K_R$ , and initial concentration,  $C_o$ , showed that the sorption of MB was favored at higher initial dye concentration and CSS dosages than the lower ones. The thermodynamic analysis showed that the sorption is spontaneous and endothermic. The prospects of regenerating the CSS was studied using four different eluting solvents in a batch desorption studies. The results of the batch desorption studies showed that both chemisorptions and ion-exchange played prominent role in the sorption process.

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### KEYWORDS

Equilibrium;  
Isotherm;  
Basic dye;  
Castor seed shell;  
Sorption;  
Thermodynamics.

### INTRODUCTION

Owing to the aesthete nature of man, the presences of dyes and pigments in wastewater generated from some of our industries have continued to burgeon. Dyes are aromatic organic compounds with structures including aryl rings which have delocalized electron systems<sup>[1]</sup>. Dye imparts colour on a material when bound to it and the colour imparted is furnished by the presence of a chromophore group. The chromogen, which is the aromatic structure, normally contains benzene, naphthalene or anthracene

rings as part of a chromogen-chromophore structure along with an auxochrome. There are more than 100,000 commercially available dyes, with over  $7 \times 10^5$  tonnes of dyes produced annually<sup>[2]</sup>. It is estimated that 2 % of dyes produced annually are discharged in effluent from manufacturing operations while 10% was discharged from textile and associated industries<sup>[3]</sup>.

Abstraction of the colored components of wastewater, using biosorbents, has proven to be an efficient and economical route to ameliorate the environmental impact of coloured wastewater. Reports

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from different studies have shown that plentiful low cost materials have been successfully applied in the removal of dyes from aqueous solution. Some of which are peat for Basic Blue 69 and Acid Blue 25<sup>[4]</sup>, giant duckweed for methylene Blue<sup>[5]</sup>; Sugar cane dust for Basic violet 10, Basic violet I and Basic green 4<sup>[6]</sup>. Rice husk for malachite green<sup>[7]</sup> carbon prepared from waste apricot for methylene blue, malachite Green and crystal violet<sup>[8]</sup>; Bagasse fly ash for orange-G and methyl violet<sup>[9]</sup>.

Previously, in our Laboratory, the ability of castor seed shell in methylene blue removal from aqua system was studied<sup>[10]</sup> but the detailed equilibrium isotherm analysis, the thermodynamics of sorption and the regeneration potential was not reported. Equilibrium relationships between sorbent and sorbate are described by sorption isotherm, usually the ratio between the quantity sorbed and that remaining in the solution at a fixed temperature at equilibrium<sup>[11]</sup>. The biosorption efficiency of varying biosorbent for different pollutants is usually reported in terms of how well the observation fit adsorption isotherm equations. The equilibrium sorption isotherm is fundamentally important in the design of sorption system for water and wastewater treatment. Equilibrium studies give the capacity of the sorbent and describe the sorption isotherm by constants whose values express the surface properties and affinity of the sorbent<sup>[6]</sup>.

The castor bean plant [*Ricinus Communis*] belongs to the Euphorbia Family [*Euphorbiaceae*], a diverse and economically important family of flowering plants. It is native to the Ethiopian region of East Africa. It has become naturalized in tropical and warm temperate regions of the world. The seeds or beans are the source of numerous economical important products. One of the nature finest natural oils is produced from it. The castor bean is enclosed in spiny seed pod or capsule. This pod or capsule is composed of three sections or carpels, which split apart at maturity. Each carpel contains a single seed. As the carpel dries and splits open, the seed is ejected. The castor seed oil is extracted from the bean while the seed pod is discarded and continued to be of environmental pollution. Thus, the present studies aimed at (I) equilibrium isotherm analysis

of the castor seed shell (CSS) for the remediation of water contaminated with basic dye, using MB as a model basic dye (II) Determination of the applicability of different equilibrium isotherm models (i.e. Langmuir I and II, Freundlich, Dubinin-Radushkevich (D-R), Temkin, Harkins-Jura and Halsey) as a function of two process variables (III) Determination of the thermodynamic parameters of the sorption process and (IV) determination of the CSS regeneration potential.

