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Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm studies of equilibrium sorption of Methylene Blue from Aqueous Solution onto Mulberry tree (Morus nigra L) roots powder

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Abstract In this study, batch adsorption experiments were conducted for the adsorption of Methylene Blue (MB) onto ground Morus Nigra L roots powder (MNLRP) surface from aqueous solution. The effects of different parameters on adsorption processes were investigated. The maximum adsorption capacity, qmax, was found to be 32.63 mg/g at 45°C. Among the all isotherms tested in this study, Langmuir isotherm model gave the best fit with R^2 and Chi square.The adsorption process was found to be physisorption process due to the calculated mean energy of adsorption calculated form Dubunin-Radushkevich (D-R) isotherm model ranged from 1.24 to 1.71 KJ/mol. This study demonstrates that MNLRP could be used to remove MB dyes from aqueous solutions.

Keywords: Adsorption, Isotherm, Methylene Blue, Mulberry tree roots.

دراسة أيزوتيرم لانجمير، فريندليش، تمكين و دوبونين – راداسكافيتش لأمتزاز صبغة الميثيلين الأزرق من المحلول المائي على مسحوق جذور شجر التوت

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الملخص في هذه الدراسة أجريت تجارب الأمتزاز لأمتزاز صبغة الميثيلين الأزرق من المحلول المائي على مسحوق جذور شجر التوت Morus Nigra L roots powder (MNLRP) وقد تم دراسة تأثير البارامترات المختلفة على عملية الأمتزاز. كانت أعلى كفاءة أمتزاز 32.63 ملي جرام/جرام عند 45 م° ومن بين جميع أيزوتيرمات الأمتزاز المستخدمة في هذه الدراسة أعطى أيزوتيرم لانجمير أفضل تناسب مع معامل الخطية R^2 و مربع كاي. وقد وجدنا أن عملية الأمتزاز تكون أمتزاز فيزيائي وذالك لأن قيمة متوسط طاقة الأمتزاز والتي تم حسابها من خلال أيزوتيرم دوبونين – راداسكافيتش تراوحت بين 1.24 – 1.71 كيلوجول/مول. توضح هذه الدراسة أن مسحوق جذور نبات التوت يمكن استخدامه لإزالة صبغة الميثيلين الأزرق من المحاليل المائية.

الكلمات المفتاحية: الأمتزاز، الأيزوتيرم، الميثيلين الأزرق، جذور شجر التوت.

1. Introduction

Dyes are miscellaneous and colorful chemicals, which are widely used in many industries to color their products such as dyeing textile;which consuming about 60% products of dyes each year**[1]** Methylene Blue (MB), Used in many industries such as paper, textile, paper, rubber, plastics, leather, cosmetics, pharmaceutical and food industries**[2]**. However, MB can have several adverse effects such as short-term inhalation leading to respiratory Function, oral ingestion leading to gastrointestinal irritation such as vomiting, diarrhoea, and severe urination, exposure to a large amount of MB creating pain in multiple places of the abdomen, chest, and head, as well as excessive sweating, mental confusion, and blood-like methyemoglobinic syndromes. Over 100,000 type of dyes are used for different purposes and about 7.5×10^5 metric tons of dyes are produced worldwide every year and most of them are completely resistant to biodegradation processes **[3]**. Environmentally, the problems of dyes is release of dye containing industrial effluents directly into the hydrosphere, which make this water unusable **[4].** Therefore, the removal of MB from wastewater is still desirable **[5]**. The methylene blue (MB) is a cation dye and its structure is shown in Figure 1 **[1]**

2.

