



Kinetics of methylene blue removal from aqueous solution using gulmohar (*Delonix regia*) plant leaf powder: Multivariate regression analysis

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ABSTRACT

Effects of process variables namely pH, dye concentration, adsorbent dosage, temperature, particle size and agitation speed on kinetics of methylene blue adsorption onto gulmohar plant leaf powder were investigated. Quadratic models were proposed to predict pseudo second order rate constant and equilibrium uptake in terms of the process variables. Model coefficients were determined by multiple regression analysis. Statistical tools like Student's *t*-test, *F*-test, ANOVA and lack-of-fit were used to define the most important process variables. The proposed models could predict the rate constant and equilibrium dye uptake with high R^2 values (0.94 and 0.947). It was found that rate constant increased with decrease in concentration, decrease in particle size, increase in adsorbent dosage, increase in agitation speed and increase in temperature. Meanwhile, it was found that equilibrium dye uptake increased with increase in concentration and decrease in dosage. Apart from these combined effects of the process variables were established through multiple regression analysis. Langmuir monolayer adsorption capacity of GUL was found to be 186.22 mg/g.

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1. Introduction

In order to satisfy the ever-growing demands in terms of quality, variety, fastness and depth of color etc., the textile industries now predominantly use synthetic dyes. Synthetic dyes or their metabolites are toxic to the aquatic life and may have carcinogenic, teratogenic and/or mutagenic effects on them [1]. Presence of dyes in water bodies reduces photosynthetic activity and primary production. Therefore, removal of dyes from effluent is of prime importance to the environmental engineers. Since most of the synthetic dyes are non-biodegradable, conventional primary and secondary processes are inefficient in removing these contaminants [2].

Among a number of physico-chemical treatments available, adsorption has been proven to be one of the most promising methods for the removal of dyes from aqueous effluents. As conventional adsorbents like activated carbons are quite expensive, identification and development of new adsorbents has gained more importance during last decade [3]. Many solid wastes, that are available in large quantities, have the potential to adsorb pollutants from aqueous effluents. Thus, exploitation of these solid wastes for the removal

of dyes from effluents will be beneficial to the mankind. Materials like bagasse fly ash [4,5], banana pith [6], orange peel [7], neem leaf powder [8], Brazilian pine-fruit shell [9], phoenix tree leaves [10], untreated guava leaf powder [11,12], pineapple stem waste [13], palm ash [14], sun flower seed hull [15] etc., have been studied.

In the present study a new adsorbent gulmohar plant leaf powder was investigated for its adsorption potential. Most of the previous work on adsorption concentrates on effects of individual process variable like pH, dye concentration, adsorbent dosage, agitation speed, particle size and temperature. However, it is quite possible that these variables can have combined effects on adsorption process. Hence, in the present work, combined effect of the process variables on the adsorption had been investigated using multiple regression analysis.

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 [10]. It is a dark green powder or crystalline solid. It is widely used as a stain and has a number of biological uses. It dissociates in aqueous solution like electrolytes. The adsorbate methylene blue was chosen as a model dye because of its well-known adsorption characteristics. MB is not regarded as acutely toxic, but it can have various harmful effects [12]. MB is a known teratogen that results in intestinal atresia when injected intra-amniotically [16]. Methylene blue may also result in hemolytic anemia, hyperbilirubinemia, and acute renal failure [17].

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Nomenclature

C_e, C_t	dye concentration at equilibrium and at time t (mg/dm^3)
D	particle dosage (g/dm^3)
d_p	particle size (μm)
K_2	pseudo second order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$)
$K_{2\text{mol}}$	pseudo second order rate constant ($\text{g mol}^{-1} \text{min}^{-1}$)
K_L	Langmuir equilibrium constant (dm^3/mg)
K_F	Freundlich equilibrium constant ($\text{mg}/\text{g})(\text{dm}^3/\text{mg})^{1/n}$
n	Freundlich isotherm parameter
q_e	equilibrium dye uptake (mg/g)
q_m	maximum monolayer dye concentration in the solid phase (mg/g)
q_t	dye uptake (mg/g)
RPS	agitation speed (s^{-1})
t	time of contact (min)
T	temperature (K)
$x,$	process variable (coded units, –)
X	process variable (un-coded units)
Y	response variable (coded, –)
β_i, β_{ij}	regression coefficients

2. Materials and methods

2.1. Adsorbate

Methylene blue was obtained from Himedia India Limited, and was used without further purification. Required amount of dye was dissolved in double distilled water to prepare $1000 \text{ mg}/\text{dm}^3$ stock solution which was later diluted to required concentrations.