## MATERIALS AND METHODS

### Sorbent and sorbate preparation

The castor seed shell [CSS] was prepared as described in our earlier treatise<sup>[10]</sup>. Methylene blue (MB), the basic dye used, as the model sorbate, in the present study is a monovalent cationic dye. It is classified as C.I. Basic blue 9, C.I. solvent blue 8, C.I.52015. It has a molecular weight of 373.90. The MB used was of analytical grade so it was used without further purification. A stock solution 1000mg/l was prepared by dissolving an appropriate quantity of MB in a liter of deionised water. The working solutions were prepared by diluting the stock solution with deionised water to give the appropriate concentration of the working solutions. The concentration of the residual MB was quantified using UV/visible spectrometer at a  $\lambda_{\max}$  corresponding to the maximum absorption for the dye solution ( $\lambda_{\max} = 661\text{nm}$ ). A calibration curve created from analysing MB solutions of different concentrations was used. All of the concentrations considered in this work resulted in absorbance values that were  $<2$  and followed Lambert-Beer's law. The amount of MB sorbed per unit mass of adsorbent (in mg/g) was calculated using the mass balance equation

### Adsorption isotherm studies

#### i) Sorbent dosage optimization

The effect of CSS dosage on the adsorption process was studied by determining the adsorption isotherms over a sorbent dosage range of 0.1g-0.8g. The initial concentration was varied from 25-300mg/l. Samples were withdrawn at a predetermined equi-

librium time and analyzed for residual MB and the amount of sorbate sorbed per unit mass of the CSS [q in mg/l] was calculated using the mass balance procedure.

## ii) Temperature optimization

The effect of temperature on the sorption characteristics was investigated by determining the adsorption isotherms at 309, 318 and 329K. The initial concentration was varied from 25-300mg/l. Samples were withdrawn at a predetermined equilibrium time and the amount of MB sorbed per unit mass of the CSS [q in mg/g] was calculated using the mass balance procedure. The thermodynamic parameters were estimated using the classical thermodynamic equations.

## Desorption studies

The CSS (1g) was loaded with the MB (200mg/L) and dried in the oven at 60°C overnight. This biomass was then placed in Erlenmeyer flasks containing 50mL of the desorbing agent solution. The sample was agitated for 120min and then the CSS was filtered. The desorbed MB concentration was quantified using UV/visible spectrophotometer. Four different eluting solvents were used: deionised water, HCl (0.1M), NaOH (0.1M) and CH<sub>3</sub>COOH (0.1M).

## RESULTS AND DISCUSSION

Basic forms of Langmuir sorption isotherm<sup>[12]</sup> have reasonable agreement with a large number of experimental isotherms including those that have different interfaces between the two phases<sup>[13]</sup>. Consequent upon this Langmuir sorption isotherm is conventionally used for the sorption of solute from a liquid solution, assuming the sorption takes place at specific homogeneous sites within the sorbent. It also assumes that once a dye occupies a site, no further sorption can take place at that site. The rate of sorption to the surface should be proportional to a driving force times an area. The driving force is the concentration of the solution and the area is the amount of bare surface. The linear form of the Langmuir isotherm equation can be represented thus:

$$q_e = \frac{q_m k_a c_e}{1 + K_a C_e} \quad (1)$$

The Langmuir isotherm equation can be linearized into four different forms and simple linear regression will result in different parameter estimates<sup>[14][15]</sup>. The more popular linear forms used are Langmuir I and II and are presented below:

$$\text{Langmuir I: } C_e/q_e = 1/q_m C_e + 1/K_a q_m \quad (2)$$

$$\text{Langmuir II: } 1/q_e = (1/K_a q_m) 1/C_e + 1/q_m \quad (3)$$

Where:  $q_e$  is the amount of MB sorbed per unit of the CSS (mg g<sup>-1</sup>),  $C_e$ , is the equilibrium concentration of the adsorbate (mg l<sup>-1</sup>) and  $q_m$  and,  $b$ , are the Langmuir constants related to maximum sorption capacity and energy of adsorption, respectively.

A plot of  $C_e/q_e$  versus  $C_e$  should indicate a straight line of slope  $1/q_m$  and intercept of  $1/K_a q_m$  for Langmuir I and a plot of  $1/q_e$  versus  $1/C_e$  should indicate a straight line of slope  $1/K_a q_m$  and intercept  $1/q_m$  for Langmuir II.

The empirical Freundlich isotherm, based on sorption on heterogeneous surface, can be derived assuming a logarithmic decrease in the enthalpy of sorption with the increase in the fraction of occupied sites and is given by:

$$q_e = K_f C_e^{1/n} \quad (4)$$

Where:  $q_e$  and  $C_e$ , are as previously defined.  $k_f$  and  $n$  are Freundlich constants related to adsorption capacity and sorption intensity respectively. Equation 4 can be linearized as presented below and the Freundlich can be determined from the plot of  $\ln q_e$  versus  $\ln C_e$ .

