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Removal of Methylene Blue Dye from Aqueous Solution Using Marrubium vulgare Leaf Powder as a Low-Cost Biosorbent

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إزالة صبغة أزرق الميثيلين من المحلول المائي باستخدام مسحوق أوراق نبات الروبيا (*Marrubium vulgare*) كمادة ماصّة حيوية منخفضة التكلفة

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Abstract:
The present study evaluates the adsorption capacity of raw Marrubium vulgare leaf powder as a biosorbent material for eliminating methylene blue (MB) dye in industrial wastewater. The results demonstrated a high removal efficiency of approximately 93.7% at neutral pH (pH = 7), highlighting the material's effectiveness under ambient conditions without the need for chemical adjustment. The maximum adsorption capacity (q_{max}) of the monolayer reached 15.06 mg/g. Equilibrium observation showed strong agreement with the Langmuir isotherm model ($R^2 = 0.9742$), indicating monolayer adsorption on a homogeneous surface. The Freundlich model further supported these findings, with an intensity parameter (n = 1.516), suggesting favorable adsorption behavior. The analytical method exhibited high sensitivity, with LOD and LOQ values of 0.008758 and 0.026539, respectively. The adsorption efficiency at neutral pH is attributed to electrostatic interactions between cationic dye molecules and the negatively charged adsorbent surface, consistent with the point of zero charge (PZC) concept. Thermodynamic analysis confirmed the spontaneous and endothermic nature of the process, as indicated by negative $\Delta G°$ values and a positive $\Delta H°$, whereas the positive $\Delta S°$ indicates enhanced disorder at the solid–liquid interface. Overall, raw marrubium vulgare leaf powder shows great promise as an affordable, environmentally friendly adsorbent for wastewater treatment applications.

Keywords: Biosorption, Methylene blue, Adsorption, Marrubium vulgare, Dyes, Extraction

الملخص
الدراسة تقيم قدرة الامتزاز لمسحوق أوراق نبات الروبيا الشائع (Marrubium vulgare) الخام كمادة مازة حيوية لإزالة صبغة الميثيلين الأزرق (MB) من مياه الصرف الصناعي. وأظهرت النتائج كفاءة إزالة عالية بلغت حوالي 93.7% عند درجة حموضة متعادلة (pH = 7) ، مما يسلط الضوء على فعالية المادة في ظل الظروف المحيطة دون الحاجة إلى تعديل كيميائي. وبلغت سعة الامتزاز القصوى (qmax) للطبقة أحادية الجزيء 15.06 ملغ/غرام. أظهرت الملاحظة التوازنية توافقاً قوياً مع نموذج إيزوثيرم لانغموير($R^2 = 0.9742$) ، مما يشير إلى امتزاز أحادي الطبقة على سطح متجانس. كما دعمت نتائج نموذج فروندليش هذه النتائج، مع عامل شدة (n = 1.516) ، مما يشير إلى سلوك امتزاز ملائم. وأظهرت الطريقة التحليلية حساسية عالية، حيث بلغت قيم حد الكشف (LOD) وحد الكمية (LOQ) حوالي 0.008758 و0.026539 على التوالي.

تُعزى كفاءة الامتزاز عند درجة الحموضة المتعادلة إلى التفاعلات الكهروستاتيكية بين جزيئات الصبغة الموجبة الشحنة الكاتيونية وسطح المادة الماصة المشحون سالباً، وهو ما يتوافق مع مفهوم نقطة الشحنة الصفرية .(PZC) وأكد التحليل الديناميكي الحراري الطبيعة التلقائية والماصة للحرارة للعملية، كما يتضح من قيم طاقة غيبس الحرة السالبة ($\Delta G0$) وقيمة الإنثالبي الموجبة ($\Delta H0$) ، في حين تشير قيمة الإنتروبي الموجبة ($\Delta S0$) إلى زيادة العشوائية عند الواجهة بين الحالة الصلبة والسائلة. بشكل عام، يظهر مسحوق أوراق نبات الروبيا الخام فعالية واعدة كمادة ماصة ميسورة التكلفة وصديقة للبيئة لتطبيقات معالجة مياه الصرف الصحي.

الكلمات المفتاحية: الامتزاز الحيوي، الميثيلين الأزرق، الامتزاز، نبات الروبيا، الأصباغ، الاستخلاص.

Introduction

The medicinal plant Rubia (Marrubium vulgare) (MV) is a member of the genus Marrubium and the family Lamiaceae, which comprises approximately 40 species distributed across temperate regions of Asia and the Mediterranean basin. This plant has been traditionally used for therapeutic purposes since ancient times. Several studies have confirmed its significant potential in chemical, biological, and pharmaceutical applications, particularly due to its antioxidant and antimicrobial properties. A study by Mittal & Nanda [1] demonstrated that Marrubium vulgare contains phenolic compounds and flavonoids, which may contribute to its antioxidant properties and its significance in pharmaceutical and therapeutic applications.

