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University of Sebha
Faculty of Science
Department of Chemistry

Graduation project submitted in fulfilment of the requirements for the degree of Bachelor

Entitled:

Isotherm, Kinetic and Thermodynamic Studies on Methylene Blue Biosorption from Aqueous Solution onto Mulberry tree (*Morus nigra* L) roots powder

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بسم الله الرحمن الرحيم

(ولا تفسدوا في الأرض بُعد إصلاحها وادغعوا خوفا وطمعا إن رحمت الله قريب من المحسنين)

صدق الله العظيم

سورة الأعراف: آية 56
Dedication

To my dear brother Featurry
Acknowledgment

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for all the help and guidance he provided throughout my education, and to the other members of my instructors
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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 Physico-Chemical characteristics of MNLRP were studied. The results showed that the pH value was 7.24, the bulk density value was 0.638 g/cm³, the internal surface area (microspores) was 627.08 mg/g using the iodine number, and ash content (metal compounds content) was 0.129%. The effects of different parameters on adsorption processes were studied. The maximum adsorption capacity, $q_{\text{max}}$, was found to be 32.63 mg/g at 45°C. The adsorption process was very fast initially and reached the equilibrium at 15 minutes. The removal percentage increased with increasing adsorbent dosage, pH solution, initial concentration, and temperature. 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. Adsorption kinetics data were modeled with different kinetic models. The results revealed that the pseudo-second order model was the best fitting model. The results from thermodynamic parameters showed that the adsorption process was spontaneous and endothermic processes and increased randomness at the solid/liquid interface. Therefore, this study demonstrates that MNLRP could be used to remove MB dyes from aqueous solutions.

Keywords: Adsorption, Equilibrium, Isotherm, Kinetic, Methylene Blue, Mulberry tree roots, Thermodynamic
CHAPTER 1

Introduction
CHAPTER 1

1. Introduction

1.1. Literature review

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. Methylene Blue (MB), are of dyes basil characterized uses multiple of which textile, paper, rubber, plastics, leather, cosmetics, pharmaceutical and food industries [1]. The cationic MB dye of formula is $C_{16}H_{18}N_3SCl^+$, with a molecular weight 319.852 g/mol. Its structure is shown in Figure 1 [2]. However, MB can have various adverse effects such as short-term inhalation leading to respiratory Function, oral ingestion leading to gastrointestinal irritation such as vomiting, diarrhea, and severe urination, exposure to a large amount of MB creating pain in multiple places of the abdomen, chest, chest and head, as well as excessive sweating, mental confusion, and blood-like methemoglobin syndromes. Over 100,000 type of dyes uses in different purposes, about $7.5 \times 10^5$ metric tons of dye produce worldwide every year and most of them are completely resistant to biodegradation processes [3]. Environmentally, the problems of dyes used especially in this industries effluents, these dyes discharge into the hydrosphere, which make this water unusable [4]. Therefore, the removal of MB from wastewater is desirable [5].

![Figure 1. Chemical structure of methylene blue](image-url)
Different separation techniques have been used in 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. Adsorption is a process in which a substance (adsorbate), in gas or liquid phase, accumulates on a solid surface (adsorbent). 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 \cite{6}. The main advantage of the adsorption processes especially using waste material from agricultural based biomass is low cost \cite{4}. The most important properties of adsorbent, which determines its usage, are the pore structure and the specific surface area \cite{6}.

Sometimes difficult to distinguish between the adsorption and absorption, Absorption is where the breakthrough atoms or molecules in the solid body regularly.

![Absorption and Adsorption Diagram](image-url)
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 the waste materials to remove dyes including a waste of agricultural such as Coir pith, Orange peel Banana peel, Rice husk, Straw, Guava (psidium guajava) leaf powder, almond shell, pomelo (Citrus grandis peel), broad bean peel, peanut hull, Citrullus lanatus rind [7]. In this study, Mulberry tree root powder (MNLRP) was used as a sorbent to remove methylene blue from aqueous solutions.
1.2. Objectives

The main objectives of this research were to:

1. Use MNLRP to remove the methylene blue dye from aqueous solutions.
2. Evaluate the effect of initial concentration, adsorbent dosage, contact time, pH, on the adsorption processes.
3. Study the isotherm models to describe the adsorption data
4. Study the adsorption kinetic models
5. Calculating of the thermodynamic parameters such as the change standard Gibbs free energy ($\Delta G^0$) and change standard enthalpy ($\Delta H^0$) and change standard entropy ($\Delta S^0$).
CHAPTER 2

Material and Methods
CHAPTER 2

2. Materials and Methods

2.1. Chemicals

The chemicals used in this study are Methylene blue, hydrochloric acid (0.05N, company ), sodium hydroxide (0.05N, Company surechem products LTD), Sodium thiosulfate solutions (0.01N, company surechem products LTD), Iodine solutions (0.01N, company DBH) and deionized water.

2.2. Materials

Mulberry tree root powder (MNLRP) was used as a sorbent. 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].

Table 1. The Scientific Classification of mulberry plantae

<table>
<thead>
<tr>
<th>Kingdom</th>
<th>Plantae</th>
</tr>
</thead>
<tbody>
<tr>
<td>Divisio</td>
<td>Tracheophytes</td>
</tr>
<tr>
<td>Phylum</td>
<td>Spermatophytes</td>
</tr>
<tr>
<td>Subphylum</td>
<td>Angiospermae</td>
</tr>
<tr>
<td>Class</td>
<td>Magnoliopsida</td>
</tr>
<tr>
<td>Order</td>
<td>Rosales</td>
</tr>
<tr>
<td>Family</td>
<td>Moreae</td>
</tr>
<tr>
<td>Subfamily</td>
<td>Moraceae</td>
</tr>
<tr>
<td>Genus</td>
<td>Morus</td>
</tr>
<tr>
<td>Scientific name</td>
<td>Morus nigra L</td>
</tr>
</tbody>
</table>

2.3. Instruments

The instruments which used in this study: mechanical shaker (Model AKI,), UV-Vis spectrophotometer (Production company jenway model 6305),
mechanical shaker equipped with a thermostatic water (Production company Clifton), pH meter (model thermo orion 4 star), furnace type 1300.