$$\ln q_e = \ln K_f + 1/n \ln C_e \quad (5)$$

Another equation usually used in the analysis of isotherm equation was proposed by Dubinin – Radushkevich,<sup>[16]</sup> thus:

$$q_e = q_s \exp(-K' \varepsilon^2) \quad (6)$$

Where:  $\varepsilon$  (Polanyi potential) is equal to  $RT \ln (1 + 1/C_e)$ ,  $q_e$  and  $C_e$  have been defined earlier  $q_m$  is the theoretical monolayer saturation capacity,  $k'$  is the constant of the adsorption energy (mol<sup>2</sup> K<sup>-1</sup> J<sup>2</sup>),  $R$  is the gas constant (KJ mol<sup>-1</sup> K) and  $T$  is the temperature (K).

$$\varepsilon = RT \ln (1 + 1/C_e) \quad (7)$$

The constant  $B$  gives the mean free energy,  $E$  or sorption per molecule of sorbate when it is transferred to the surface of the solid from the solution

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and can be computed using following relationship<sup>[17]</sup>:

$$E = 1/\sqrt{2k} \quad (8)$$

A plot of  $\ln q_e$  versus  $\varepsilon^2$  enables the determination of the D-R isotherm constants.

Temkin isotherm contains a factor that explicitly takes into account adsorbing species-adsorbate interactions. This isotherm assumes that<sup>[18]</sup>: (1) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate interactions, and (ii) Adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy.

The Temkin isotherm is given as:

$$q_e = \frac{RT \ln(KT C_e)}{b} \quad (9)$$

Equation (9) can be linearized as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (10)$$

$$\text{Where } B_1 = \frac{RT}{b} \quad (11)$$

A plot of  $q_e$  versus  $\ln C_e$  enables the determination of the isotherm constants  $B_1$  and  $K_T$  from the slope and intercept, respectively.  $K_{Tis}$  the equilibrium binding constant (l/mol) corresponding to the maximum binding energy and constant  $B_1$  is related to the heat of adsorption.

The Harkins-Jura adsorption isotherm can be expressed<sup>[19]</sup> as:

$$1/q_e^2 = (B/A) - (1/A) \log C_e \quad (12)$$

The Harkins-Jura equation account for multilayer adsorption and can be explained with the existence of a heterogeneous pore distribution. The Harkins – Jura isotherm constants are obtained from the plot of  $1/q_e^2$  versus  $\log C_e$ .

Halsey adsorption isotherm can be given as:

$$\ln q_e = [1/n \ln K] - 1/n \ln C_e \quad (13)$$

This equation is suitable for multilayer adsorption. The fitting of this equation to the experimental data is a pointer to the heteroporous nature of the adsorbent<sup>[20]</sup>. The Halsey adsorption isotherm parameters can be obtained from the plot of  $\ln q_e$  versus  $\ln C_e$ .

### Error analysis

The constant parameters of the isotherm equations for the adsorption of MB unto CSS were cal-

culated by regression using the linear form of the isotherm equations. In order to evaluate the fit of the equation to the experimented data obtained from the optimization processes employed an error function is required. In this study, the linear coefficient of determination was used. The linear coefficient of determination,  $r^2$ , found from the evaluation of data by the linear model was calculated with the aid of the equation:

$$r^2 = \frac{S_{2xy}}{S_{xx}S_{yy}} \quad (14)$$

Where  $S_{xx}$  is the sum of squares of x

$$S_{xx} = \frac{\sum x_i^2 - \sum i^n = 1 x_i}{n}$$

Where  $S_{yy}$  is the sum of squares of y

$$S_{yy} = \frac{\sum y_i^2 - \sum i^n = 1 y_i}{n}$$

Where  $S_{xy}$  is the sum of squares of x and y and

$$S_{xy} = \frac{\sum x_i y_i - (\sum i^n = 1 x_i)(\sum i^n = 1 y_i)}{n} \quad (15)$$

### Sorbent Dosage Optimization.

In order to understand the effect of CSS dosage on the sorption of MB, isotherm experiments were carried out and the data obtained were analysed using the seven aforementioned isotherm equations. Isotherms were determined for five different sorbent dosages (0.1-0.8g). The different equilibrium adsorption isotherm equation parameters and the coefficients of determinations ( $r^2$ ) are presented in TABLE 1.