Water pollution represents one of the most critical global environmental challenges, mainly driven by rapid industrialization, agricultural expansion, and population growth. Inadequate waste management practices and the absence of proper environmental planning have led to the severe degradation of environmental components, including soil, air, and water resources. It is estimated that thousands of chemical compounds are introduced into the environment annually, with their impact depending on their concentration, physicochemical properties, and biological interactions [2]. Dyes are considered among the most hazardous water pollutants due to their extensive use in textile, leather, paper, plastics, and cosmetic industries. They are characterized by complex molecular structures and high stability, making them resistant to biodegradation and persistent in the environment. Even at low concentrations, dyes adversely affect water quality by reducing light penetration and inhibiting photosynthetic processes in aquatic ecosystems. Furthermore, they may transform into more toxic compounds or bioaccumulate within the food chain, endangering human health and ecosystems [3,4]. MB is considered one of the most extensively employed dyes due to its environmental persistence. Its release into aquatic systems obstructs light penetration, disrupts sensitive biochemical processes in aquatic organisms, and may cause severe health effects in humans, including cardiovascular and neurological disorders, cyanosis, jaundice, tissue damage, and even carcinogenic effects [2,5]. Various techniques have been employed for the removal of organic pollutants from aqueous solutions, including chemical precipitation, membrane separation, ion exchange, solvent extraction, and electrodialysis. Among these methods, adsorption is considered one of the most efficient and versatile techniques [6].

Conventional adsorbents such as activated carbon, silica, and alumina have demonstrated high efficiency. However, their high cost has encouraged the exploration of low-cost alternative natural adsorbents [7]. Natural materials, often derived from agricultural waste, are abundant and economically attractive. Accordingly, extensive research has been conducted on various natural biosorbents such as orange peels, olive leaves, palm fronds, and date seeds, which are used to remove organic contaminants, such as dyes [8-10].

Several analytical techniques are available for determining the concentration of MB in aqueous solutions. Among them, UV–Vis's spectrophotometry is widely used due to the strong absorption characteristics of the dye in the visible region, allowing accurate quantification at specific wavelengths. The present study aims to evaluate the efficiency of MV leaf powder as a low-cost natural adsorbent for the removal of MB dye from aqueous solutions. The effects of various operational parameters, including pH, contact time, initial dye concentration, adsorbent dosage, stirring speed, and temperature, were investigated to assess adsorption performance under different experimental conditions

2. Experimental

2.1 Materials

All chemicals were of analytical grade and were used directly as received from the supplier without any further purification. The reagents included methylene blue (MB) dye obtained from BDH Chemicals, hydrochloric acid (HCl) supplied by T-Baker Lab Chemicals, and sodium hydroxide (NaOH) supplied by Merck.

2.2 Apparatus

All laboratory measurements and experimental analyses in this study were carried out using a set of high-precision scientific instruments. A pH meter (Thermo) was used to measure the pH, and a mill (Homer) was used to prepare the sample. For spectrophotometric analysis and physicochemical characterization of the samples, a UV–Vis's spectrophotometer (Analytik Jena) and a Fourier Transform Infrared (FTIR) spectrometer (PerkinElmer) were employed. In addition, the experimental procedures involved the use of a mechanical shaker and an electric heater

(Stuart) to control operating conditions, along with a water bath (model HH-S) to maintain a constant temperature throughout the experiments.

2.3 Collection and Preparation of the Adsorbent

A sample of MV plant leaves was collected in late December 2023 from the Al-Gharbiyat area (a suburb of Sirte city, Libya). Only the leaves were utilized in this study, while the remaining parts of the plant were excluded. The collected leaves were thoroughly washed several times with tap water to remove dust and surface impurities, followed by rinsing with distilled water to eliminate any adhering ions. The leaves were then air-dried under shade at room temperature, avoiding direct exposure to sunlight, dust, and humidity in order to preserve their physicochemical properties. The leaves were periodically turned to ensure uniform drying and to prevent microbial degradation under high humidity conditions. The drying process was maintained for approximately 20–25 days. After complete drying, the leaves were crushed and finely powdered and subsequently stored in dark paper bags under dry conditions, away from moisture [11,12]. Finally, Fourier Transform Infrared (FTIR) spectroscopy was employed to characterize the active functional groups present on the surface of the prepared MV leaf powder.

2.4 Prepare MB stock solution

The MB stock solution (500 ppm) was prepared by dissolving 0.5 g of the dye powder in one liter of distilled water, ensuring complete dissolution. Subsequently, working solutions with concentrations ranging from 5 to 15 ppm were obtained through stepwise dilution as required. For pH adjustment, 0.1 M solutions of hydrochloric acid (HCl) and sodium hydroxide (NaOH) were prepared. [13]

2.5 Batch Adsorption Method

The adsorption procedure was performed by bringing a specified mass of the adsorbent into contact with a known volume of the dye solution at the desired concentration in a 50 mL conical flask. The flasks were tightly sealed to prevent any evaporation or contamination during the experiment. To achieve equilibrium between the solid and liquid phases, the flasks were placed on a mechanical shaker operating at a constant and appropriate agitation speed to ensure homogeneous distribution and effective contact between the adsorbent particles and the solute. In order to determine the optimal operating conditions and to better understand the adsorption behavior, a set of experiments was performed to evaluate the influence of several independent variables. This included solution pH, contact time, initial dye concentration, and adsorbent dosage, in addition to temperature and agitation speed. This approach enabled a comprehensive evaluation of the adsorption efficiency under well-controlled laboratory conditions.