2.4. Sample Preparation

The Morus nigra L roots (MNLR) were collected from Samno Village, Albowanise State, north of Sebha City, Libya. The collected MNLR were washed with distilled water for several times in order to remove all the dirt particles and were left on clean paper to dry under room temperature. These dry roots were grounded with grinder and sieved using different sieves of 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 all investigations. MNLRP with Particle sizes of 0.250 mm was used adsorbent material in all experiments throughout this work.
2.5. 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 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.

2.6. equilibrium concentration of Methylene blue solution

The equilibrium concentration of methylene blue after adsorption on MNLRP was determined using UV-Vis spectrophotometer (Production company Jenway model 6305 at 660 nm, on the base of Beer–Lambert law. Figure 2 shows the calibration curve in the range (1-8 mg/L) and maximum of the wavelength happens has largest absorption for 8 mg/L concentration.

![Calibration curve](image)

\[ y = 0.1883x - 0.0019 \]
\[ R^2 = 0.9999 \]

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

2.7.1. Physico-Chemical characteristics of MNLRP

2.7.2. Determination of pH

The pH were determined according to the method of ASTM D3838-80 with slight modification as follows; 1.0 g of each MNLRP was weighed and transferred into a 250 ml beaker and 100 ml of deionized water was added and stirred for 1 hr.

2.7.3. Ash Content Determination

Ash content determination was done according to the ASTM D2866-94 method. Dry MNLRP sample (0.30 g) was placed into a porcelain crucible and heating at 1000 °C. The furnace was left on for 1 hr after. Then, the crucible with content was transferred to desiccators and allowed to cool at room temperature. The crucible and content was reweighed and the weight lost was recorded as the ash content of the MNLRP sample \( (W_{\text{ash}}) \). Then the % ash content (dry basis) was calculation by the following equation:

\[
Ash(\%) = \frac{100 \times W_{\text{ash}}}{W_0}
\]

Where: \( W_{\text{ash}} \) is the ash content of the MNLRP sample

\( W_0 \) is the initial mass of the MNLRP sample

2.7.4. Moisture Content Determination

Moisture content, MC, was determined according to ASTM 2867-99. Each MNLRP sample (4.0 g) was weighed and dried in a furnace continuously. The drying sample was constantly reweighed every 10 minutes interval until a
constant weight \((W'_p)\) was obtained. The crucible and its content was retrieved and cooled in desiccators. The difference in weight \((W_0 - W'_p)\) was recorded and the moisture content (MC) calculated from the following equation:

\[
MC = \frac{W_0 - W_p}{W_0} \times 100
\]

(2)

Where: \(W_p = \) weight of MNLRP retrieved from the furnace and \(W_0 = \) initial dry weight of the MNLRP sample.

2.7.5. Pore Volume Determination

Each MNLR sample (1.0943, 0.9007, 0.8154 0.8026 g) was immersed in water for 60 minutes using a vacuum pump in order to displace air from the pores. The samples were superficially dried and reweighed. The pore volume was calculated as increase in weight \((\partial W)\) divided by the density \((\ell)\) of water at \(20^\circ C\) by the following equation:

\[
\frac{\partial W}{\ell_{20}} = pore volume
\]

(3)

2.7.6. Determination of Iodine Number

The Iodine number was determined according to the modified ASTM D 4607-94 method as modified by Okuo and Ozioko (2001) by following equation:

\[
\frac{v - x}{y} \times \frac{v}{w} \times M(126.9)
\]

(4)

Where: \(x = \) volume of the thiosulphate used for sample free aliquot, \(y = \) volume of thiosulphate used for blank solution, \(w = \) weight of sample, \(M = \)
molarity of iodine solution used and \( v = \) volume of iodine solution used for titration.

2.7.7. The Bulk Density determination

Bulk density \((Bd)\) of MNLRP were determined according to ASTM D 2854-96. The bulk density and were calculated by using the following equation [9].

\[
\text{Bulk densities}(Bd) = \frac{\text{mass of sample}}{\text{volume}}
\]  

(5)

2.7.8. Adsorption experiments

2.7.8.1. Selective adsorbent dosage

Adsorbent dosage MNLRP at different doses (0.10, 0.20, 0.30, 0.40, 0.50 g) were added into the flasks with 15mL of (MB) solution (60 mg/L), and then agitated for 60 min and 400 rpm. Then, the concentration of filtrated MB left in solution measured the absorption of each solution using UV-Vis spectrophotometer (jenway model 6305).

2.7.8.2. Equilibrium study

0.1 g MNLRP was added into the flasks of 15 mL MB (80 mg/L) and then agitated at 400 rpm for contact times ranging from 15 min to 135 min at different temperature (25, 35 and 45 °C). Then, the concentration of filtrated MB left in solution measured the absorption of each solution using UV-Vis spectrophotometer (Jenway model 6305).
2.7.8.3. Study the effect of initial (MB) concentration

0.1 g MNLRP was added to each 15 ml of 40, 50, 70, 90, 120 mg/L MB at different temperature (25, 35 and 45°C). The mixtures was stirred at 400 rpm for 60min. Then, the concentration of filtrated MB left in solution measured the absorption of each solution using UV-Vis spectrophotometer (Jenway model 6305).

2.7.8.4. Study the pH

The adsorption capacity of the MB dye on MNLRP was studied at different values of pH. The pH was changing by adding drops of HCl (0.05N) or NaOH (0.05N) for the purpose of reaching pH (1.75, 2.74, 2.90, 4.83, 6.07, 8.49, 10.35, 11.14, 12.32). Then, the concentration of filtrated MB left in solution measured the absorption of each solution using UV-Vis spectrophotometer (Jenway model 6305).

2.7.9. Mathematical adsorption models

2.7.9.1. Calculation of removal percentage and adsorption capacity

The removal percentage and adsorption capacity of the amount MB dye adsorbed onto MNLRP was calculated using the following equation:

\[
R \% = \frac{C_0 - C_e}{C_0} \times 100
\]  \hspace{1cm} (6)

\[
q_t = \frac{C_0 - C_t}{m_s} \times V
\]  \hspace{1cm} (7)

\[
q_e = \frac{C_0 - C_e}{m_s} \times V
\]  \hspace{1cm} (8)
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)[10].