The analysis of the experimenter data with Langmuir I and II showed that the monolayer sorption capacity,  $q_m$ , reduced from 166.67 mg/g to 21.14 mg/g and 81.97 to 15.04 mg/g respectively when the CSS dose was varied from 0.1-0.8g, at fixed sorbate volume. It is apparent that by increasing the dosage of the CSS, the number of sorption sites, available for sorbent-sorbate interaction is increased, thereby resulting in the increased percentage of dye removal from the solution. The dwindling capacity of the CSS for the dye molecules as the CSS dose was increased from 0.1-0.8g was attributed to two reasons. The increased sorbent dose, at constant dye concentration and volume, will lead to unsaturation of sorption sites through the sorption

**TABLE 1 : Equilibrium isotherm parameters and correlation coefficients calculated for the sorption of MB by CSS at different CSS dosages (g)**

Isotherm Temperatures (K)			
Equations 309 318 328			
<b>Langmuir I</b>			
q <sub>m</sub> (mg/g)	166.67	200.00	303.03
b (L/mg)	0.251	0.112	0.039
r <sup>2</sup>	0.9785	0.9675	0.9905
<b>Langmuir II</b>			
q <sub>m</sub> (mg/g)	81.97	113.64	256.41
b (L/mg)	0.961	0.263	0.048
r <sup>2</sup>	0.9518	0.9824	0.9997
<b>Freundlich</b>			
K <sub>f</sub> (L/g)	31.17	21.16	12.89
1/n	0.5338	0.6609	0.8077
r <sup>2</sup>	0.9955	0.9936	0.9894
<b>D-R</b>			
q <sub>m</sub> (mol/g)	74.65	76.77	80.85
E (kJ/mol)	2.443	1.510	0.888
r <sup>2</sup>	0.7217	0.7416	0.7897
<b>Temkin</b>			
B <sub>1</sub>	27.815	34.181	42.01
K <sub>T</sub> (L/mg)	4.96	2.055	0.03
r <sup>2</sup>	0.9297	0.925	0.9505
<b>Harkins Jura</b>			
A	384.62	270.27	222.22
B	1.000	0.9730	1.0889
r <sup>2</sup>	0.8702	0.7324	0.6732
<b>Halsey</b>			
n	1.873	1.514	1.230
K =	1.836	2.015	2.050
r <sup>2</sup>	0.9955	0.9937	0.9974

process<sup>[21][22]</sup> and secondly may be due particulate interaction such as aggregation, resulting from high sorbent dose<sup>[23]</sup>. Such aggregation would lead to a decrease in total surface area of the sorbent and an increase in diffusion path length<sup>[21]</sup>. The value of q<sub>m</sub> and K<sub>a</sub> were plotted against the CSS dosage (m<sub>s</sub>) (Figure 1 and 2) and the corresponding linear plot of the values of q<sub>m</sub> and K<sub>a</sub> against m<sub>s</sub> were regressed to derive a mathematical relationship with coefficients of determination r<sup>2</sup>: 0.7956 for Langmuir I and 0.8559 for Langmuir II (for q<sub>m</sub> versus m<sub>s</sub>) and 0.7925 for Langmuir I and 0.9914 for Langmuir II (for K<sub>a</sub> versus m<sub>s</sub>) therefore q<sub>m</sub> and K<sub>a</sub> can be ex-

pressed as a function of m<sub>s</sub> as follows:

<p>Langmuir I</p> $q_m = -189.41m_s^{150.86}$ $K_a = 0.9673m_s^{0.2402}$	<p>Langmuir II</p> $q_m = 90.774m_s^{78.575}$ $K_a = 1.9743m_s^{0.704}$
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The effect of isotherm shape can be used to predict whether a sorption system is favourable or unfavourable both in fixed bed system as well as in batch process<sup>[24]</sup>. Hall et al.,<sup>[25]</sup> opined that the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, K<sub>R</sub>, which can be defined by the following relationship:

$$K_{R} = 1/1+ K_a C_o(16)$$

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Where:  $K_R$  is a dimensionless separation factor,  $C_o$ , is the initial concentration ( $\text{mg l}^{-1}$ ) and,  $b$ , is the Langmuir constant ( $\text{L mg}^{-1}$ ). The parameter  $K_R$  indicates the shape of the isotherm accordingly:

Values of $K_R$	Types of Isotherm
$K_R > 1$	Unfavorable
$K_R = 1$	Linear
$0 < K_R < 1$	Favorable
$K_R = 0$	Irreversible

The relationship between  $K_R$  and  $C_o$  is presented in Figure 3 and 4. From both Langmuir I and II the  $K_R$  values indicated that sorption was more favored at higher initial dye concentration and CSS dosages than the lower ones.

The linearities of both the Langmuir I and II are presented in TABLE 1. The linearities of both plots were high (i.e.  $>0.9000$ ) but the linearities of Langmuir II plots were higher.

The linear plots of  $\ln q_e$  versus  $\ln C_e$  at each CSS dosage revealed that the adsorption of MB onto CSS occurred on a heterogeneous site on the CSS. The Freundlich adsorption isotherm constants and the correlation coefficients are presented in TABLE 1. The values of  $1/n$  were less than unity, which is a pointer to the favourable nature of the sorption of MB onto CSS [26]. The values of  $1/n$  obtained ranged between 0.6116 and 0.5338. Values similar to this have been reported by [9] for the adsorption of Auramine-O (AR), Congo red (CR), Orange-G (OG) and Methyl Violet (MV) by mesoporous fertilizer plant waste carbon.