2.6 Capacity and Removal Efficiency

The adsorption capacity (Qe) was used to assess the impact of the above-mentioned parameters. It was determined by calculating the difference between the initial concentration (Co, mg/L) and the equilibrium concentration (Ce, mg/L) of the solution (equation 1), which reflects the impact of various adsorption processes: [14]

$$Qe = \frac{Co - Ce}{M} \times V \text{ --------------- (1)}$$

Where Qe represents the dye adsorption capacity (mg/g), V is the volume of the solution (L), and M is the mass of the adsorbent (g). Accordingly, the dye removal efficiency (%R) was calculated as follows: [13]

$$\%R = \frac{Co - Ce}{Co} \times 100 \text{ --------- (2)}$$

3. Results and Discussion:

3.1 FTIR Spectroscopy

FTIR spectroscopy analysis was performed on the powdered of the untreated Rubia plant leaves using a Perkin Elmer FTIR spectrometer, covering the wavenumber range from 650 to 4000 cm^{-1}. Based on the IR spectrum shown in Figure (1), a band was observed at 3339.54 cm-1, corresponding to the O−H stretching vibration present in the polysaccharides that make up the plant fibers [15]. Another band appeared at 2918.7 cm-1, attributed to the C−H stretching in the carbon chain. A band at 1730.27 cm-1 indicates the presence of a C=O bond, suggesting the existence of carbonyl groups. Additionally, a band at 1031 cm-1 was recorded, corresponding to C−O bonds present in the chemical structure of the sample.

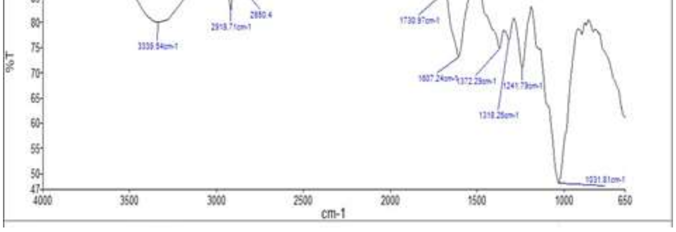


Figure 1: FTIR spectrum of the adsorbent Rubia leaves (marrubium vulgare).

3.2 Biosorption of MB dye by MV adsorbent

- **Study of Factors Affecting Adsorption**

The adsorption of MB dye onto RV leaf powder was examined by assessing the effects of pH, contact time, adsorbent dosage, agitation speed, initial dye concentration, and temperature.

- **Effect of pH**

To investigate the influence of solution pH on the adsorption efficiency of MB dye, nine samples were prepared at a fixed initial concentration of 10 ppm and a volume of 25 mL for each sample. The pH values were adjusted in the range 2–10 with HCl and NaOH 0.01M. All other experimental conditions and parameters were kept constant. MV leaf powder (0.05 g) was used as the adsorbent.

The results of the study (Figure 2) demonstrate a remarkable capacity of the adsorbent of removing MB dye from aqueous solution. The adsorption efficiency is more pronounced under acidic conditions, with a noticeable improvement in performance as the pH decreases. The highest removal efficiency was recorded at pH = 4, reaching approximately 88%, which highlights the significant role of the functional groups present on the surface of the adsorbent in enhancing the interaction with cationic dye molecules under the studied conditions. Furthermore, results also show that the adsorbent maintains relatively stable performance over a pH range of 4 to 8, indicating good operational flexibility in water treatment applications without the need for strict chemical adjustment of the medium. This behavior can be attributed to the electrostatic balance between the surface charge of the adsorbent and the charge of the dye molecules, which promotes electrostatic attraction and enhances binding efficiency. Accordingly, the MV powder can be considered a promising adsorbent from both environmental and economic perspectives due to its ability to achieve high removal efficiencies under conditions close to natural water neutrality [16].

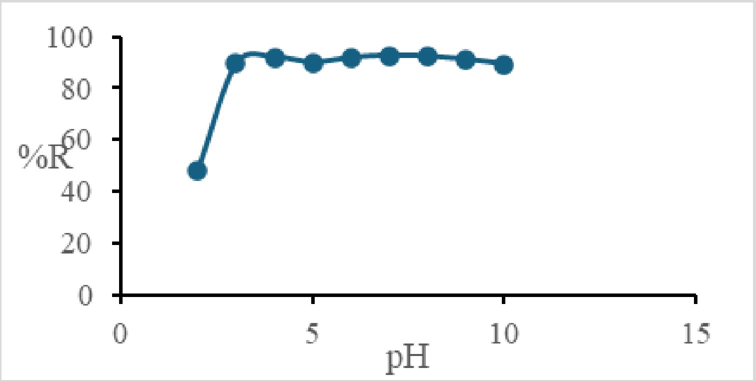


Figure 2: Effect of pH on the adsorption of MB dye

- Effect of Adsorbent Dose

The effect of adsorbent dosage was evaluated using ten samples with varying masses ranging from 0.01 to 0.1 g. All other experimental conditions were kept constant. Figure (3) demonstrates the influence of adsorbent dosage on dye removal efficiency. The removal efficiency increases progressively with increasing adsorbent dosage, reaching a plateau at approximately 50 mg. This trend is attributed to the limited availability of adsorption sites at lower adsorbent dosages compared with the number of dye molecules present in the solution, the specific surface area and the number of active sites increase accordingly, leading to a marked enhancement in removal efficiency. At equilibrium, the removal efficiency remains nearly constant, ranging between 89% and 91%, despite further increases in dosage up to 100 mg. This suggests that the system has approached equilibrium conditions, where most of the available dye molecules have been adsorbed onto the active sites. Consequently, any additional increase in adsorbent dosage provides excess adsorption sites without contributing to further improvement in removal. At this stage, the dye concentration becomes the limiting factor governing the adsorption process [17].

