

Adsorption of methylene blue onto gulmohar plant leaf powder: Equilibrium, kinetic, and thermodynamic analysis

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Abstract

Batch adsorption of methylene blue onto gulmohar plant leaf powder (GUL) was investigated. The effects of pH, initial dye concentration, particle size, dosage, agitation speed, and temperature were studied. Langmuir and Freundlich isotherm models were used to test the equilibrium data. The linear regression coefficient R^2 and non-linear regression coefficient χ^2 were used to elucidate the best fitting isotherm model. The Langmuir isotherm was found to be the best fitting isotherm model. The monolayer adsorption capacities of GUL were found to be 120, 178, and 253 mg/g at temperatures of 293, 303, and 313 K, respectively. The pseudo-second order model best fits the adsorption kinetics. The multi-linearity obtained in the intra-particle diffusion plot showed that both external diffusion and internal diffusion resistances are important in controlling the overall adsorption rate. Gibb's free energy values obtained confirmed that the process was feasible and spontaneous ($\Delta G = -24.44, -23.90, \text{ and } -22.75 \text{ kJ/mol}$). The value of ΔH (-49.12 kJ/mol) indicated that an exothermic chemisorption had taken place. The value of ΔS (-0.084 kJ/mol) suggested that the randomness decreased after adsorption. High values of q_m indicate that GUL can be a potential substitute for activated carbon.

Keywords: Gulmohar, methylene blue, adsorption, isotherm, kinetics.

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1. Introduction

Dyes are used by plastic, paper, tannery, textile, and many other industries to color their end products. A significant portion of the dyes remains unconsumed and, therefore, let out in the effluent. The presence of dyes in aqueous effluents poses a serious ecological threat. It reduces light penetration in water bodies and interferes with metabolic activities of aquatic life.¹ Dyes are mostly resistant to biodegradation and therefore are not removed by conventional treatment techniques. Many dyes and/or their metabolites are known to have carcinogenic, mutagenic, and teratogenic effects on aquatic life and humans.² Therefore, it is essential to treat effluents before letting them out. The biological and physical/chemical methods available for the removal of dyes from aqueous effluents include anaerobic/aerobic treatment, coagulation, flocculation, oxidation, ozonation, membrane separation, and adsorption. Among these methods, adsorption has been proven to be more efficient, offering advantages over

conventional processes.^{3,4} Though activated carbon has been widely used as an adsorbent for the removal of a wide range of organic molecules and metals, high costs and regeneration difficulties hamper large-scale application of activated carbon.² This has prompted many researchers to study the feasibility of using low cost substances as alternate adsorbents. Because many agro-wastes are either arbitrarily discarded or set on fire, exploitation and utilization of these materials should bring economic and social benefits to mankind.² Materials like neem leaf powder,⁵ bagasse fly ash,⁶ sugarcane dust,⁷ rice husk,⁸ banana pith,⁹ coir pith,¹⁰ orange peel,¹¹ shells of bittim,¹² chemically treated guava leaf powder,¹³ phoenix tree leaves,¹⁴ citrus grandis,¹⁵ unburned carbon,¹⁶ etc., have been studied. Thus, in the present work, adsorption potential of gulmohar plant leaf powder (GUL) was investigated. Gulmohar is a flamboyant flowering tree (*Delonix regia*, *Caesalpinaceae* family). For several weeks in spring and summer it is covered with exuberant clusters of flame-red flowers, 100 to 150 mm across. The delicate, fern-like leaves are composed of small individual leaflets, which fold up at the onset of dusk. Gulmohar grows 10 to 13 m tall, but its elegant wide-spreading

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umbrella-like canopy can be wider than its height. Gulmohar is naturalized in India and is widely cultivated as a street tree.

2. Materials and Methods

Mature gulmohar leaves were washed thoroughly with distilled water to remove dust and other impurities. Washed plant leaves were dried overnight at 343 K in a hot air oven. Dried leaves were then ground in a domestic-mixer-grinder. After grinding, the powder was screened in a sieve shaker. Screened powders were again washed and dried. Different sized GULs were then stored in plastic containers for further use.