The results obtained when the data obtained were analysed using the D-R Isotherm equation are presented in TABLE 1. The theoretical monolayer saturation capacity,  $q_m$  decreased as the sorbent dosage increased (74.65-12.90). The mean free energy,  $E$ , of sorption per molecule of sorbate when it is transferred to the surface of the solid from infinity in the solution was calculated using equation (8) and the values obtained are presented in TABLE 1. The,  $E$ , values similar to what were obtained from the present studies have been reported [9][10] for the sorption of AR, CR, OG and MC onto mesoporous fertilizer plant waste carbon and the sorption of OG and MV onto bagasse fly ash. The D-R isotherm equation represents poor description of the sorption of MB onto CSS as shown in the values of the  $r^2$  obtained (0.8456-0.9212).

A plot of,  $q_e$ , versus  $\ln C_e$  enabled the analysis of the adsorption data with Temkin isotherm equation. The isotherm constants were obtained from the linear plots and the values obtained are presented in TABLE 1. The equilibrium binding constant,  $K_T$  ( $\text{l/mol}$ ) corresponding to the maximum binding energy increased from 4.93 to 21.007 as the sorbent dose was increased while the Temkin constant,  $B_1$ , related to the heat of adsorption reduced from 27.815-3.727 as the sorbent dose increased. The linearities of these plots were also high.

In order to investigate the possibility of the adsorption of MB onto CSS via a multilayer adsorption process, the experimental data were analysed

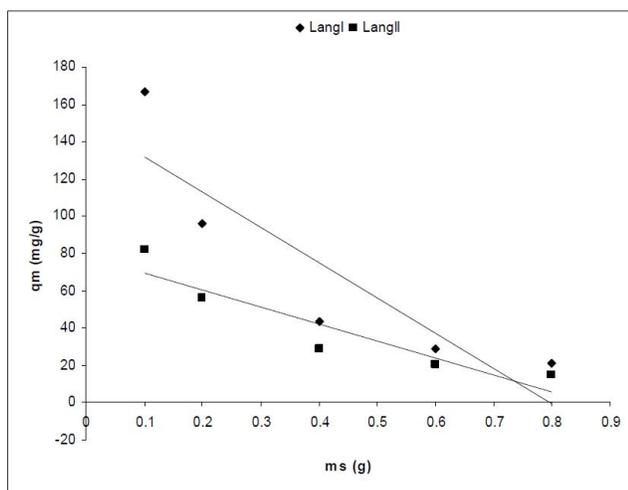


Figure 1 : Plot of  $q_m$  versus CSS dosage (g)

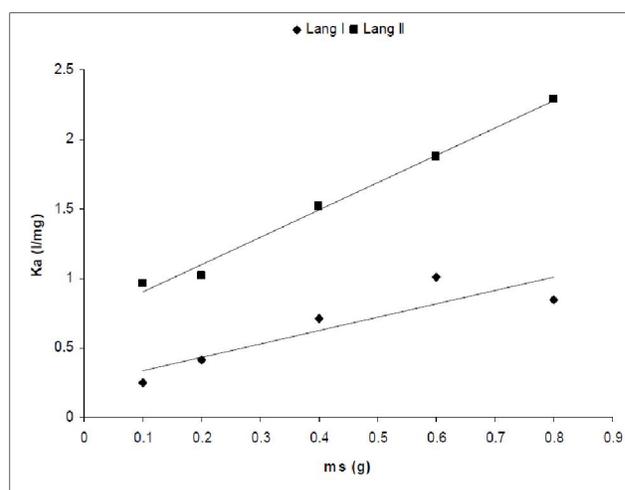


Figure 2 : Plot of  $k_a$  versus CSS dosage (g)

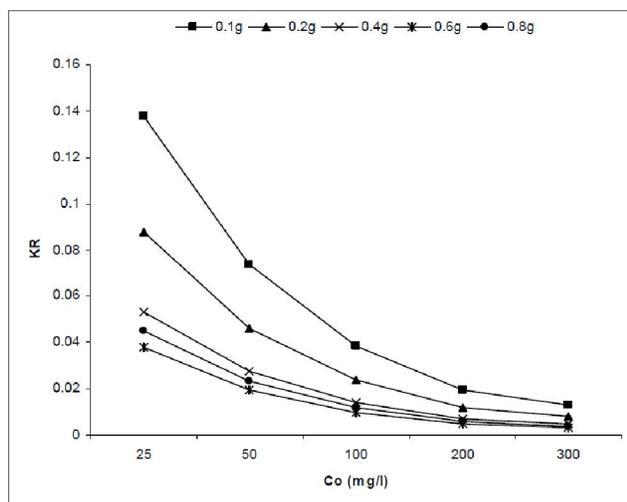


Figure 3 : Langmuir I plot of  $K_R$  versus  $C_o$  (mg/l)