### 2.7.9.2. Adsorption Kinetics

The adsorption MNLRP onto the prepared adsorbent was evaluated using pseudo-first order, pseudo-second order, intraparticle diffusion.

**A. Pseudo-First order model**

Pseudo first-order kinetic model can be written as:

\[
\frac{dq_t}{dt} = k_1 (q_e - q_t)
\]

Integration of Eq. (9) for the boundary conditions \( t = 0 \) to \( t \) and \( q_t = 0 \) to \( t \), gives

\[
ln(q_e - q_t) = ln q_e - k_1 t
\]

Where: \( q_e \) and \( q_t \) are the amounts of MB (mg/g) at equilibrium and at time \( t \), respectively, and \( k_1 \) is the pseudo-first order equilibrium rate constant (min\(^{-1}\)). The values of \( q_e \) and \( k_1 \) were determined from the linear plot of \( ln(q_e - q_t) \) against \( t \), (\( ln q_e = \) intercept) and (\( k_1 = \) slope).

**B. Pseudo-Second order model**

Pseudo second-order kinetic model can be written as:

\[
\frac{dq_t}{dt} = k_2 (q_e - q_t)^2
\]
Integrating Eq. (11) for the boundary condition \( t = 0 \) to \( t \) and \( q_t = 0 \) to \( q_t \), gives:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
\]  \hspace{1cm} (12)

\[
k_2 q_e^2 = h = \frac{1}{\text{intercept}} \hspace{1cm} (at \ t = 0)
\]  \hspace{1cm} (13)

Where: the expression in equation (h) denotes the initial sorption rate (mg/g min) at \( t = 0 \). \( q_e \) and \( q_t \) refer to the amount of (MB) (mg/g) adsorbed at equilibrium and at any time, \( t \) (min), respectively and \( k_2 \) is the equilibrium rate constant of pseudo-second order adsorption (g/mg min). \( q_e \), \( k_2 \) and \( h \) can be determined from the slope and intercept of the straight lines in plot of \( t/q_t \) versus \( t \).

C. Intraparticle Diffusion model

Intraparticle diffusion model used to identify the diffusion mechanisms (internal surface and pore diffusion). The intra-particle diffusion is a function of \( t^{1/2} \) and can be defined by Eq. (13):

\[
q_t = k_d t^{1/2} + C
\]  \hspace{1cm} (14)

Where: \( C \) (mg/g) is the intercept and \( k_d \) (mg/gmin\(^{1/2}\)) is the intraparticle diffusion rate constant (slope) [11]

2.7.9.3. Adsorption Isotherm Models

The isotherm models are used for investigating maximum adsorption capacity of adsorbents, which establishing the relation between the amounts of adsorbate adsorbed onto the surfaces of an adsorbent and concentration
A. Langmuir isotherm model

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

\[
\frac{C_e}{q_e} = \frac{1}{K_L \times q_{max}} + \frac{C_e}{q_{max}}
\]  

(15)

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

\[
q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}
\]  

(16)

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).

From an important characteristics of Langmuir isotherm is the dimensionless separation parameter \( R_L \) which is expressed as:

\[
R_L = \frac{1}{1 + b C_0}
\]  

(17)

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 model

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

\[
lnq_e = lnK_F + \frac{1}{n} lnC_e
\]  

(18)

Equation (18) can be also rewritten as:
\[ q_e = K_F C_e^{1/n} \]  

(19)

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 model

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:

\[ q_e = \frac{RT}{b} \ln(A_T C_e) = B \ln(A_T C_e) \]  

(20)

Equation (20) can be also rewritten as:

\[ q_e = B \ln(A_T) + B \ln(C_e) \]  

(21)

It is linear relationship between and \( \ln(C_e) \). The intercept is \( B \ln(A_T) \) and the slope is \( B \). Where \( A_T \) = Temkin isotherm equilibrium binding constant (L/g) \( b \) = Temkin isotherm constant, \( R \) = universal gas constant (8.314 mol\(^{-1}\)K\(^{-1}\)) \( T \) = Temperature (K). \( B \) = Constant related to heat of sorption (J/mol). \( b \) = heat of sorption.[12]

D. Dubinin–Radushkevich (D-R) isotherm model

Dubinin–Radushkevich is expressed as:

\[ q_e = (q_s) \exp\left(-K_{ad} \varepsilon^2\right) \]  

(22)

The linear form of the D–R equation can be expressed as:
\[
\ln(q_e) = \ln(q_s) - (K_{ad} \varepsilon^2)
\]  
(23)

\[
\varepsilon = RT \ln\left[1 + \frac{1}{C_e}\right]
\]  
(24)

\[
E = \left[\frac{1}{\sqrt{2K_{ad}}}\right]
\]  
(25)

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 \((mol^2/KJ^2)\) and \(\varepsilon\) = D–R isotherm constant where R, T and \(C_e\) represent the gas constant (8.314 J/mol K), absolute temperature (K) and adsorbate equilibrium concentration (mg/L), respectively, E is energy of adsorption [4, 13, 14]. If this value is between 8 and 16 kJ/mol, the adsorption type can be explained by ion-exchange (chemical adsorption) and which lies within the range of 1–8 kJ/mol for the physisorption processes [15].