Methylene blue (MB, chemical formula: $C_{16}H_{18}N_3SCl$; FW: 319.86 g mol⁻¹, λ_{max} = 662 nm, class: thiazine, C.I. Classification Number: 52015) is the most important basic dye. It dissociated into methylene blue cation and chloride anion. Dissociated MB is preferentially adsorbed onto many solids. For this reason, MB was used in the present study. The MB dye was obtained from Ranbaxy Laboratories Limited (India) and used without further purification. The dye is not regarded as acutely toxic, but it can have various harmful effects. On inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, diarrhea, and gastritis.⁵ Stock solution was prepared by dissolving the required amount of dye in double distilled water, which was later diluted to required concentrations. All the solutions were prepared in double distilled water. Solution pH was adjusted by adding either 0.1 N HCl or 10% Na₂CO₃ as required. The batch adsorption experiments were carried out by varying initial pH, initial dye concentrations, temperature, adsorbent dosage, particle size, and agitation speed. For each run, accurately weighed GUL was added to 100 cm³ of aqueous dye solution taken in a 250 cm³ conical flask and the mixture was agitated in an incubated shaker at constant RPM and temperature. Samples were withdrawn at regular time intervals using a fine tip syringe to minimize carryover of adsorbent particles with the sample. Samples were immediately centrifuged (Remi Research centrifuge) to separate remaining adsorbent particles. Concentrations of the dye solutions were determined by measuring the absorbance of the solution at the characteristic wavelength (λ_{max} = 662 nm) of MB using a double beam UV-Vis. spectrophotometer (Systronics 2201). Samples were diluted if the absorbance exceeded 0.8. Final concentration was then determined from the calibration curve already prepared.

2.1. Equilibrium isotherms

Equilibrium data commonly known as adsorption isotherms are basic requirements for the design of adsorption systems. Langmuir and Freundlich isotherms were used to describe the equilibrium characteristics of adsorption in the present study. The Langmuir isotherm¹⁷

basically assumes homogenous surface energy distribution. The Langmuir isotherm assumes that the adsorption rate is proportional to the number of vacant sites on the adsorbent and fluid phase concentration, while the desorption rate is proportional to the number of sites covered with adsorbate molecules. Thus, at dynamic equilibrium the dye concentration in the solid phase can be expressed as:

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \quad (1)$$

Where:

q_e = equilibrium dye concentration in the solid phase, mg g⁻¹

q_m = maximum monolayer dye concentration in the solid phase, mg g⁻¹

C_e = equilibrium dye concentration in the aqueous phase, mg dm⁻³

K_L = Langmuir equilibrium constant, mg⁻¹ dm³

Eq. (1) can then be rearranged into linear form as follows:

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \quad (2)$$

By plotting $1/q_e$ versus $1/C_e$, the Langmuir constants q_m and K_L can be obtained. The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless separation parameter, which is defined as:

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

R_L indicates the nature of adsorption. Adsorption is favorable when the value of R_L is between 0 and 1.¹⁸ Another adsorption isotherm commonly used for liquid phase adsorption on a surface having heterogeneous energy distribution is the Freundlich isotherm.¹⁹ It is expressed as follows:

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

K_F and n are indicators of adsorption capacity and adsorption intensity, respectively.²⁰ Rearranging Eq. (4) we get:

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

A plot of $\ln q_e$ vs. $\ln C_e$ yields a straight line. From the slope and intercept of the plot, n and K_F can be estimated.

The value of the Freundlich constant (n) should lie in the range of 1 to 10 for favorable adsorption.

An accurate isotherm is important for design purposes. Linear regression is commonly used to determine the best fitting model and to determine isotherm constants;¹⁶ however, linearization of a non-linear model leads to different axial settings and hence influences the determination process. To overcome this problem, the non-linear Chi-square (χ^2) test had been proposed as an alternate method of determination.^{21, 22} Thus, in the present study both R^2 and χ^2 were used to identify the best fitting isotherm model.

2.2. Adsorption kinetic studies

The transient behavior of the dye sorption process is commonly analyzed using pseudo-first order,²³ pseudo-second order,²⁴⁻²⁷ and intra-particle diffusion models.²⁸ However, the pseudo-first order model could not explain the adsorption of MB onto GUL. Therefore, in the present paper only the pseudo-second order and intra-particle diffusion models are discussed.

2.3. Pseudo-second order model

Ho's most widely used pseudo-second order kinetic model²⁴⁻²⁷ is expressed in its linear form as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

Where:

t = time, min

q_t = dye concentration in the solid phase at time t, mg g⁻¹

K_2 = pseudo-second order rate constant, g mg⁻¹ min⁻¹

Values of q_e and K_2 can be obtained from the slope and intercept of the plot t/q_t vs. t.