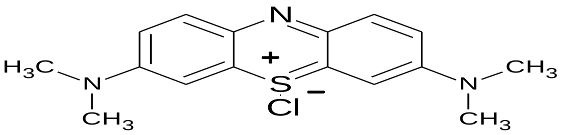

Figure 1. Chemical structure of methylene blue

Different separation techniques have been used for the removal of dyes from aqueous solutions, such as coagulation, flocculation, ion exchange, membrane filtration, photo-catalysis and photo-oxidation. However, the disadvantages of these methods are a long running time, produce a large amount of heat, high cost, and not environmentally friendly. One of the most economically methods is adsorption, which uses to remove pollutants like dyes from the hydrosphere emerging as a growing alternative technique for the decolonization of dye containing effluents. The major advantage of the adsorption processes especially using waste material from agricultural based biomass is low cost **[4].** There are two types of adsorption; physical adsorption, which is done by Van der Waals forces, dipole interactions, and hydrogen binding and chemical adsorption, which is done by electrons exchange between adsorbent and adsorbate **[6]**. Granular activated carbon has been marked by the Environmental Protection Agency of (US-EPA) as the best available technology for organic and inorganic chemicals removal. However, it is still considered expensive adsorbent and the higher the quality the greater the cost. All the processes used for activation such as chemical and thermal regeneration of spent carbon are still expensive, impractical on a large-scale and produces additional effluent and results in considerable loss of the adsorbent **[5].** Many previous studies have earlier been conducted on using waste materials to remove dyes including agricultural wastes such as Coir pith, Orange peel Banana peel, Rice husk , Straw, Guava leaf powder, almond shell, pomelo, broad bean peel, peanut hull ,Citrullus lanatus rind and etc. **[7].** In this study, Mulberry tree root powder (MNLRP) was used as a sorbent to remove methylene blue from aqueous solutions.

3. Materials and methods

3.1. Adsorbent Preparation: The Morus nigra L roots (MNLR) were collected from Samno Village, Albowanise State, North of Sebha City, Libya. Mulberry trees Classified scientifically of genus Morus of the family Moraceaeis grow in the areas of multi-around the world Asia, Europe, North America, South America, and Africa, in southern Asia used the Leaves for silk production by silkworm **[8].** The collected MNLR were washed with distilled water for several times in order to remove all the dirt particles and left on clean paper to dry under room temperature. These dry roots were grounded with grinder and then sieved using sieves of sizes 0.250-0.50 mm. This produced a uniform material for the complete set of adsorption tests, which was stored in an air-tight plastic container for future work. Particle sizes, 0.250 mm, of MNLRP were used in all experiments throughout this work.

3.2.Preparation of Standard Solutions: Stock standard solution of (MB) with a concentration of 500 mg/L was prepared by dissolving (MB) in deionized water and it was kept in refrigerator for further experiments. The desired (MB) concentrations were prepared from the stock solution of 500 mg/L by adding deionized water to standard MB solution making fresh dilutions for each sorption experiment. Standard curve was used in order to determine the desire concentration.

3.3.Adsorption experiments: The concentration of MB before and after adsorption on MNLRP was determined using UV-Vis spectrophotometer (Jenway model 6305) at 660 nm, on the base of Beer–Lambert law, shows the calibration curve (Figure 2) in the range of concentration (1-8 mg/L) and maximum of the wavelength happens has largest absorption for 8 mg/L. The concentration of filtrated MB left in solution measured.

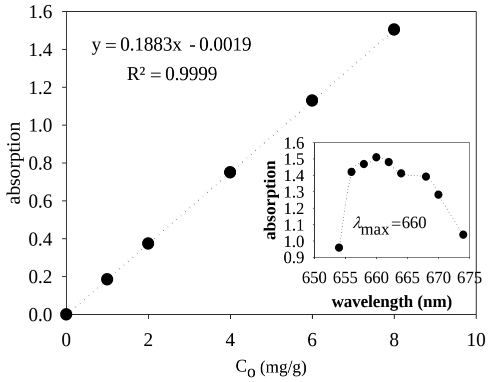

Figure 2. Calibration curve (1-8 mg/L) and maximum of the wavelength (8 mg/L)

3.4.Mathematical adsorption models: Adsorption capacity of the amount MB dye adsorbed onto MNLRP was calculated using the following equations:

$$q_e = \frac{C_0 - C_e}{m_s} \times V \qquad \textbf{(1)}$$

Where: C_0 and C_e (mg/L) are the initial and the final concentrations of adsorbates in flasks, respectively, C_t (mg/L) is the concentrations of adsorbates at time t. V is the volume of the solution (L) and m_s is the mass of dry adsorbent used (g)[9].