with Harkins-Jura adsorption isotherm equation. The linearities of these plots were the poorest amongst all the isotherm equations tested (0.656-0.7145). Harkins-Jura isotherm constants, derived from the plots of  $1/q_e^2$  versus  $\log C_e$ , and the correlation coefficients,  $r^2$ , of the plots are presented in TABLE 1.

The heteroporosity of the CSS and the multilayer adsorption tendency of the sorption of MB onto CSS were tested using Halsey isotherm equation by plotting  $\ln q_e$  versus  $\ln C_e$ . The isotherm constants and the correlation coefficients are presented in TABLE 1.

### Temperature optimization

The effect of temperature optimization on the sorption isotherm of MB onto CSS was studied at 309, 318 and 329 K and the results are presented in TABLE 2. The linearities of both Langmuir I and II were high and the values of the monolayer sorption capacities  $q_m$  (mg/g) increased with increase in temperature. Since the sorption increased when temperature rose, therefore the system was endothermic<sup>[27][6]</sup>.

The linear plot of  $\ln q_e$  versus  $\ln C_e$ , at each temperature, indicates that adsorption of MB onto CSS also agrees with the description of the Freundlich isotherm equation (TABLE 2). The Freundlich adsorption isotherm constants and the correlation coefficients of the plots are presented in TABLE 2. The values of  $K_f$  and  $1/n$ , determined from the application of Freundlich isotherm equation, changed with the rise in temperature. The Freundlich con-

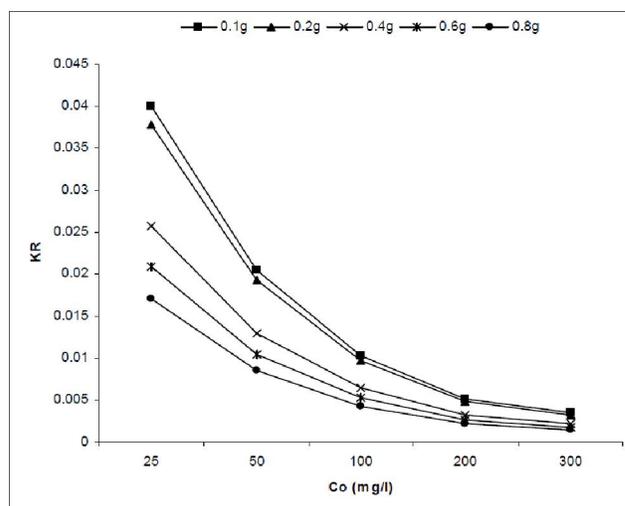


Figure 4 : Langmuir II plot of  $K_R$  versus  $C_o$  (mg/l)

stant  $1/n$  is a measure of the deviation from linearity of the adsorption<sup>[28]</sup> and the numerical values of  $1/n$  were less than unity, indicating that the adsorption of MB onto CSS was favourable at all the temperature studied.

The constants obtained from the plots of  $\ln q_e$  versus  $\varepsilon^2$  (D-R isotherm plot) are presented in TABLE 2. The mean free energy  $E$ , reduced with increase in temperature from 2.443 to 0.888 (KJ/mol) as the temperature of the MB solution increased. A low value of,  $E$ , has been reported for the sorption of Orange-G (2.236 kJ/mol) and Methyl violet (1.290 KJ/mol) by bagasse fly ash<sup>[9]</sup>. The theoretical monolayer saturation capacity value,  $q_m$ , increased with increase in temperature. In comparison with the applications of other isotherm equations, the linearities of D-R isotherm plots for the sorption of MB unto CSS were poor (TABLE 2).

The heat of adsorption of MB by CSS and the possible interactions of MB molecules on the surfaces of the CSS particles were studied at different temperatures using Temkin isotherm equation. The linearities ( $r^2$  of the plots of  $q_e$  versus  $\ln C_e$  and the derived isotherm constants, at studied temperatures, are presented in TABLE 2. The Temkin isotherm constants, presented in TABLE 2 show, that the heat of adsorption ( $B_1$ ) increases with increase in temperature, indicating endothermic adsorption<sup>[29]</sup>.