2.4. Intra-particle diffusion

Weber & Morris proposed the intra-particle diffusion model to explain the transient behavior of dye adsorption. Accordingly, if a plot of dye uptake versus $t^{0.5}$ is a straight line passing through the origin, then the effect of external film resistance is negligible. On the other hand, if the intercept deviates from the origin, this shows the importance of the external film resistance. The value y-intercept is a qualitative measure of film thickness. A multi-linearity of the Weber plot is an indication of the presence of different size pores (micro-, meso-, and nano-pores) in the adsorbent.

2.5. Thermodynamic analysis

The Langmuir isotherm constant, K_L , was used to estimate the thermodynamic parameters Gibbs free energy (ΔG), change in enthalpy (ΔH), and change in entropy (ΔS). Negative ΔG indicates the spontaneity of the

adsorption process. ΔH is used to identify the exothermic or endothermic nature of adsorption. A positive value of ΔS indicates increased randomness of adsorbate molecules on the solid surface than in the solution.

The free energy of adsorption (ΔG) can be related with the Langmuir adsorption constant⁶ by the following expression:

$$\Delta G = -RT \ln K_L \quad (7)$$

Also, enthalpy and entropy changes are related to the Langmuir equilibrium constant by the following expression:⁶

$$\ln K_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (8)$$

Thus, a plot of $\ln K_L$ vs. $1/T$ should be a straight line. ΔH and ΔS values could be obtained from the slope and intercept of this plot.

3. Results and Discussion

3.1. Effect of initial pH

Initial pH is an important factor that affects adsorption. Effect of pH on adsorption of MB onto GUL was analyzed over a pH range from 2.4 to 9.0. Dye uptake was found to increase with increase in initial solution pH. When the solution initial pH was increased from 2.4 to 9.0, dye uptake increased from 13.78 to 43.75 mg/g. It was evident that dye uptake was significantly affected by the solution pH. This behavior could be explained with reference to the zero point charge of the material. Zero point charge of a material is the solution pH at which the adsorbent exhibits a net zero surface charge in the absence of any specific adsorption. In the present study, zero point charge was determined by using the powder addition method.²⁹ pH_{zpc} was found to be 7.5 (Figure 1).

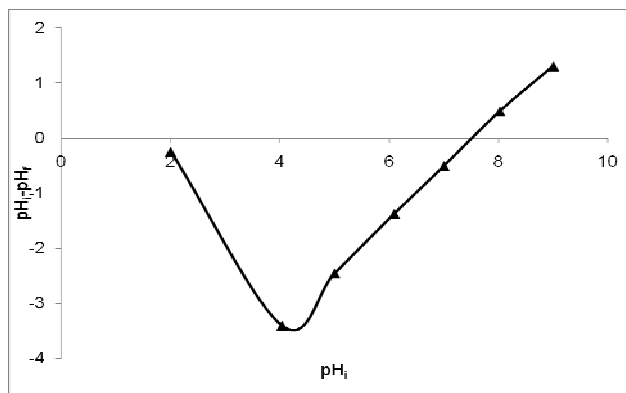


Figure 1. pH_{zpc} of GUL. (Powder addition method)

Thus, at a pH below 7.5 (pH_{zpc}), sorbent surface was likely to have a net positive charge and, therefore, adsorption of cationic dye was low. On the other hand, when solution pH was greater than 7.5, the adsorbent surface was likely to have a net negative charge which favored adsorption of cationic dyes. Similar trends were observed by Kumar and Porkodi (2007),²⁹ Bulut and Aydin (2006),³⁰ and Kumar and Kumaran (2005)³¹ during adsorption of MB on different adsorbents. Since the optimum pH was close to the natural solution pH, for further studies pH was not adjusted.

The transient behavior of adsorption could be well explained by second order kinetic model ($R^2 > 0.92$). Second order rate constants and maximum specific uptakes predicted by Ho's pseudo second order model at different initial pH values are presented in Table 1.

pH	K_2 , $\text{g mg}^{-1} \text{ min}^{-1}$	$q_{m, \text{pre}}$, mg g^{-1}	$q_{m, \text{exp}}$, mg g^{-1}	R^2
2.40	0.000700	20.481	13.78	0.9222
4.00	0.001773	39.323	37.98	0.9551
6.00	0.002332	45.130	42.55	0.9957
8.00	0.002150	46.019	42.70	0.9958
9.00	0.003589	45.548	43.75	0.9984

3.2. Effect of initial concentration

The effect of initial dye concentration on adsorption of MB onto GUL is illustrated in Figures 2 to 4.