3.4.1.Adsorption Isotherm

A. Langmuir isotherm: The linear form of the Langmuir equation can be expressed as:

$$\frac{C_e}{q_e} = \frac{1}{K_L \times q_{max}} + \frac{C_e}{q_{max}} \qquad \textbf{(2)}$$

And the non-linear form of the Langmuir equation can be expressed as:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \qquad \textbf{(3)}$$

Where: q_e is the adsorption capacity at equilibrium (mg/g),q_{max} is the maximum adsorption capacity (mg/g), k_L is the Langmuir equilibrium constant (L/mg), C_e is the equilibrium solution concentration (mg/L). An important characteristics of Langmuir isotherm is the dimensionless separation parameter $R_L$which is expressed as:

$$R_L = \frac{1}{1 + K_L C_0} \qquad \textbf{(4)}$$

Where: the values of (R_L=1) process of adsorption process is unfavorable, when (R_L=1) indicative that adsorption is linear, when (R_L=0) this indicate irreversible adsorption, when R_L between 0 and 1 represent favorable adsorption.

B. Freundlich isotherm: The Freundlich isotherm is used to describe adsorption heterogeneous systems. The linear form of the Freundlich equation can be expressed as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad \textbf{(5)}$$

Equation (18) can be also rewritten as:

$$q_e = K_F C_e^{1/n} \qquad \textbf{(6)}$$

Where: K_F and n are Freundlich constants, indicating the adsorption capacity and the adsorption intensity, respectively. K_F and n are, respectively, determined from the intercept and slope of plotting $\ln q_e$ versus $\ln C_e$.

C. Temkin isotherm: The Temkin isotherm model can be used in evaluating characteristic energies of an adsorption process. The adsorption is characterized by a uniform distribution of binding energies, which is up to some maximum binding energy. The Temkin isotherm is expressed as:

$$q_e = \frac{RT}{b} \ln\left(A_T C_e\right) = B \ln\left(A_T C_e\right) \qquad \textbf{(7)}$$

Equation (7) can be also rewritten as:

$$q_e = B \ln\left(A_T\right) + B \ln\left(C_e\right) \qquad \textbf{(8)}$$

It is linear relationship between and $\ln(C_e)$. The intercept is B $\ln(A_T)$ and the slope is B. Where: A_T is Temkin isotherm equilibrium binding constant (L/g), b is Temkin isotherm constant, R is universal gas constant ($8.314 \mathrm{mol}^{-1} \mathrm{K}^{-1}$), T (K), B is constant related to heat of sorption (J/mol), b is heat of sorption **[10].**

D. Dubinin–Radushkevich isotherm: Dubinin–Radushkevich isotherm is one of the important methods to determine the adsorption type and expressed as:

$$q_e = \left(q_S\right) \exp\left(-K_{ad} \varepsilon^2\right) \qquad \textbf{(10)}$$

The linear form of the D–R equation can be expressed as

$$\ln\left(q_e\right) = \ln\left(q_S\right) - \left(K_{ad} \varepsilon^2\right) \qquad \textbf{(11)}$$

$$\varepsilon = \mathrm{R\,T} \ln\left[1 + \frac{1}{\mathrm{C_e}}\right] \qquad \textbf{(12)}$$

$$E = \left[\frac{1}{\sqrt{2K_{ad}}}\right] \qquad \textbf{(13)}$$

Where: q_e amount of adsorbate in the adsorbent at equilibrium (mg/g); q_s = theoretical isotherm saturation capacity (mg/g); K_{ad} =D–R isotherm constant ($\mathrm{KJ}^{-1} \mathrm{mol}^{-1}$) and ε=D–R isotherm constant, R the gas constant (8.314 J/mol K), T (K) and E energy of adsorption **[4, 11, 12]**. However, if E is between 8 and 16 kJ/mol, the adsorption type is explained by ion-exchange and chemical adsorption, while if E lies within the range of 1–8 kJ/mol, the adsorption type is explained by Ven Der Wells for the physisorption processes **[13].**