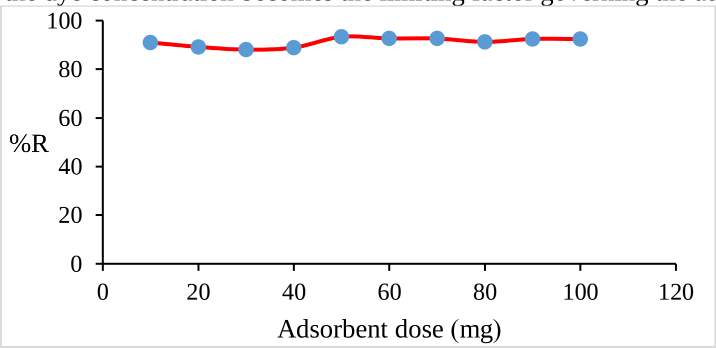


Figure 3: Effect of adsorbent dose on the adsorption of MB dye

- **Effect of Contact Time**

The kinetics of adsorption were examined by performing six experiments at different contact times ranging from 5 to 30 minutes. This study was conducted to evaluate the time required to achieve adsorption equilibrium. Figure (4) illustrates the effect of shaking time on the adsorption efficiency of the studied biosorbent towards MB dye. The results indicate that the adsorption rate was rapid during the initial stage, with approximately 85% of the dye removed within the first 10 minutes. This behavior can be attributed to the abundance of available active sites on the adsorbent surface, in addition to the high concentration gradient that enhances the transfer of dye molecules from the bulk solution to the adsorbent. The maximum removal efficiency (90%) was achieved at a shaking time of 20 minutes. Beyond this point, no significant improvement in removal efficiency was observed, indicating that the system had reached adsorption equilibrium and that the adsorbent surface had become saturated. These findings are consistent with those reported by Mosoarca et al. [18], where similar observation was reported on the adsorption behavior of lignocellulosic materials

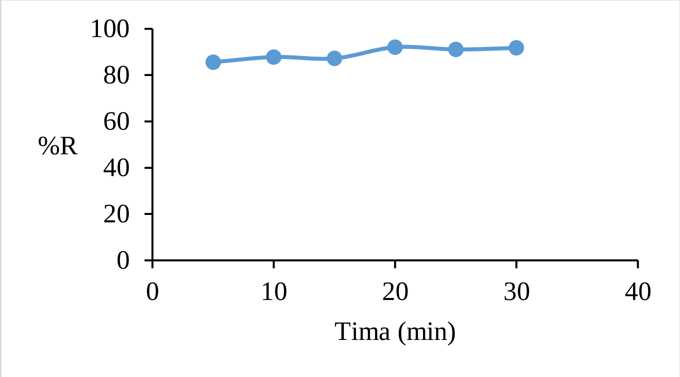


Figure 4: Effect of shaking time (min) on the adsorption of dye

Effect of Agitation Speed (Shaking Speed)

The effect of agitation speed was examined by conducting five experiments at different shaking rates (50, 100, 150, 200, and 250 rpm). As shown in Figure (5), the effect of shaking speed on dye adsorption shows that the removal effectiveness increases gradually with increasing agitation rate, reaching an optimum at 100 rpm where the maximum removal efficiency above 90% was attained. The boundary layer around the adsorbent surface thins at higher shaking rates, which explains this improvement. Shaking speed higher than this, the efficiency of elimination plateaus or decreases slightly. This behavior is attributed to the high turbulence of the fluid, which, on the one hand, limits the effective interaction of the dye molecules with the adsorbent surface and, on the other hand, causes partial desorption due to shear pressures. Results show that agitation speed higher than 100 rpm does not improve the adsorption process significantly [19].

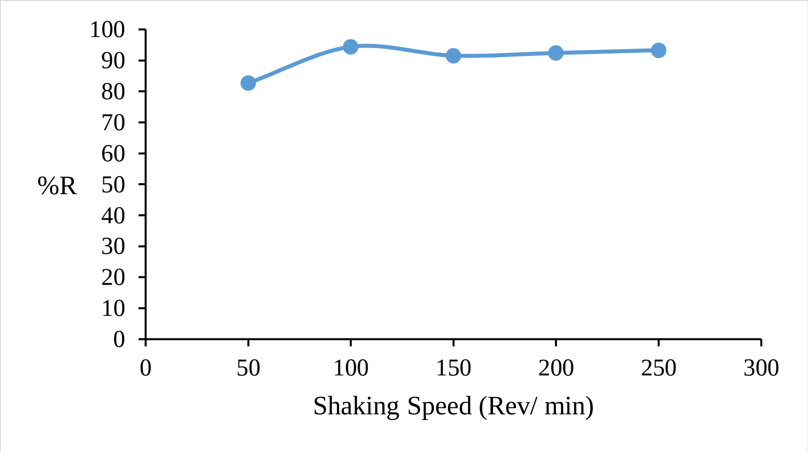
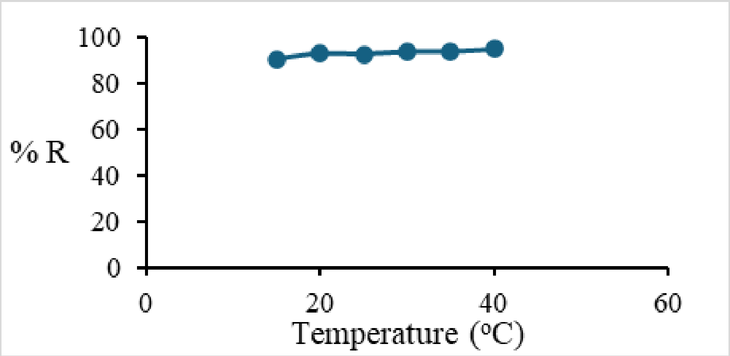