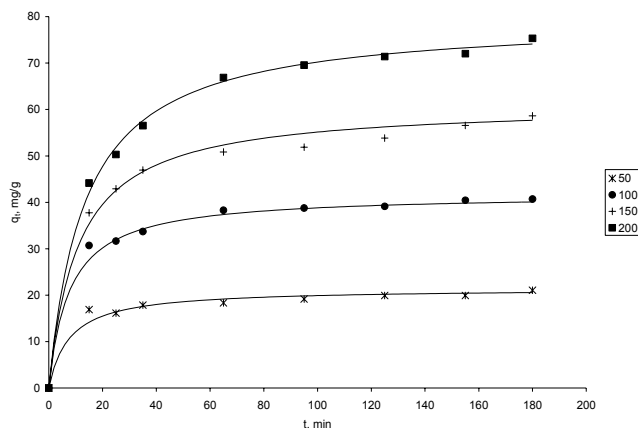


Figure 2. Effect of initial concentration on adsorption of MB onto GUL. (Particle size = 125 μm ; RPM = 150; $T = 303 \text{ K}$; $C_0 = 50$ to 200 mg/L ; $D = 2 \text{ g/L}$)

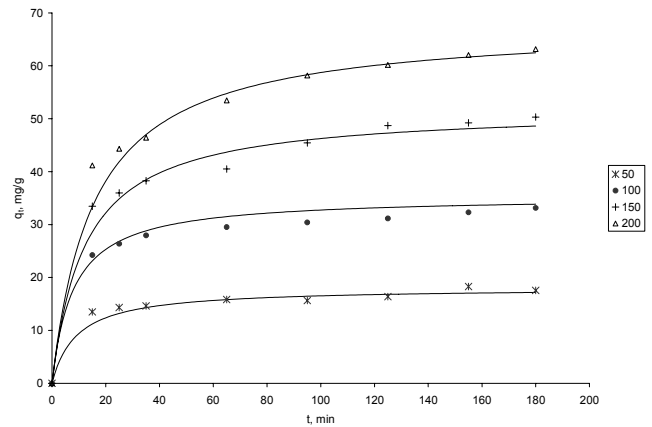


Figure 3. Effect of initial concentration on adsorption of MB onto GUL. (Particle size = 125 μm ; RPM = 150; $T = 313 \text{ K}$; $C_0 = 50$ to 200 mg/L ; $D = 2 \text{ g/L}$)

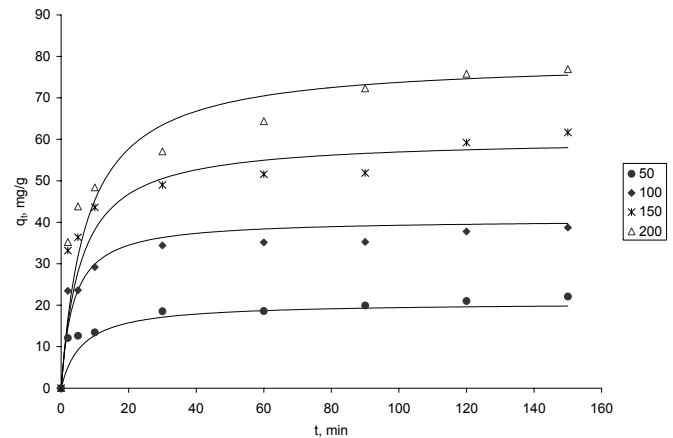


Figure 4. Effect of initial concentration on adsorption of MB onto GUL. (Particle size = 125 μm ; RPM = 150; $T = 323 \text{ K}$; $C_0 = 50$ to 200 mg/L ; $D = 2 \text{ g/L}$)

The pseudo-second order model fits the data well ($R^2 > 0.99$). Values of pseudo-second order kinetic parameters, K_2 & q_e , along with coefficients of determination are given in Table 2. K_2 decreased with increase in initial concentration, while q_e increased with increase in concentration. The dependencies of K_2 and q_e with C_0 can be expressed by the following correlations:

$$K_2 = \frac{C_0}{aC_0^2 + bC_0 + c} \quad (9)$$

$$q_e = \frac{C_0}{a' + b'C_0} \quad (10)$$

T, K	C ₀ , mg/g	Pseudo-second order model			Intra-particle diffusion model		
		K ₂ , g mg ⁻¹ min ⁻¹	q _{e,pre} , mg/g	R ²	K _i , mg g ⁻¹ min ^{-0.5}	I, mg g ⁻¹	R ²
303	50	0.0061	21.33	0.9973	0.45	14.73	0.930
303	100	0.0031	42.21	0.9995	1.87	22.89	0.975
303	150	0.0014	60.70	0.9972	3.06	27.13	0.940
303	200	0.0009	79.77	0.9991	5.45	23.33	0.996
313	50	0.0060	18.37	0.9933	0.38	11.97	0.915
313	100	0.0036	33.97	0.9985	1.23	19.99	0.937
313	150	0.0014	53.49	0.9966	1.66	27.55	0.952
313	200	0.0011	67.26	0.9986	2.93	29.60	0.995
323	50	0.0078	22.15	0.9955	1.19	11.14	0.941
323	100	0.0068	38.77	0.9976	2.89	18.79	0.943
323	150	0.0028	61.23	0.9905	3.93	28.46	0.936
323	200	0.0046	68.05	0.9995	5.04	30.64	0.940