2.7.10. Thermodynamic parameters

One of the important methods used to calculate thermodynamic parameters such as the change in standard free energy \(\Delta G^0\), enthalpy \(\Delta H^0\), and entropy \(\Delta S^0\) is the Van’t Hoff equation which are given by the following equations:

\[
\ln K_0 = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R}
\]  
(26)

\[
\Delta G^0 = -RT \ln K_0
\]  
(27)

Where: \(K_0\) is thermodynamic equilibrium constant it can be calculated through the following equation:
\[ K_S = \frac{q_e \times v_1}{C_e \times v_2} \]  

(28)

Where: \( v_1 \) is the activity coefficient of the adsorbed solute, and \( v_2 \) is the activity coefficient of the solute in equilibrium suspension, when equilibrium concentration approaching to zero the ratio tends to unity as follows:

\[ \lim_{C_e \to 0} \frac{ln q_e}{C_e} = K_0 \]  

(29)

Representationally, \( ln \frac{q_e}{C_e} \) vs \( C_e \) can be account \( K_0 \) from the intercept [18]

The activation energy, \( E_a \) of adsorption was also calculated from the linearized Arrhenius equation

\[ lnK_2 = lnK_0 - \frac{E_a}{RT} \]

Where: \( K_2 \) is the rate constant second-order of adsorption (g/mol min), \( K_0 \) is the independent temperature factor (g/mol min), \( E_a \) is the activation energy of adsorption (KJ mol\(^{-1}\)), R is the gas constant (Jmol\(^{-1}\)K\(^{-1}\)) and T is the solution temperature (K). A plot of \( ln k_2 \) vs. 1/T gives a straight line, and the corresponding activation energy was determined from the slope of the linear plot[19].

2.7.11. Statistical Methods

In this study we will use Coefficient of determination \( (R^2) \), Chi-squared test \( (\chi^2) \), Sum of the Squares of the Errors (SSE), Hybrid fractional error function (HYBRID), Marquardt’s Percent Standard Deviation (MPSD), for interpretation of results process can be represented this relations statistical as the following equations:
\[ \chi^2 = \sum_{i=1}^{n} \frac{(q_{e,exp} - q_{e,calc})^2}{q_{e,calc}} \]  

(30)

\[ SSE = \sum_{i=1}^{n} (q_{e,calc} - q_{e,exp})^2 \]  

(31)

\[ HYBRID = \frac{100}{n-p} \sum_{i=1}^{n} \frac{(q_{e,exp} - q_{e,calc})^2}{q_{e,exp}} \]  

(32)

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

(33)

Where: \( q_{e,calc} \) is the equilibrium capacity obtained from the adsorption model (mg / g) and \( q_{e,exp} \) is the 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 [20].
CHAPTER 3

Results and Discussion
CHAPTER 3

3. Results and Discussion

3.1. Characteristics of the MNLRP

Table 2 shows the physico-chemical characteristics of MNLRP. Iodine Number value is 627.08 $mg/g$, the internal surface area (microspores) is determined by calculating the Iodine Number, which is milligrams sorbent by one gram of adsorbent from aqueous solutions. the high amount of iodine sorbent indicates higher efficiency for surface area [21]. Bulk Density value is 0.638 $g/cm^3$, which is in the range allowed to use MNLRP by the American Water Works Association (AWWA) value is 0.25 $g/cm^3$. The content of ash was found to low as shown in Table 2 This is probably due to high content of organic materials comparing to metals. The size of pores were found to be 1.265 $cm^3/g$, which the higher pores volume increases opportunity to remove the large compounds [9].

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size (mm)</td>
<td>0.50-0.25</td>
</tr>
<tr>
<td>pH</td>
<td>7.240</td>
</tr>
<tr>
<td>Ash Content(%)</td>
<td>0.129</td>
</tr>
<tr>
<td>Moisture Content(%)</td>
<td>11.287</td>
</tr>
<tr>
<td>Pore Volume ($cm^3/g$)</td>
<td>1.265</td>
</tr>
<tr>
<td>Bulk Density($g/cm^3$)</td>
<td>0.681</td>
</tr>
<tr>
<td>Iodine Number($mg/g$)</td>
<td>627.08</td>
</tr>
</tbody>
</table>

3.2. Characterization of MNLRP surface

Figure 3 shows the FT-IR spectra for MNLRP before and after adsorption of MB. The spectrum showed the functional groups, which represent
adsorption sites on MNLRP such as stretching of the O–H or N–H group at the range 3200-3500 cm\(^{-1}\), CH group at 2800-3000 cm\(^{-1}\), stretching C=O at 1700-1600 cm\(^{-1}\), stretching C-C between 1400-1500 cm\(^{-1}\) and stretching C-O at 1050-1260 cm\(^{-1}\). Also, the spectrum shows the bonds before and after adsorption process. It was noted that the spectra of before and after adsorption are very close in wavenumber. This indicates that there are no chemical bonds between MB and MNLRP, therefore, the adsorption of MB on MNLRP is physisorption [22].

![FTIR spectra for MNLRP before and after adsorption process](image)

**Figure 3.** FTIR spectra for MNLRP before and after adsorption process
3.3. Effect of adsorbent dosage

The results show that 100 mg of MNLRP was the best weight for a higher adsorption efficiency and Figure 4 shows the dosages effect of MNLRP on $R\%$ and $q_e$. However, it is clear that the $R\%$ increased with increasing dosages from 100mg to 500mg. This could be due to the increase in the number of adsorption sites on the surface as dosages increase. On the other hand, the decreasing efficiency of adsorption with increasing dosages was also noted, which probably due to the lack of saturation sites of adsorption at higher dosage. In addition, the adsorption capacity refers to mg dyes/g adsorbent MNLRP [23].

![Graph showing the effect of adsorbent dosages on R% and qe](image)
3.4. Effect of contact time

Figure 5 shows the relationship between the contact time, the removal percentage of MB from solution after adsorption and the adsorption capacity at different time periods. It is noted that the time to reach the equilibrium of MB and MNLRP adsorption is very fast and short within 15 minutes. This could be considered as a natural of physical adsorption due to requiring a short period of time for the equilibrium between the adsorbent and the adsorbate [6]. 87.5% of the MB dye was removed with 15 minutes. The time equilibrium of 60 minutes for adsorption in all experiments was chosen.