Figure 5: Effect of shaking speed (rpm) on the adsorption of dye

- Effect of Temperature

The influence of temperature was studied by performing adsorption experiments at six different temperatures (15, 20, 25, 30, 35, and 40 °C), while maintaining all other experimental conditions constant as previously defined. The adsorption behavior illustrated in Figure (6) provides a quantitative evaluation of the effect of temperature on the efficiency of the adsorption process. The results indicate a slight increase in removal efficiency with rising temperature in the initial stage. This behavior can be attributed to the decrease in solution viscosity and the improvement in mass transfer properties, which enhance the diffusion of dye molecules toward the active sites on the surface of the adsorbent [20]. The maximum removal efficiency was recorded at 20°C, reaching approximately

92%, which indicates a high adsorption performance of the adsorbent. As the temperature increased further up to 40 °C, no significant changes in adsorption efficiency were observed. These results demonstrate the high thermodynamic stability of the adsorbent material. [21]. Moreover, this trend can be explained by the incremental occupancy of available binding sites on the adsorbent's surface, where the supply of additional thermal energy does not lead to any significant increase of the adsorption [22].



igure 6 Effect of temperature (oC) on the adsorption of dye

- Effect of Initial Dye Concentration

To examine the effect of the initial dye concentration, experiments were conducted over a concentration range of 5-30 ppm under fixed operating conditions, including an adsorbent dose of 0.05 g, pH 7, and constant agitation. Figure (7) illustrates the effect of the initial concentration of MB dye on the adsorbent. The results reveal a clear inverse relationship between the initial concentration and the removal efficiency. At low concentrations (5 mg/L), a high removal efficiency of approximately 95% was achieved, which can be attributed to the abundance of available active sites relative to the number of dye molecules in the solution. As the concentration increased gradually to 30 mg/L, the removal efficiency decreased to about 80%. This decline is primarily associated with the progressive saturation of the active adsorption sites on the surface of the adsorbent, leading to increased competition among dye molecules for the limited available sites [23]. These results indicate that the adsorbent possesses a finite adsorption capacity, beyond which its efficiency diminishes. Accordingly, these findings are essential for determining the optimal adsorbent dosage and predicting its performance in treating wastewater containing varying concentrations of organic dyes.

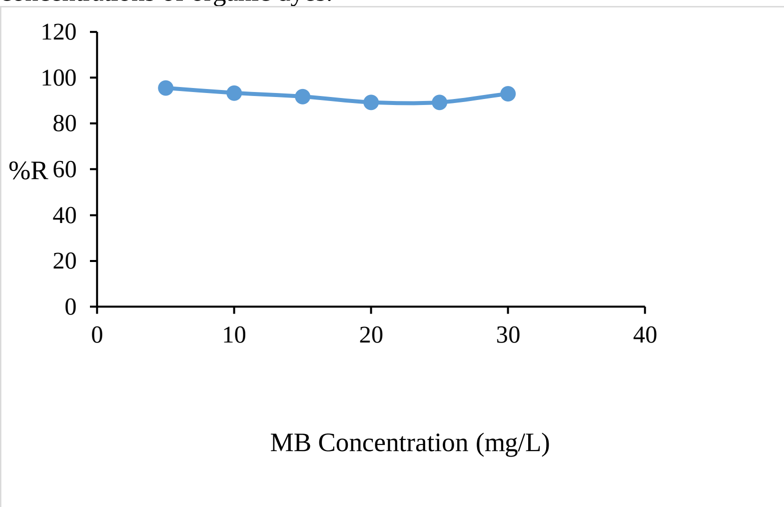


Figure 7: Effect of initial concentration (mg/L) of MB solution on dye adsorption pH=7, shaking speed= 10 rpm, m=0.5g, t= 20min)

- Validation of the Method

The analytical method for studying MB adsorption was evaluated for key performance parameters following the report by Lambarki et al. [24].

4. Limit of Detection and Limit of Quantification (LOD & LOQ)

The LOD and LOQ were computed using the following equation based on blank data and standard concentrations prior to adsorption:

$$\text{LOD} = \frac{3.3\,\sigma}{S} \text{-------------------------- (3)}$$

$$LOQ = \frac{10\,\sigma}{S} \quad \text{----------------------------------} \quad (4)$$

Where (σ) standard deviation of blank signals and (S) slope of the calibration curve. This ensures accurate sensitivity estimation and reliable measurement of MB before adsorption. Table 1, provides the validation constants for the analytical method suitability.

Table 1: The validation constants for the analytical method suitability.Sample

Sample	r	R^2	σ	LOD	LOQ
	0.9987	0.9975	0.000513	0.008758	0.026539

5. Adsorption Isotherm

The distribution of dye ions between the solution (liquid phase) and the adsorbent material (solid phase) can be interpreted using several theoretical models, particularly after the system reaches equilibrium. Among the most important models that explain these interactions are the Langmuir the Freundlich models.