Statistical Methods: In this study, the correlation Coefficient (R^2), Chi-squared test (χ^2), Sum of the Squares of the Errors (SSE), Hybrid fractional error function (HYBRID) and Marquardt's Percent Standard Deviation (MPSD) were used for interpretation of results process. These relations are shown as the following equations:

$$\chi^2 = \sum_{i=1}^{n} \frac{\left(q_{e,\exp} - q_{e,calc}\right)^2}{q_{e,calc}} \qquad \textbf{(14)}$$

$$SSE = \sum_{i=1}^{n} \left(q_{e,calc} - q_{e,\exp}\right)^2 \qquad \textbf{(15)}$$

$$\mathrm{HYBRID} = \frac{100}{n-p} \sum_{i=1}^{n} \frac{\left(q_{e,\exp} - q_{e,calc}\right)^2}{q_{e,\exp}} \qquad \textbf{(16)}$$

$$\mathrm{MPSD} = 100 \times \sqrt{\frac{1}{n-p} \sum_{i=1}^{n} \left[\frac{\left(q_{e,\exp} - q_{e,calc}\right)}{q_{e,\exp}}\right]^2} \qquad \textbf{(17)}$$

Where: $q_{e,cal}$ is the equilibrium capacity obtained from the adsorption model (mg/g) and q_{max} is then equilibrium capacity (mg/g) from the experimental data n is the number of data points, and p is the number of parameters in isotherm equations and kinetic equations **[14].**

3. Results and Discussion

3.1.Isotherm study

A. Langmuir isotherm model: Figure 3 shows Langmuir isotherm model for adsorption MB on MNLRP and the parameters are listed in

Temp	298K	308K	318K
Langmuir isotherm model			
q_{max}	22.71	27.85	32.63
K_L	0.4082	0.3928	0.3377
R^2	0.9877	0.9875	0.9799
χ^2	0.2425	0.0547	0.0769
SSE	2.0733	0.4854	0.8424
HYBRID	7.5□25	1.8772	2.4632
MPSD	16.397	8.9038	9.4210
Freundlich isotherm model			
K_F	1.6320	1.8290	1.9290
1/n	0.489	0.604	0.658
R^2	0.9269	0.9679	0.9902
χ^2	0.4712	0.2641	0.1183
SSE	3.6782	3.3931	1.5041
HYBRID	14.977	8.9193	3.8333
MPSD	23.669	19.31	10.928
Temkin isotherm model			
B	164.15	180.41	205.39
A_T	1.746	1.7190	1.7030
R^2	0.9791	0.9976	0.9823
χ^2	0.1985	0.0214	0.1697
SSE	1.6533	0.2018	1.5361
HYBRID	6.5572	0.7120	□5.688
MPSD	14.802	6.0370	15.543

D-R isotherm model			
E (KJ/mol)	1.24	1.48	1.71
q_s (mg/g)	16.218	16.969	16.563
R^2	0.9776	0.9748	0.9289
χ^2	0.1985	0.5249	0.9500
SSE	1.6533	6.3943	9.1935
HYBRID	6.5572	18.688	26.398
MPSD	14.802	29.511	31.000

B. The maximum adsorption capacities q_{max} were 22.71, 27.85, 32.63 mg/g at 25, 35 and 45°C, respectively. It was noted that the maximum adsorption capacity was increased with increasing temperature. This refers that the process of adsorption is endothermic.

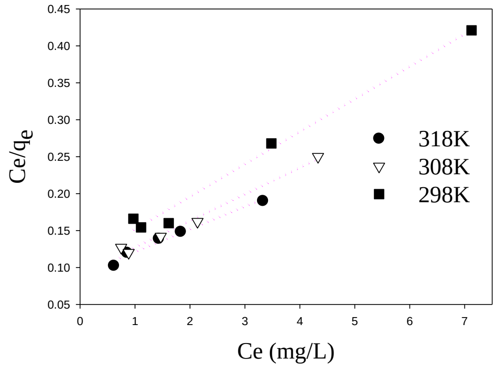

Figure 3. Langmuir isotherm model of MB solution on MNLRP under condition 400rpm, 60 min, dosage 0.1g, 15mL, pH=7, 298, 308 and 318K

The R_L values were found to be 0.0577, 0.049, 0.0338, 0.0265 and 0.02 for initial concentration 40, 50, 70, 90, 120 mg/L, respectively as shown in Figure 4. This means that the Langmuir isotherm was favourable for adsorption of MB on MNLRP under these conditions used in this study.