![Graph showing the relationship between contact time, removal percentage, and adsorption capacity.](image)

**Figure 5. Effect of time contact time on the removal and adsorption efficiency under conditions**
Co 80 mg/L, 400 rpm, dosag0.1g, 15ml, pH=7, room temperature

3.5. Effect of initial concentration

Through the drawing in Figure 6 shown to increase the adsorption efficiency (\(q_e\)) with increased initial MB concentration, it was found that the
amount of dye adsorbed per unit mass of adsorbent at equilibrium equal to 5.2805, 6.4666, 8.04, 9.7961, 10.671 (mg/g) for concentrations 40, 50, 70, 90, 120 mg/L respectively, and decrease the removal percentage ($R\%$) with increased initial MB concentration it was found that the removal percentage equal to 88.36, 87.514, 78.796, 74.38, 60.47% for initial concentrate ions 40, 50, 70, 90, 120 mg/L, due to the saturation of adsorption sites on the adsorbent surface with increased initial MB concentration, where dependent removal percentage on the relationship between the MB concentration and the available binding sites on an adsorbent surface[24].

![Graph](image.png)

**Figure 6.** Effect of initial concentration on removal and adsorption efficiency under condition dosage 0.1 g, 15ml, pH=7, 400 rpm, 60min, room temperature

### 3.6. Effect of pH

**Figure 7** shows the effect of the pH solution on $R\%$ and $q_e$. It was found that the $R\%$ increased with increasing pH to reach the maximum of $R\%$ 99.3%
at pH 12.32 while the minimum of $R\%$ was 16.29% at pH 1.75. This could be probably explained as: In acidic solution the adsorbent surface is positively charged, where functional groups on the surface is working on removal the hydrogen ion mechanism wise following:

\[
\begin{align*}
\text{ROH}_2(S) + H_3O^+(aq) & \leftrightarrow \text{ROH}_2(S) + H_2O(L) \\
\text{RNH}_2(S) + H_3O^+(aq) & \leftrightarrow \text{RNH}_3(S) + H_2O(L) \\
\text{RCOOH}(S) + H_3O^+(aq) & \leftrightarrow \text{RCOOH}_2^+(S) + H_2O(L)
\end{align*}
\]

In basic solution the adsorbent surface is negatively charged, where hydroxyl ion in solution is working on removal the hydrogen atom from the surface of MNLRP mechanism wise following:

\[
\begin{align*}
\text{ROH}_2(S) + OH^-(aq) & \leftrightarrow \text{RO}^-(S) + H_2O(L) \\
\text{RNH}_2(S) + OH^-(aq) & \leftrightarrow \text{RNH}^-(S) + H_2O(L) \\
\text{RCOOH}(S) + OH^-(aq) & \leftrightarrow \text{RCOO}^-(S) + H_2O(L)
\end{align*}
\]

The pH solution before adsorption and after-adsorption was determined by pH meter. The results showed that the value of pH in acidic solution after adsorption increase, which could be due to hydrogen ion concentration decrease, however, in basic solution hydroxyl ion concentration decrease[22, 25, 26].
Figure 7. Effect of pH on the removal percentage and adsorption capacity under condition Co 120 mg/L, 400rpm, 60 min, dosag 0.1g, 15ml, room temperature

3.7. pH at point of zero charge

$pH_{pzc}$ method has been used to evaluate the charge on the solid surface. At this point $pH_{pzc}$, initial pH is equal to final pH because of lack change surface charge at this point, therefore, the change surface charge can happen before and after this point. Figure 8 shows the determination of $pH_{zpc}$ method for MNLRP surface[25, 29]. It was found that $pH_{pzc}$ is equal to 6.07 a similar finding has been obtained in a previous study on adsorption of methylene blue and malachite green by *Daucus carota* [30]
3.8. Effect of temperature

Figure 9 Shows the effect of temperature on removal percentage and adsorption efficiency. It was noted that the percentage removal and adsorption efficiency increase with increased the solution temperature. The removal percentages are to be 94.06, 96.39%, 97.23% at 25, 35 and 45°C, respectively, for initial concentration 120 mg/L. Also, the adsorption efficiencies are to be 16.9312, 17.3505, 17.5 (mg/g). This indicates that nature of adsorption is endothermic processes. This may be due to increase interaction between MB and active sites at the surface with increasing the temperature leading to an increase in the removal percentage and adsorption efficiency, and thermodynamic equilibrium constant increase [27]. This can be explained by Le Chatelier’s Principle, which is commonly expressed ”suggests that a stress applied to a system at equilibrium will lead to a shift in the position of the equilibrium which minimizes the effect of that stress” [28].
3.9. Adsorption kinetic studies

Study of the adsorption kinetic models for the interaction between MB and MNLRP surface were investigated at different time, t and all kinetic data are Table 3. The adsorption processes in general could be divided into two stages: a rapid adsorption process and followed by a slow adsorption state until reaching equilibrium state as shown in

One of an important parameter in order to design adsorption system is the adsorption kinetics. Three models had been studied to investigate the adsorption kinetics, Pseudo-first order, Pseudo-second order and intra-particle diffusion as shown in chapter 2. However, the statistical analysis of $R^2$, $\chi^2$, HYBRID and MPSD were also studied. In the case of the pseudo-first order model, it was
found that the $R^2$ value was low and high value of $\chi^2$. Therefore, pseudo-first order model cannot explain the kinetics of the interaction MB onto MNLRP as shown in Figure 10. In the other case, the intraparticle diffusion model was used to explain adsorption kinetics in this study as well. It was appeared that the plots do not pass through the origin, therefore, this indicates that the intraparticle diffusion is not the only rate limiting step, the intercept in this model gives information about the thickness of the boundary layer (amount of MB, in milligrams, adsorbed per gram of MNLRP), the graph for this model shown in Figure 12. On the other case, Pseudo-second order model was used to illustrate the adsorption kinetics. It was became clear that the interaction between MB and MNLRP surface belongs to pseudo-second order model based on the results from $R^2$, $\chi^2$, HYBRID and MPSD as listed in Table 3. The $R^2$ value for this model is 0.9999 at 25, 35 and 45 °C. Therefore, kinetic adsorption processes of MB onto MNLRP surface depends on the both of concentration of MB and MNLRP. [11, 19, 31]

![Figure 10. relationship of the kinetics data by First-order model under conditionsCo80mg/L, 400rpm,dosag 0.1g, 15ml, pH=7, 298,308 and 318K](image-url)
Figure 11. relationship of the kinetics data by second-order model under conditions Co 80 mg/L, 400rpm, dosag 0.1g, pH=7