The conformity of the sorption of MB onto CSS to the description of Harkins – Jura isotherm equation was very low. This is clearly expressed in the

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**TABLE 2 : Equilibrium isotherm parameters and correlation coefficients calculated for the sorption of MB by CSS at different Temperatures (K)**

Isotherm Equations Sorbent dosages (g)					
Langmuir I	0.1	0.2	0.4	0.6	0.8
$q_m$ (mg/g)	166.67	96.15	43.67	28.90	21.14
$b$ (L/mg)	0.251	0.414	0.711	1.012	0.844
$r^2$	0.9785	0.9353	0.9685	0.9604	0.9558
Langmuir II					
$q_m$ (mg/g)	81.97	56.18	28.65	20.41	15.04
$b$ (L/mg)	0.961	1.017	1.518	1.877	2.293
$r^2$	0.9518	0.9902	0.9958	0.9961	0.9949
Freundlich					
$K_f$ (L/g)	31.17	23.76	14.40	11.38	9.09
$1/n$	0.5338	0.6116	0.5617	0.5601	0.5464
$r^2$	0.9955	0.9983	0.9928	0.9903	0.9892
D-R					
$q_m$ (mol/g)	74.65	45.15	24.26	17.02	12.90
$E$ (kJ/mol)	2.443	2.752	3.172	3.467	3.666
$r^2$	0.7217	0.8456	0.8882	0.9125	0.9212
Temkin					
$B_1$	27.815	16.258	7.6193	5.0878	3.7266
$K_T$ (L/mg)	4.96	7.938	12.859	17.434	21.007
$r^2$	0.9297	0.9133	0.9424	0.9411	0.9394
Harkins Jura					
$A$	384.62	77.519	21.930	9.775	5.666
$B$	1.000	0.519	0.443	0.312	0.273
$r^2$	0.8702	0.7145	0.6672	0.6574	0.656
Halsey					
$n$	1.873	1.635	1.780	1.785	1.830
$K =$	1.836	177.57	115.29	76.72	56.75
$r^2$	0.9955	0.9983	0.9928	0.9903	0.9892

linearities ( $r^2$  values) of the Harkins – Jura isotherm equation. The Harkins-Jura isotherm parameters, obtained at varying temperatures are presented in TABLE 2.

The high possibility of the CSS surface being heteroporous was expressed when the data obtained from this study were analysed with Halsey isotherm equation. The linearities of the plots were very high ( $>0.99$ ). The Halsey constant,  $n$  values decrease with increasing temperature, which show that adsorption increased with a decrease in  $n$  values indicating that the process is endothermic.

### Sorption thermodynamics

The thermodynamic parameters of a sorption process are required to determine the spontaneity of the biosorption process. Both energy and entropy factors must be considered in order to determine which process will occur spontaneously. The Gibbs free energy change,  $\Delta G^\circ$ , is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if,  $\Delta G^\circ$ , is a negative quantity. The free energy of the sorption reaction, considering the sorption equilibrium constant,  $k_a$ , is given by the following equation:

$$\Delta G^\circ = -RT \ln K_a \quad (17)$$

Where:  $\Delta G^\circ$  is the standard free energy change (J), R the Universal gas constant,  $8.314 \text{ J mol}^{-1} \text{ K}$ , and T is the absolute temperature (K)

Considering the relationship between free energy and equilibrium constant, change in equilibrium constant with temperature can be obtained in the differential form as follows<sup>[6]</sup>:

$$\frac{d \ln K_L}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (18)$$

After integration, the integrated form of equation (18) becomes:

$$\ln K_L = \frac{\Delta H^\circ}{RT} + Y \quad (19)$$

Where: Y is a constant. Equation (19) can be rearranged to obtain

$$-RT \ln K_L = \Delta H^\circ - TRY \quad (20)$$

Let

$$\Delta S^\circ = RY \quad (21)$$

Substituting Eqs (20) and (21), the Gibbs free energy change,  $\Delta G^\circ$ , can be represented as follows:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (22)$$

The thermodynamic parameters Gibbs free energy change  $\Delta G^\circ$ , was calculated using Langmuir II constant. The  $\Delta G^\circ$  value change with increase in temperature and the negative values of  $\Delta G^\circ$  confirm the feasibility of the process and the spontaneous nature of the sorption of MB onto CSS.  $\Delta G^\circ$  values similar to what was obtained from the present studies have been reported for dye adsorption on different sorbents<sup>[30][31][9]</sup>.