Langmuir Isotherm:-

Langmuir's model assumes adsorption occurs on a homogeneous monolayer surface with a finite number of identical sites. The linear form of the Langmuir equation is given as follows: [25].

$$\frac{1}{qe} = \frac{1}{Qm} + \frac{1}{b\,Qm\,Ce} \quad \text{--------------------------------} \quad (5)$$

Where: Langmuir constant = (b) represents the adsorption energy, Ce = is the equilibrium concentration (mg/L), q_e = is the amount adsorbed at equilibrium (mg/g), and q_m = is the maximum adsorption capacity (mg/g).

By plotting the reciprocal of the adsorption capacity ($1/q_e$) against the reciprocal of the equilibrium concentration (1/Ce), a straight line is obtained (Figure 8). From the slope and intercept of this line, the Langmuir constants can be estimated.

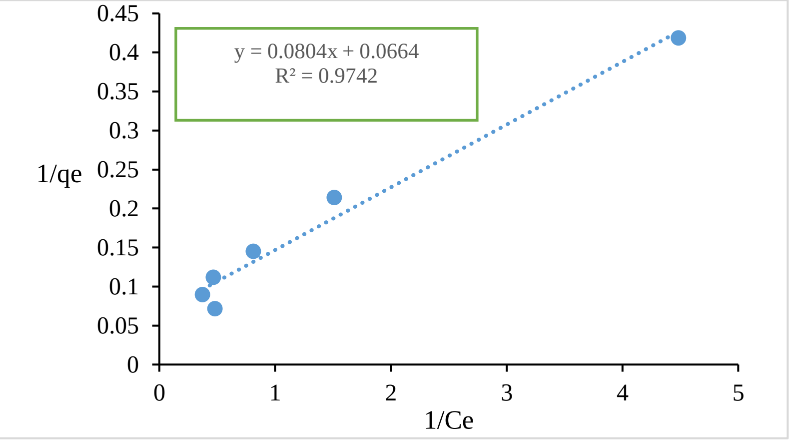


Figure 8: Langmuir Isotherm Model for the adsorption of MB dye by MV leaves

To evaluate the adsorption characteristics of MB dye onto the adsorbent, the linear formulation of the Langmuir isotherm was utilized. The empirical data demonstrated strong alignment with the model, validated by the high correlation coefficient value. (R^2 = 0.9742), suggesting monolayer adsorption on a homogeneous surface with energetically equivalent active sites. Based on the linear regression equation (y = 0.0804x + 0.0664), the maximum adsorption capacity (q_{max}) was calculated to be 15.06 mg/g, while the Langmuir constant (KL) was found to be 0.826 L/mg, indicating a strong affinity between the adsorbent surface and dye molecules. These results corroborate the findings reported in previous study conducted by Nandiyanto et al. [26]. Furthermore, the dimensionless separation factor (RL) values ranged from 0.195 to 0.046 for initial dye concentrations between 5 and 25 mg/L. Since all RL values fall within the range of $0 < RL < 1$, the adsorption process is considered favorable. The decrease in RL values with increasing initial concentration further confirms the enhanced favorability of adsorption at higher dye concentrations [27].

- **Freundlich Isotherm:-**

This model describes the adsorption on heterogeneous surfaces. The empirical constants n and K can be determined from the slope and intercept, respectively, by plotting log qe against log Ce, as expressed in Equation (6) [28].

$$qe = K_f \; Ce^{(1/n)} \quad \text{--------------------------} (6)$$

Where: qe = amount of dye adsorbed at equilibrium (mg/g), Ce = dye concentration at equilibrium in solution (mg/L), Kf = constant of adsorption capacity, and n is the adsorption intensity (indicator of surface heterogeneity). However, for the practical use, the previous equation was linearized as:

$$\text{Log (qe)} = \log (\text{Kf}) + (1/n) \log(\text{Ce}) \quad \text{-- ----(7)}$$

This linear form (Figure 9) allows one to plot log(qe) versus log(Ce), where the slope equals 1/n. The intercept = log (Kf). From this plot, both Kf and n can be determined experimentally. The results indicate a good fit with the Freundlich model ($R^2 = 0.9374$), confirming its suitability for describing the adsorption process. This suggests a heterogeneous adsorbent surface with sites of varying energies. The adsorption intensity was found equal to n = 1.516. Table 2 falls within the favorable range (1–10), indicating strong interaction between MB molecules and the adsorbent surface. The adsorption capacity (Kf = 6.320 mg/g) is moderate, likely due to a limited number of active sites, low surface porosity, and possible pore blockage by natural impurities in the raw material [29].

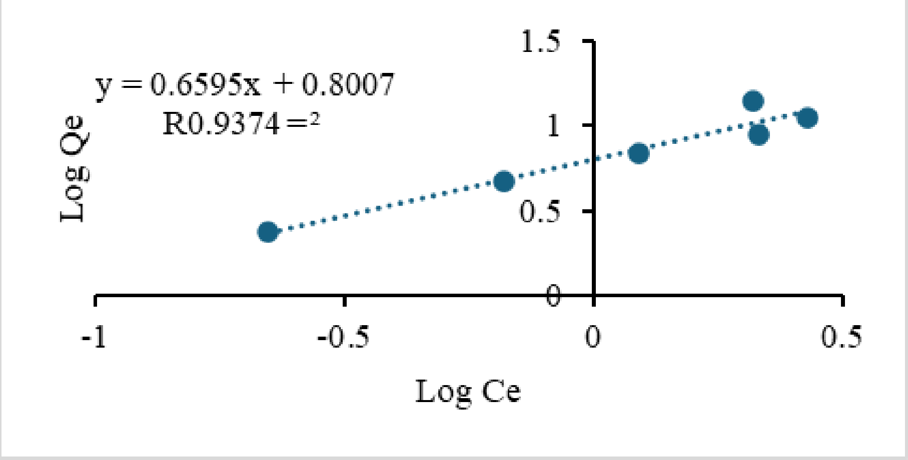


Figure 9: Freundlich Isotherm Model

Table 2: The comparison between both thermal conditions of all of the studiet sample.