Figure 12. relationship of the kinetics data by Intraparticle diffusion model under conditions Co 80 mg/L, 400rpm, dosag 0.1g, 15ml, pH=7, 298, 308 and 318K
Table 3. The adsorption kinetic parameters for adsorption of MB on MNLRP at different temperatures, 400rpm, 80mg/L, 0.1g, 15ml, pH=7

<table>
<thead>
<tr>
<th>Temperatures (K)</th>
<th>298K</th>
<th>308K</th>
<th>318K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_{e,exp}$ (mg/g) after 4 hours</td>
<td>11.609</td>
<td>11.677</td>
<td>11.861</td>
</tr>
</tbody>
</table>

**Pseudo-First order model**

| $q_{e,calc}$ (mg/g) | 0.3045 | 0.1857 | 0.1801 |
| $k_1$ (min$^{-1}$)  | 0.0149 | 0.0149 | 0.0119 |
| $R^2$              | 0.780  | 0.9072 | 0.9493 |
| $\chi^2$           | 419.7  | 711.1  | 757.6  |
| SSE               | 127.8  | 132.0  | 136.4  |
| HYBRID            | 220.2  | 226.2  | 230.1  |
| MPSD              | 56.22  | 56.82  | 57.29  |

**Pseudo-Second order model**

| $q_{e,calc}$ (mg/g) | 11.561 | 11.655 | 11.820 |
| $h$ (mg g$^{-1}$ min$^{-1}$) | 41.494 | 75.188 | 80.645 |
| $k_2$ (g mg$^{-1}$ min$^{-1}$) | 0.3100 | 0.5510 | 0.5770 |
| $R^2$ | 0.9999 | 0.9999 | 0.9999 |
| $\chi^2$ | 0.00019 | 0.00004 | 0.00014 |
| SSE | 0.0023 | 0.00048 | 0.0017 |
| HYBRID | 0.0039 | 0.0008 | 0.0028 |
| MPSD | 0.2387 | 0.1087 | 0.1996 |

**Intraparticle diffusion model**

| $K_d$ (mg/g min$^{1/2}$) | 0.039 | 0.0194 | 0.0166 |
| $C$ (mg/g) | 11.158 | 11.442 | 11.641 |
| $R^2$ | 0.6426 | 0.846  | 0.9426 |
3.10. Isotherm study

3.10.1. Langmuir isotherm model

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. Figure 13 shows Langmuir isotherm model for adsorption MB on MNLRP and the parameters are listed in Table 4. The graph were selected maximum adsorption capacity and Langmuir equilibrium constant by slope and intercept the values of $q_e$ are 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 13](image-url)

Figure 13. Langmuir isotherm model of MB solution on MNLRP under condition 400rpm, 60 min, dosag 0.1g,15ml, pH=7, 298, 308 and 318K
The statistical analysis highest value for $R^2$ indicates that the Langmuir isotherm is clearly the better fitting isotherm to the experimental data, the isotherm and statistical data for this model are listed in Table 4 [32].

The $R_L$ values are to be 0.0577, 0.049, 0.0338, 0.0265 and 0.02 for initial concentration 40, 50, 70, 90, 120 mg/L, respectively. This means that the Langmuir isotherm was favorable for adsorption of MB on MNLRP under these conditions used in this study [33].

![Figure 14. Relationship between RL and initial MB concentration](image)

3.10.2. 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 15 and the parameters are listed in Table 4.

![Figure 15. Freundlich isotherm model for adsorption MB on MNLRP under condition 400rpm, time 60 min, dosag 0.1g, 15ml, pH=7, 298,308 and 318K](image)

3.10.3. Temkin isotherm

The heat of adsorption (b) were determined by Figure 16 using equation 20 and the parameters are listed in Table 4. They were to be, 180.41, 164.15, 205.39 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 [34]. The maximum binding energy calculating from Temkin isotherm equilibrium binding constants ($A_r$ L/g) was to be 1.746, 1.703,1.719 L/g at 25, 35 and 45°C, respectively [35].
3.10.4. Dubinin–Radushkevich (D-R) isotherm

Figure 17 shows the plot of equation 22 from the adsorption data used in this study and the parameters are listed in Table 4. The type of adsorption was determined by calculating the value of adsorption energy (E) on the surface by equation 25 chapter 2. $K_{ad}$ value was obtained slope of $\ln(q_e) VS \varepsilon^2$ plots, values of E are equal to 1.24, 1.48, 1.71 KJ/mol these values. This means that adsorption of MB on MNLRP is physical adsorption.
The statistical analysis values of correlation coefficient ($R^2$), Chi-squared test $\chi^2$, SSE, HYBRID and MPSD were tested in order to find the best fit of isotherm model [32]. The isotherm and statistical data for this model are listed in Table 4. 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.
Table 4. Isotherm parameters for adsorption of MB on MNLRP at different temperatures, 400rpm, 60min, 0.1g, 15ml, pH=7