2.2. Adsorbent

Gulmohar is a flamboyant tree in flower (*Delonix regia*). The delicate, fern-like leaves are composed of small individual leaflets, which fold up at the onset of dusk. Gulmohar gets 10–13 m tall. Gulmohar is naturalized in India and is widely cultivated as a street tree. Fallen gulmohar plant leaves were collected from the university garden and thoroughly washed with raw water to remove impurities. Leaves were washed with distilled water again and dried in a hot air oven at 70°C till they become crisp. The dried leaves were first hand crushed and then ground in a domestic mixer-grinder. Ground gulmohar plant leaf powders (GUL) were size separated using rotary sieve shakers and stored in plastic containers.

Since the plant leaves have porous structure they can effectively adsorb dye molecules. The functional groups on the leaf surface can attract ionic dye molecules of opposite charge which lead to increase in dye removal efficiency. Infrared spectra of the biomass sample were obtained using a Fourier transform infrared spectrometer (PerkinElmer Spectrum RX1). The sample, prepared as KBr disc, was examined within the range $400\text{--}4000 \text{ cm}^{-1}$ to identify the functional groups responsible for the sorption. FTIR of GUL is shown in Fig. 1. IR spectrum showed a band at 3400 cm^{-1} due to O–H stretching. Bands at 2925 and 2854 cm^{-1} are due to C–H stretching, and 1630 cm^{-1} is due to C=C stretching. Peaks at 700 , 1080 and 1235 cm^{-1} showed possible presence of halo compound. Another peak at 1390 cm^{-1} indicated the presence of phenolic group. IR spectra also indicated the absence of C=O group. Thus, it is inferred from IR spectrum that adsorbent contains hydrocarbon having hydroxyl groups. Therefore it is predicted that the functional groups that are responsible for the electrostatic attraction of MB cations onto GUL is $-\text{OH}^{-1}$ and halo groups.

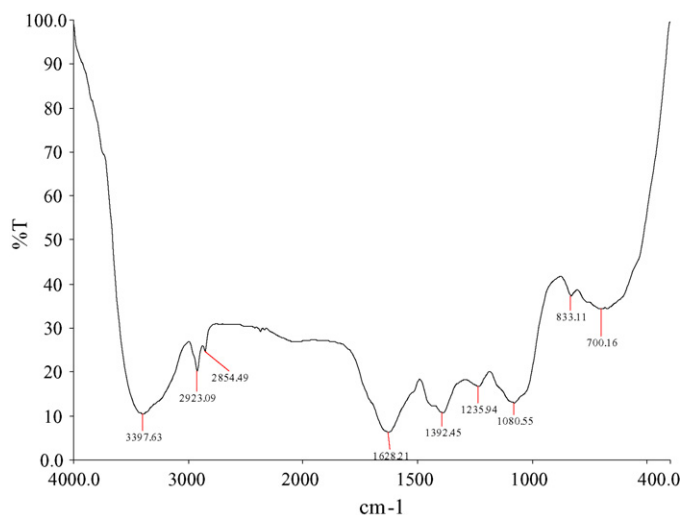


Fig. 1. FTIR spectrum of GUL.

pH zero point charge (pH_{zpc}) of the adsorbent was determined by powder addition method described by Kumar and Porkodi [18]. 0.5 g of GUL was added to 100 cm^3 conical flask containing 50 cm^3 of 0.1 M NaCl solution. The electrolyte solution with the GUL was equilibrated for 24 h. After equilibration the final pH (pH_f) was recorded. Several batches were carried out with different initial solution pH (pH_i). The pH was adjusted using 0.1 M HCl and 0.1 M NaOH solution. Change in solution pH ($\Delta\text{pH} = \text{pH}_i - \text{pH}_f$), was recorded for each solution and a plot of ΔpH versus initial pH was prepared. The pH at which ΔpH becomes zero is called pH_{zpc} .

Moisture content, fixed carbon, volatile matter and ash content were determined by proximate analysis. About 1 g of GUL sample weighed accurately and taken in a crucible was dried in hot air oven at $105 \pm 5^\circ\text{C}$ for 1 h. The loss of weight on drying was reported as percentage moisture content. The remaining sample was placed (covered with lid) in a muffle furnace and heated at $925 \pm 20^\circ\text{C}$ for 7 min. The loss in weight was reported as volatile matter. The residue was again heated (without lid) at $700 \pm 50^\circ\text{C}$ for 30 min. The loss in weight was reported as ash. The fixed carbon was then determined by calculating the difference. Bulk density was calculated by weighing 100 cm^3 (untapped) of sample. Proximate analysis and density measurement was carried out thrice and the average values had been reported in Table 1.