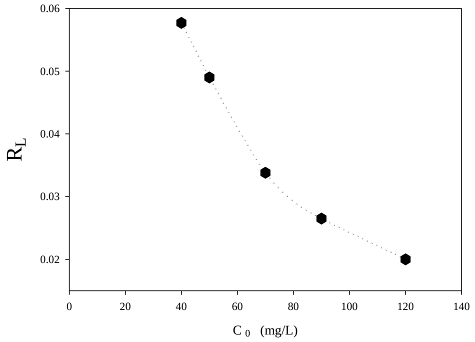

Figure 4. R_L versus initial concentrations

C. Freundlich isotherm: The Freundlich isotherm is based on the formation of a multi-layer adsorbate MB on the outer surface of the adsorbent MNLRP as shown in Figure 5 and the parameters are listed in

Temp	298K	308K	318K
Langmuir isotherm model			
q_{max}	22.71	27.85	32.63
K_L	0.4082	0.3928	0.3377
R^2	0.9877	0.9875	0.9799
χ^2	0.2425	0.0547	0.0769
SSE	2.0733	0.4854	0.8424
HYBRID	7.5□25	1.8772	2.4632
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Temkin isotherm model			
B	164.15	180.41	205.39
A_T	1.746	1.7190	1.7030
R^2	0.9791	0.9976	0.9823
χ^2	0.1985	0.0214	0.1697
SSE	1.6533	0.2018	1.5361
HYBRID	6.5572	0.7120	□5.688
MPSD	14.802	6.0370	15.543
D-R isotherm model			
E (KJ/mol)	1.24	1.48	1.71
q_s (mg/g)	16.218	16.969	16.563
R^2	0.9776	0.9748	0.9289
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HYBRID	6.5572	18.688	26.398
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D. [12].

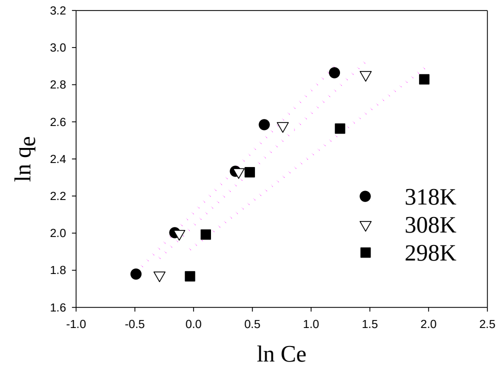

Figure 5. Freundlich isotherm model for adsorption MB on MNLRP under condition 400rpm, time 60 min, dosage 0.1g, 15mL, pH=7, 298,308 and 318K

E. Temkin isotherm: The heat of adsorption b were determined by slope where b=RT/B Figure 6 and the parameters are listed in

Temp	298K	308K	318K
Langmuir isotherm model			
q_{max}	22.71	27.85	32.63
K_L	0.4082	0.3928	0.3377
R^2	0.9877	0.9875	0.9799
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SSE	1.6533	6.3943	9.1935
HYBRID	6.5572	18.688	26.398
MPSD	14.802	29.511	31.000

F. The *b* values were to be 205.39, 180.41, 164.15 J/mol at 25, 35 and 45 °C, respectively. The heat of adsorption was lower than 80 KJ/mol. This means that adsorption of MB on MNLRP is physical adsorption. The maximum binding energy calculating from Temkin isotherm equilibrium binding constants (A_T,L/ was to be 1.746, 1.703,1.719 L/g at 25, 35 and 45°C, respectively

G. D-R isotherm: Figure 7 shows the plot $\ln q_e$ VS ε^2 and the parameters are listed in

Temp	298K	308K	318K
Langmuir isotherm model			
q_{max}	22.71	27.85	32.63
K_L	0.4082	0.3928	0.3377
R^2	0.9877	0.9875	0.9799
χ^2	0.2425	0.0547	0.0769
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SSE	1.6533	6.3943	9.1935
HYBRID	6.5572	18.688	26.398
MPSD	14.802	29.511	31.000

H. . The type of adsorption was determined by calculating the value of adsorption energy (E) on the surface. The values of E are equal to 1.24, 1.48, 1.71 KJ/mol. This means that adsorption of MB on MNLRP is physical adsorption**. [15]**