Langmuir Isotherm				**Freundlich Isotherm**		
R^2	Q_{max}	K_L	R_L	R^2	N	K_f
0.9742	15.06	0.826	0.195 – 0.039	0.9374	1.516	6.32

6. **Adsorption kinetic**

- **Pseudo-first-order kinetic model**

The pseudo-first-order kinetic model for the adsorption of the MB dye onto the adsorbent is presented in Figure (10) and the results indicate that the relationship between the natural logarithm of the difference between the adsorption capacity at equilibrium and the amount adsorbed at a given time versus contact time does not exhibit a clear linear behavior according to the pseudo-first-order model [30]. The linear equation is expressed as ($y = 0.0111x - 1.1885$) with a very low coefficient ($R^2 = 0.0065$). This extremely low value strongly confirms the poor applicability of the model to the experimental data indicating conclusively that the pseudo-first-order kinetic model is not suitable for describing the adsorption behavior of the dye. This pronounced deviation from linearity suggests that the adsorption dynamics cannot be characterized by a straightforward single-site physisorption model due to its inherent complexity in nature and may follow a higher-order kinetic model or governed by multiple mechanisms such as intraparticle diffusion [31].

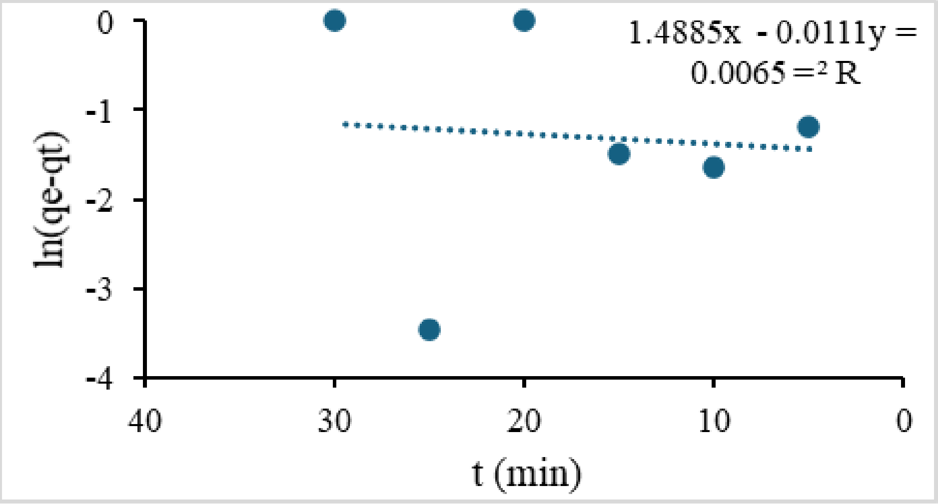


Figure 10: Pseudo first order kinetic model for the adsorption of dye

- Pseudo second order kinetic model for the adsorption of MB dye

The adsorbent exhibits a remarkable adsorption performance in the removal of MB dye from aqueous solutions. Kinetic analysis, as illustrated in Figure (11), indicated a high compatibility of the adsorption process with the pseudo-second-order kinetic model, validated by an outstanding determination coefficient (R2 = 0.9998), indicating an almost perfect fit between the experimental data and the applied mathematical model [32]. Furthermore, the pseudo-second-order rate constant (k_2) was determined to be 0.335 g/mg min, reflecting a relatively high adsorption rate. Suggesting a rapid response of the active sites on the adsorbent surface toward binding dye molecules, thereby enhancing the overall kinetic efficiency of the adsorption process, which is consistent with recent findings reported in the literature [33]. Table 3 shows the summary of the kinetic model constants for the adsorption of MB dye.