<table>
<thead>
<tr>
<th>Temperatures K</th>
<th>298K</th>
<th>308K</th>
<th>318K</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir isotherm model</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_{\text{max}}$ (mg / g)</td>
<td>22.71</td>
<td>27.85</td>
<td>32.63</td>
</tr>
<tr>
<td>$K_L$</td>
<td>0.4082</td>
<td>0.3928</td>
<td>0.3377</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9877</td>
<td>0.9875</td>
<td>0.9799</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>0.2425</td>
<td>0.0547</td>
<td>0.0769</td>
</tr>
<tr>
<td>SSE</td>
<td>2.0733</td>
<td>0.4854</td>
<td>0.8424</td>
</tr>
<tr>
<td>HYBRID</td>
<td>7.5725</td>
<td>1.8772</td>
<td>2.4632</td>
</tr>
<tr>
<td>MPSD</td>
<td>16.397</td>
<td>8.9038</td>
<td>9.4210</td>
</tr>
<tr>
<td><strong>Freundlich isotherm model</strong></td>
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</tr>
<tr>
<td>$K_f$</td>
<td>1.6320</td>
<td>1.8290</td>
<td>1.9290</td>
</tr>
<tr>
<td>$1/n$</td>
<td>0.489</td>
<td>0.604</td>
<td>0.658</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9269</td>
<td>0.9679</td>
<td>0.9902</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>0.4712</td>
<td>0.2641</td>
<td>0.1183</td>
</tr>
<tr>
<td>SSE</td>
<td>3.6782</td>
<td>3.3931</td>
<td>1.5041</td>
</tr>
<tr>
<td>HYBRID</td>
<td>14.977</td>
<td>8.9193</td>
<td>3.8333</td>
</tr>
<tr>
<td>MPSD</td>
<td>23.669</td>
<td>19.231</td>
<td>10.928</td>
</tr>
<tr>
<td><strong>Temkin isotherm model</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$b$</td>
<td>164.15</td>
<td>180.41</td>
<td>205.39</td>
</tr>
<tr>
<td>$A_T$</td>
<td>1.746</td>
<td>1.7190</td>
<td>1.7030</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9791</td>
<td>0.9976</td>
<td>0.9823</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>0.1985</td>
<td>0.0214</td>
<td>0.1697</td>
</tr>
<tr>
<td>SSE</td>
<td>1.6533</td>
<td>0.2018</td>
<td>1.5361</td>
</tr>
<tr>
<td>HYBRID</td>
<td>6.5572</td>
<td>0.7120</td>
<td>5.6887</td>
</tr>
<tr>
<td>MPSD</td>
<td>14.802</td>
<td>6.0370</td>
<td>15.543</td>
</tr>
<tr>
<td><strong>D-R isotherm model</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_{ad}$ (mol$^2$ / J$^2$)</td>
<td>0.325×10$^{-6}$</td>
<td>0.2284×10$^{-6}$</td>
<td>0.1715×10$^{-6}$</td>
</tr>
<tr>
<td>$E$ (KJ/mol)</td>
<td>1.24</td>
<td>1.48</td>
<td>1.71</td>
</tr>
<tr>
<td>$q_s$ (mg / g)</td>
<td>16.218</td>
<td>16.969</td>
<td>16.563</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9776</td>
<td>0.9748</td>
<td>0.9289</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>0.1985</td>
<td>0.5249</td>
<td>0.9500</td>
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<tr>
<td>SSE</td>
<td>1.6533</td>
<td>6.3943</td>
<td>9.1935</td>
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<tr>
<td>HYBRID</td>
<td>6.5572</td>
<td>18.688</td>
<td>26.398</td>
</tr>
<tr>
<td>MPSD</td>
<td>14.802</td>
<td>29.511</td>
<td>31.000</td>
</tr>
</tbody>
</table>
3.11. Thermodynamic study

Thermodynamic parameter using the equations 34 chapter 2 was used as shown in Figure 18 and listed in Table 5. The thermodynamic equilibrium constant were obtained intercept of $\ln q_e/C_e$ vs $C_e$ plot. The change in standard free energy ($\Delta G^0$) is calculated from equation 35, the change in standard enthalpy ($\Delta H^0$) and entropy ($\Delta S^0$) are calculated from the slope and intercept of plot $\ln K_o$ versus $1/T$ respectively, as shown in Figure 19 and listed in Table 5. The values of $\Delta G^0$ are to be -1.730, -2.124 and -2.234 KJ/mol at 25, 35 and 45°C, respectively. This indicates that the interaction occurs spontaneous, obviously, becoming more spontaneous with increasing temperature (more favorable at higher temperature). Also, the $\Delta H^0$ and $\Delta S^0$ values are to be 12.61 KJ/mol and 59.35 J/(mol.K), respectively as listed in Table 5. The positive value of $\Delta H^0$ means that the adsorption of MB on MNLRP is endothermic processes. This explains the increase in removal percentage and adsorption efficiency with increased temperature. The positive value of $\Delta S^0$ means that the adsorption of MB on MNLRP is irreversible [36]. In addition, adsorption process is accompanied increase in entropy[37].

![Figure 18. Thermodynamic equilibrium constant at different temperature](image-url)
The activation energy are calculated from the slope of plot \( \ln K_2 \) vs. 1/T, as shown in Figure 20 and listed in Table 5. The value of \( E_a \) is to be 24.75 KJ/mol. This is confirmed that the adsorption process of MB onto MNLRP is physical adsorption process due to the physical adsorption the activation energy value is lower than 40 kJ/mol [19, 34].
Figure 20. Plots of $\ln k_2$ vs $1/T$ for the Arrhenius

Table 5. Thermodynamic parameters for adsorption of MB on MNLRP

<table>
<thead>
<tr>
<th>Temp</th>
<th>$K_v$ (L g$^{-1}$)</th>
<th>$\Delta G^0$ (KJ mol$^{-1}$)</th>
<th>$\Delta H^0$ (KJ mol$^{-1}$)</th>
<th>$\Delta S^0$ (J mol$^{-1}$K$^{-1}$)</th>
<th>$E_a$ (KJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298K</td>
<td>2.0103</td>
<td>-1.730</td>
<td>12.61</td>
<td>59.35</td>
<td>24.75</td>
</tr>
<tr>
<td>308K</td>
<td>2.2917</td>
<td>-2.124</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>318K</td>
<td>2.3279</td>
<td>-2.234</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4. Conclusion

Based on the results of these experiments, the following conclusions can be achieved:

- MNLRP characterized properties Physico-Chemical qualify to remove dyes.
- The basic solution fits the removal of MB dye more than acidic solution.
- The Langmuir isotherm model and statistical analysis, the adsorption of MB on MNLRP indicates to formation of mono-layer.
- The kinetic study adsorption of MB on MNLRP indicates that interaction belong to pseudo-second order model.
- Heat of adsorption, adsorption energy and activation energy for adsorption of MB on MNLRP indicates that the adsorption is physisorption.
- Adsorption of MB on MNLRP is spontaneous, endothermic and increased randomness at the solid/liquid interface.
- MNLRP can be used to remove MB from ecosystems.
5. Future work