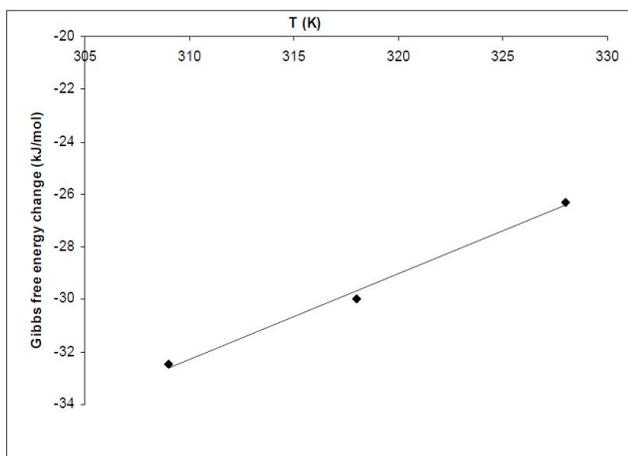


Figure 5 : Plot of  $\Delta G^\circ$  versus T (K)

The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  calculated from the plot of Gibbs free energy change,  $\Delta G^\circ$ , versus absolute temperature Figure 5 are  $-0.3259$  and  $-133.31$  respectively. The enthalpy change,  $\Delta H^\circ$ , is positive indicating that the biosorption reaction is endothermic. The negative value of  $\Delta S^\circ$  shows a reduction in the degree of disorderliness or randomness at the solid/liquid interface during the biosorption of MB onto CSS.

### Desorption studies

In order to investigate the possibilities of CSS regeneration for reuse and the recovery of the sorbed dye, batch desorption studies was carried out. It has been reported that desorption studies could be used to elucidate the mechanism of an adsorption process<sup>[32]</sup>. Mall et al<sup>[32]</sup> opined that if the dye adsorbed on the adsorbent could be desorbed by water, it can be said that the attachment of the dye onto the adsorbent is by weak bonds. If strong acid or strong base can desorb the dye the attachment of the dye to the sorbent is regarded as ion exchange. If organic acid can desorb the dye, the adsorption of the dye onto the adsorbent is taken to be chemisorptions.

Different eluting solvents (deionised water, HCl, NaOH, and  $\text{CH}_3\text{COOH}$ ), that cut across these classifications, were used in the desorption of the MB from the CSS. The results obtained are presented in Figure 6. A very low desorption of the dye was observed when NaOH and deionised water was used while appreciable amount of the dye was desorbed

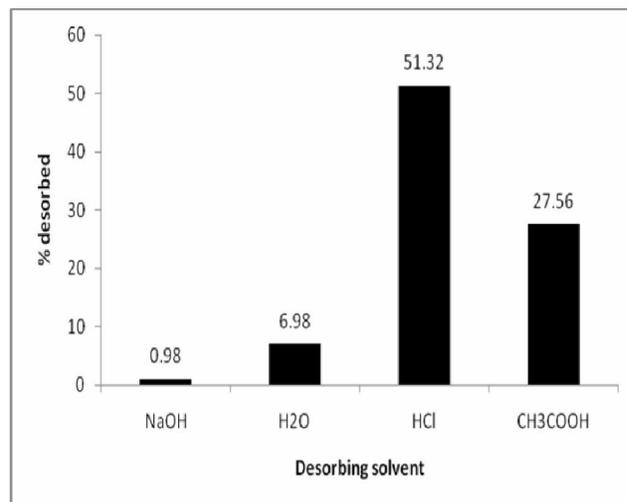


Figure 6 : Batch desorption of MB from CSS using different eluting solvents

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when HCl and CH<sub>3</sub>COOH were used separately. Optimum dye desorption was got, when HCl was used as the eluting solvent (Figure 6). The appreciable amount of dye desorbed with the use of both HCl and CH<sub>3</sub>COOH could be ascribed to the role of both ion exchange and chemisorptions in the uptake of MB by CSS.

An overview of the total amount of the dye desorbed from the CSS showed that 86.85% of the dye adsorbed was desorbed by all the eluting solvent used. The undesorbed portion of the dye in the sorbate could be ascribed to the complex formation between the MB and the active sites on the CSS; hence the inability of the eluting solvents to completely desorb the dye.

### CONCLUSION

The ability of CSS to attenuate MB in aqua system was studied using equilibrium isotherm analysis. Langmuir I and II, Freundlich, Dubinin-Radushkevich (D-R); Temkin; Harkins –Jura and Halsey isotherm equation were used to describe the sorption process, when two process variables (sorbent dosage and temperature) were optimized by method of continuous variation. Freundlich, Langmuir (I and II) and Halsey isotherm equations had better correlations ( $r^2$ ) than the other isotherm equations fitted into the experimental data. The thermodynamic analysis of the sorption process indicates that the system is spontaneous, endothermic and a reduction in the degree of disorderliness or randomness at the solid/liquid interface occurred during the biosorption of MB onto CSS. The results of the desorption studies showed that both chemisorptions and ion-exchange played prominent role in the sorption of MB by CSS.

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