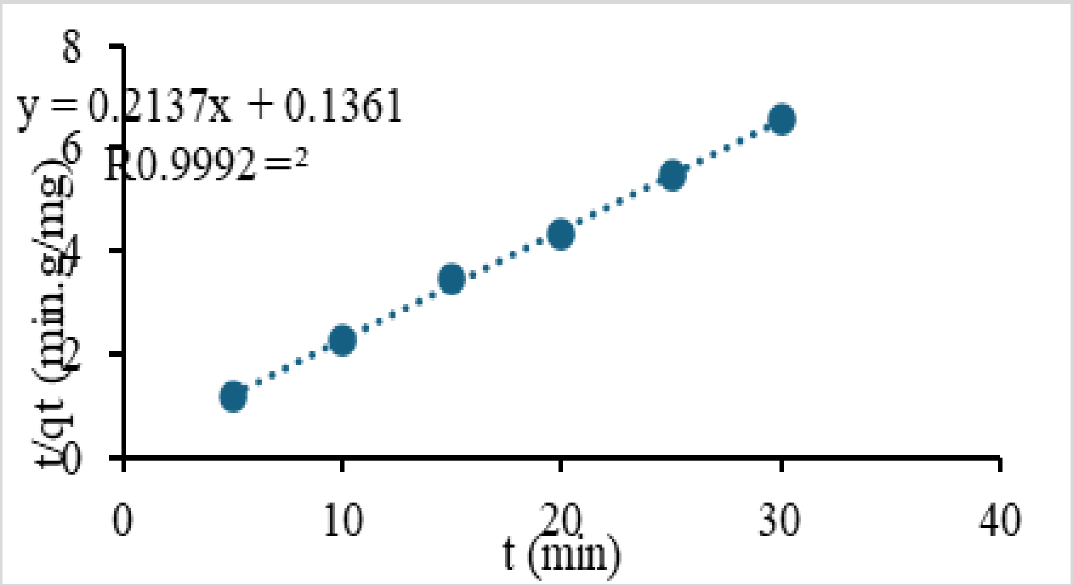


Figure 11: Pseudo second order kinetic model for dye adsorption by MV leaves.

Table 3: Summary of the kinetic model constants for the adsorption of MB dye.

Models		Sample
Types	Constants	
Pseudo first order kinetic model	K1 (min-1)	0.0111
	qe (mg.g-1)	0.2257
	R2	0.0065
Pseudo second order kinetic model	K2 (g. min-1. mg-1)	0.335
	qe (mg.g-1)	4.679
	R2	0.9992

Thermodynamic Study:-

All calculated Gibbs free energy change (ΔG°) values were negative (Table 4), indicating that the adsorption process is spontaneous at all the studied temperatures. From a thermodynamic perspective, since both the enthalpy change (ΔH°) and the entropy change (ΔS°) are positive, the process becomes thermodynamically favorable only when the T ΔS° term exceeds ΔH°, i.e., at higher temperatures. The enthalpy change (ΔH°) was found to be 16.45 $kJ\cdot mol^{-1}$. Furthermore, ΔG° became more negative with increasing temperature, demonstrating that the spontaneity of the adsorption process is enhanced at elevated temperatures. Similar thermodynamic behavior, characterized by negative ΔG° values and positive ΔH° and ΔS° values indicating a spontaneous and endothermic adsorption process (Figure 13). Similarly, as reported for MB adsorption onto rice husk [34].

Table 4: Thermodynamic parameters for the adsorption of MB dye.

T (oC)	T (K)	ΔH°	ΔS°	ΔG°
15	288.15	16.4559	70.54678	-3.87216
20	293.15	16.4559	70.54678	-4.22489
25	298.15	16.4559	70.54678	-4.57762

30	303.15	16.4559	70.54678	-4.93036
35	308.15	16.4559	70.54678	-5.28309
40	313.15	16.4559	70.54678	-5.63583

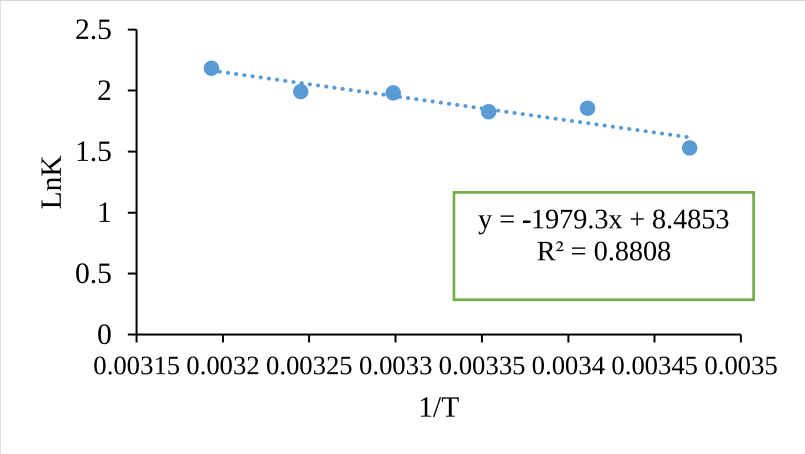


Figure 13 Thermodynamic Study for the adsorption of MB dye.

Conclusion

The results of this study indicate that Marrubium vulgare (Rubia leaf) powder is a highly effective biosorbent and an environmentally friendly and efficient substitute for eliminating organic dyes from liquid phases. The material demonstrated significant performance under neutral conditions, which helped to eliminate the need for preliminary chemical treatments and decreasing the operational expenses of the water treatment processes. From a modeling point of view, the analysis showed that the adsorption process is consistent with the monolayer model on a homogeneous surface, which implies a uniform adsorption process with active sites having the same energy. Statistically, the data confirmed the better fitting of this model compared to other isotherm models, thus improving the physicochemical interpretation of the adsorption process. The thermodynamic results indicate that the adsorption process is spontaneous and endothermic in nature and take place with increased efficiency at high temperature. Such behavior suggests that the process is controlled by strong interaction forces, which are probably electrostatic in nature owing to the electrostatic attraction between cationic dye molecules and the active functional groups on the adsorbent's surface. The present study, therefore, highlights the promising potential of raw plant-based wastes as low-cost and environment-friendly adsorbents for the development of efficient water treatment systems, which are able to remove pollutants even at low concentrations, thus supporting the advancement of sustainable environmental technologies in industrial applications.

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