Because of small-time not perform studies the following:

- Preparation Activated Carbon from MNLRP
- MNLRP use as a sorbent to remove acidic dyes from aqueous solution
- MNLRP use as a sorbent to remove heavy metals from aqueous solution
- MNLRP use as a sorbent to remove phenol and aniline from aqueous solution
6. References


Enclosures
### Enclosure A - selective adsorbent dosage, 400rpm, 60 min, 60 mg/L, pH=7, room temperature

<table>
<thead>
<tr>
<th>dosage (g)</th>
<th>$C_e$ (mg / L)</th>
<th>$q_e$ (mg / g)</th>
<th>$R%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1005</td>
<td>5.9094</td>
<td>8.0733</td>
<td>90.151</td>
</tr>
<tr>
<td>0.2002</td>
<td>1.4376</td>
<td>4.3877</td>
<td>97.604</td>
</tr>
<tr>
<td>0.3011</td>
<td>0.5760</td>
<td>2.9610</td>
<td>99.040</td>
</tr>
<tr>
<td>0.4009</td>
<td>0.5880</td>
<td>2.2246</td>
<td>99.020</td>
</tr>
<tr>
<td>0.5006</td>
<td>0.4920</td>
<td>1.7641</td>
<td>99.180</td>
</tr>
</tbody>
</table>

### Enclosure B - determination pHpzc and study effect pH on the removal and adsorption efficiency, 400rpm, 60min, 120mg/L, 0.1g, room temperature,

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Final pH</th>
<th>$q_e$ (mg / g)</th>
<th>$R%$</th>
<th>$C_e$ (mg / L)</th>
<th>Initial pH - Final pH</th>
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</thead>
<tbody>
<tr>
<td>1.75</td>
<td>2.50</td>
<td>2.933</td>
<td>16.295</td>
<td>100.446</td>
<td>0.75</td>
</tr>
<tr>
<td>2.74</td>
<td>3.28</td>
<td>9.178</td>
<td>50.991</td>
<td>67.8100</td>
<td>0.54</td>
</tr>
<tr>
<td>2.90</td>
<td>3.71</td>
<td>10.708</td>
<td>59.489</td>
<td>48.6130</td>
<td>0.81</td>
</tr>
<tr>
<td>4.83</td>
<td>5.90</td>
<td>12.699</td>
<td>70.553</td>
<td>35.3370</td>
<td>1.07</td>
</tr>
<tr>
<td>6.07</td>
<td>6.22</td>
<td>15.719</td>
<td>87.330</td>
<td>15.2020</td>
<td>0.15</td>
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<tr>
<td>8.49</td>
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<td>17.620</td>
<td>97.891</td>
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<tr>
<td>10.35</td>
<td>6.32</td>
<td>17.811</td>
<td>98.948</td>
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<tr>
<td>11.14</td>
<td>7.38</td>
<td>17.831</td>
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<td>1.12400</td>
<td>-3.76</td>
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<tr>
<td>12.32</td>
<td>11.45</td>
<td>17.890</td>
<td>99.391</td>
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<td>-0.87</td>
</tr>
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</table>
Enclosure C 1 – study the effect of contact time, 400rpm, 80mg/L, 0.1g, 15ml, pH=7,

\[ C_t (mg/l) \quad q_t (mg/g) \]

<table>
<thead>
<tr>
<th>Time</th>
<th>Room temp</th>
<th>25°C</th>
<th>35°C</th>
<th>45°C</th>
<th>Room temp</th>
<th>25°C</th>
<th>35°C</th>
<th>45°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>5.1551</td>
<td>3.3860</td>
<td>2.813</td>
<td>1.7191</td>
<td>11.1380</td>
<td>11.492</td>
<td>11.5785</td>
<td>11.7421</td>
</tr>
<tr>
<td>60</td>
<td>4.4115</td>
<td>3.3260</td>
<td>2.666</td>
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<td>11.2590</td>
<td>11.501</td>
<td>11.6000</td>
<td>11.7724</td>
</tr>
<tr>
<td>90</td>
<td>3.6362</td>
<td>3.1260</td>
<td>2.400</td>
<td>1.2889</td>
<td>11.3749</td>
<td>11.531</td>
<td>11.6400</td>
<td>11.8100</td>
</tr>
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</table>

Enclosure C 2 - kinetics data

- **First order model**

- **Second order model**

- **Intraparticle diffusion model**


<table>
<thead>
<tr>
<th>Time</th>
<th>ln ( q_e - q_t )</th>
<th>ln ( q_e - q_t )</th>
<th>ln ( q_e - q_t )</th>
<th>( \frac{v}{q_t} )</th>
<th>( \frac{v}{q_t} )</th>
<th>( \frac{v}{q_t} )</th>
<th>( t^{1/2} )</th>
<th>( q_t )</th>
<th>( q_t )</th>
<th>( q_t )</th>
<th>( 25°C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3.873</td>
<td>11.192</td>
<td>11.485</td>
<td>11.691</td>
<td>11.742</td>
</tr>
<tr>
<td>15</td>
<td>-0.875</td>
<td>-1.650</td>
<td>-1.772</td>
<td>1.340</td>
<td>1.306</td>
<td>1.283</td>
<td>5.477</td>
<td>11.492</td>
<td>11.579</td>
<td>11.600</td>
<td>11.772</td>
</tr>
</tbody>
</table>
Enclosure D1- study the effect of initial concentration, 400rpm, 60min, 0.1g, 15ml,pH=7,

\[
C_e (mg / L) \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \q
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<thead>
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<th>Langmuir Isotherm Data</th>
<th>Freundlich Isotherm Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_e/qe$</td>
<td>$C_e$</td>
</tr>
<tr>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td></td>
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</tr>
<tr>
<td>45</td>
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</tbody>
</table>

<table>
<thead>
<tr>
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<th>Temkin Isotherm Data</th>
<th>D-R Isotherm Data</th>
</tr>
</thead>
<tbody>
<tr>
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<td>$q_e (mg / g)$</td>
<td>$\ln C_e$</td>
</tr>
<tr>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td></td>
<td></td>
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</tbody>
</table>