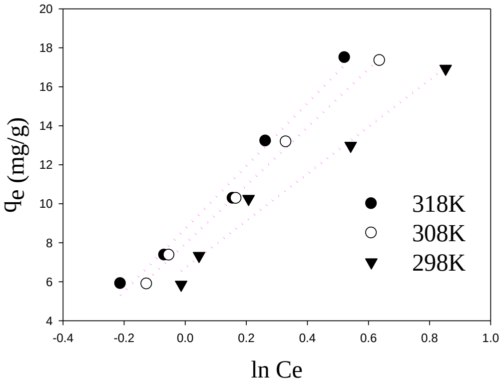

Figure 6. Temkin isotherm model for adsorption MB on MNLRP under condition 400rpm, time 60 min, dosage 0.1g, 15mL, pH=7, 298,308 and 318K

Table 1. Isotherm parameters for adsorption of MB on MNLRP at different temperatures

Temp.	298K	308K	318K
Langmuir isotherm model			
q_{max}	22.71	27.85	32.63
K_L	0.4082	0.3928	0.3377
R^2	0.9877	0.9875	0.9799
χ^2	0.2425	0.0547	0.0769
SSE	2.0733	0.4854	0.8424
HYBRID	7.5□25	1.8772	2.4632
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q_s (mg/g)	16.218	16.969	16.563
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MPSD	14.802	29.511	31.000

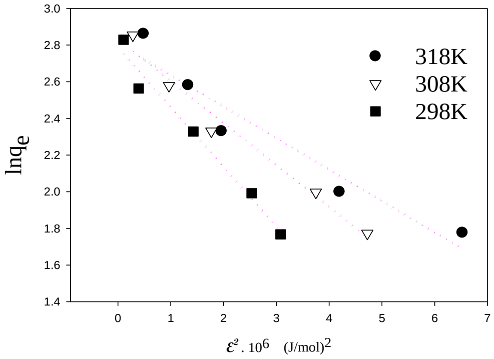

Figure 7. D-R isotherm model for adsorption MB on MNLRP under condition400rpm, time 60 min, dosage 0.1g, 15mL, pH=7, 298,308 and 318K.

The statistical analyses of isotherm models are listed in

Temp.	298K	308K	318K
Langmuir isotherm model			
q_{max}	22.71	27.85	32.63

K_L	0.4082	0.3928	0.3377
R^2	0.9877	0.9875	0.9799
χ^2	0.2425	0.0547	0.0769
SSE	2.0733	0.4854	0.8424
HYBRID	7.5□25	1.8772	2.4632
MPSD	16.397	8.9038	9.4210
Freundlich isotherm model			
K_F	1.6320	1.8290	1.9290
1/n	0.489	0.604	0.658
R^2	0.9269	0.9679	0.9902
χ^2	0.4712	0.2641	0.1183
SSE	3.6782	3.3931	1.5041
HYBRID	14.977	8.9193	3.8333
MPSD	23.669	19.31	10.928
Temkin isotherm model			
B	164.15	180.41	205.39
A_T	1.746	1.7190	1.7030
R^2	0.9791	0.9976	0.9823
χ^2	0.1985	0.0214	0.1697
SSE	1.6533	0.2018	1.5361
HYBRID	6.5572	0.7120	□5.688
MPSD	14.802	6.0370	15.543
D-R isotherm model			
E (KJ/mol)	1.24	1.48	1.71
q_s (mg/g)	16.218	16.969	16.563
R^2	0.9776	0.9748	0.9289
χ^2	0.1985	0.5249	0.9500
SSE	1.6533	6.3943	9.1935
HYBRID	6.5572	18.688	26.398
MPSD	14.802	29.511	31.000

The statistical analysis values of correlation coefficient (R^2), Chi-squared test (χ^2), SSE, HYBRID and MPSD were tested in order to find the best fit of isotherm model**.** It was found that the Langmuir isotherm is clearly the better fitting isotherm to the experimental data, the isotherm and statistical data for this model **[13]**. The Langmuir isotherm is based on the formation of a monolayer adsorbate MB on the outer surface of the adsorbent MNLRP, and after that there is no further adsorption. The highest value for R^2 indicates that the Langmuir isotherm is clearly the better fitting isotherm to the experimental data used in this study.

Conclusion: The Langmuir isotherm model and statistical analysis, the adsorption of MB on MNLRP indicates to formation of mono-layer. The R_L values Indicates that the Langmuir isotherm was favourable for adsorption of MB on MNLRP under these conditions used in this study Heat of adsorption, adsorption energy for adsorption of MB on MNLRP indicates that the adsorption is physisorption.

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