Values of the coefficients in these equations determined by non-linear regression are listed in Table 3. High R² (> 0.99) implies that the correlations fit well with the experimental data. By substituting the Eqs. 9 and 10 in Eq. 6, it is possible to predict the kinetics of MB adsorption onto GUL for any unknown initial concentration in the range of 50 to 200 mg/dm³. Figures 2 to 4 illustrate the comparison of the predicted data with the experimental data. Slopes and intercepts of the intra-particle diffusion plots at various concentrations are given in Table 2. It can be observed that the intercept values increase with increase in initial dye concentration of the solution. The greater the intercept value, the higher is the boundary layer thickness. Similar observations were earlier made by Mane et al. (2007).⁶ Thus, it is evident from the observation that the boundary layer effects are predominant at higher initial dye concentration.

T, K	k ₂				q _e		
	A	b	C	R ²	a'	b'	R ²
303	8.851	-849	28545	0.9999	0.0012	2.272	0.9999
313	9.521	-1033	36131	0.9979	0.0012	2.710	0.9983
323	5.808	-705	27135	0.9995	0.0007	2.392	0.9981

3.3. Effect of particle size

Effect of particle size is shown in Figure 5. The effect of particle size on the removal of MB was studied by using four different size particles (40, 125, 230, and 548 μm) keeping all other parameters constant (C₀ = 200 mg/dm³, T = 303 K, agitation speed = 150 RPM, pH = 7, D = 2 g/L). The specific uptake of dye increased from 33.12 to 63.88 mg/g when particle size decreased from 548 to 40 microns.

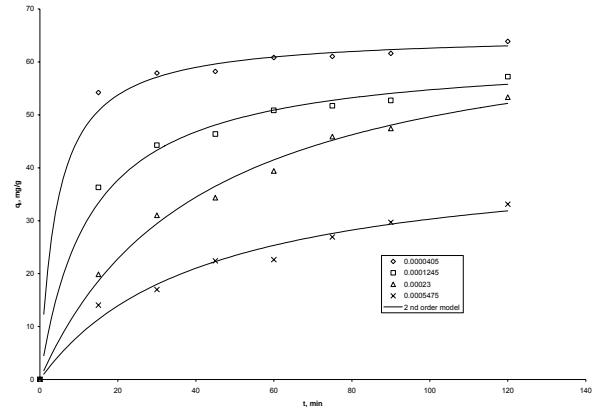


Figure 5. Effect of particle size on adsorption of MB onto GUL. (pH = 7; RPM = 150; T = 303 K; C₀ = 200 mg/L; D = 2 g/L)

An increase in uptake with decreasing particle size can be ascribed to adsorption being limited to the external surface area of the adsorbent, as small particles have a larger external surface area.³² For smaller particles, equilibrium was achieved much more rapidly, while equilibrium was reached slowly with larger particles. This may be due to the fact that dye molecules may take a longer time to reach the adsorption site. The pseudo-second order model explained the kinetics well (R² > 0.96). Second order rate constants and maximum specific uptakes predicted by Ho's pseudo-second order model are presented in Table 4.

d _p , μm	Pseudo-second order model			
	K ₂ , g mg ⁻¹ min ⁻¹	q _{m,pre} , mg g ⁻¹	q _{m,exp} , mg g ⁻¹	R ²
40	0.003566	65.301	63.880	0.9990
125	0.001272	61.703	57.220	0.9960
230	0.000342	70.281	53.345	0.9870
548	0.000559	42.921	33.118	0.9599

Second order rate constant decreased with increase in size. These observations are in agreement with those of Qada et al. (2006),³² Ho and McKay (1999),³³ and Poots et al. (1976).³⁴

The following empirical relationships fit the experimental data.

$$q_e = 65.92 - 59535 d_p, R^2 = 99.4 \quad (11)$$

$$\log K_2 = -5.954 - 0.7792 \log d_p, R^2 = 87.7 \quad (12)$$