2.3. Batch kinetic studies

The adsorption potential of the GUL was investigated by conducting a series of batch kinetic studies. The effects of important parameters such as pH (2–9), initial dye concentration ($50\text{--}200 \text{ mg}/\text{dm}^3$), adsorbent dose ($0.5\text{--}2.5 \text{ g}/\text{dm}^3$), particle size ($40\text{--}530 \mu\text{m}$), agitation speed ($50\text{--}200 \text{ RPM}$), and temperatures ($303\text{--}323 \text{ K}$) that are known to affect the adsorption process were studied. To 100 cm^3 of MB solution of desired concentration taken in 500 cm^3 conical flask, required amount of GUL was added. The mixture was agitated in a rotary shaker for at least two hours. Liquid

Table 1
Physical and chemical properties of GUL.

Moisture content (%)	4.9
Volatile matter (%)	85.5
Ash (%)	7.8
Fixed carbon (%)	1.8
Bulk density (kg/m^3)	418.0
pH_{zpc}	7.5

samples for concentration measurements were withdrawn from the mixture at regular time intervals. Fine tip syringes were used to draw the samples to avoid/minimize carryover of adsorbent particles with the test sample. Samples were immediately centrifuged. Concentration of MB in the aqueous phase was determined by measuring the optical density of the supernatant solution using a double beam UV–vis. Spectrophotometer (Systronics 2201) at the characteristic wavelength ($\lambda_{\max} = 662 \text{ nm}$) of MB. If the absorbance was greater than 1.0 the sample solution was suitably diluted before measuring the absorbance.

2.3.1. Kinetic models

Adsorption of dyes onto agro-wastes mostly follows either pseudo first order [19] or pseudo second order model [20–22]. However, since pseudo first order model could not fit the kinetic data well in the present study it is not discussed here. Ho's pseudo second order kinetic model explained the kinetic data well. The linearized form of the pseudo second order kinetic model is given below:

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

By plotting t/q_t versus t , equilibrium uptake and pseudo second order rate constant can be determined.

2.4. Equilibrium studies

Equilibrium data commonly known as adsorption isotherms are basic requirements for the design of adsorption systems. 100 cm^3 of MB solutions of various concentrations ($C_0 = 10\text{--}400 \text{ mg/dm}^3$) were taken in 500 cm^3 flasks. One gram each GUL was added to the solution and the mixtures were agitated in incubated rotary

shakers (pH 7, RPM = 150, $T = 303 \text{ K}$, particle size = $125 \mu\text{m}$) for 24 h to ensure equilibrium. Langmuir [23] and Freundlich [24] isotherms were used to describe the equilibrium.

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

$$\text{Freundlich isotherm : } q_e = K_F C^{1/n} \quad (3)$$

Values of Langmuir and Freundlich isotherm parameters were determined by non-linear regression using Excel-solver. Chi square and R^2 values were employed to find out optimum isotherm.

3. Results and discussion

3.1. Effect of pH

One of the important factors that affect adsorption is pH. The effect of pH on adsorption of MB onto GUL was studied by varying pH from 2.4 to 9. Adsorption of MB onto GUL followed pseudo second order kinetics and the parameters are shown in Table 2. Dye uptake increased with increase in solution pH. The influence of the solution pH on the dye uptake could be explained on the basis of pH zero point charge (pH_{zpc}). An amphoteric molecule contains both positive and negative charges depending on the functional groups present in the molecule. The net surface charge of such molecules is influenced by the pH of their surrounding environment. By either loosing or gaining protons (H^+) they can become more negatively or more positively charged. The value of the pH at which the net charge on a solid surface becomes zero, in the absence of specific sorption, is called the zero point charge. In Fig. 2 plots of ΔpH ($\text{pH}_i - \text{pH}_f$) versus pH_i , and pH_f versus pH_i are shown. From the figure pH_{zpc} of GUL was found to be 7.5 [18,25]. As already mentioned in Section 2.2 when solution

Table 2
Pseudo second order kinetic parameters for the adsorption of MB onto GUL.

T (K)	C_0 (mg/dm ³)	D (g/dm ³)	d_p (μm)	RPM	pH	k_2 (g mg ⁻¹ min ⁻¹)	$q_{m,\text{pre}}$ (mg/g)	R^2
303	100	2.0	125	150	2.40	0.00070	20.48	0.9222
					4.00	0.00177	39.32	0.9551
					6.00	0.00233	45.13	0.9957
					8.00	0.00215	46.02	0.9958
					9.00	0.00359	45.55	0.9984
303	50	2.0	125	200	7.50	0.0061	21.33	0.9973
					100	0.0031	42.21	0.9995
					150	0.0014	60.70	0.9972
					200	0.0009	79.77	0.9991
313	50	2.0	125	200	7.50	0.0060	18.37	0.9933
					100	0.0036	33.97	0.9985
					150	0.0014	53.49	0.9966
					200	0.0011	67.26	0.9986
323	50	2.0	125	200	7.50	0.0078	22.15	0.9955
					100	0.0068	38.77	0.9976
					150	0.0028	61.23	0.9905
					200	0.0046	68.05	0.9995
303	100	0.50	125	200	7.50	0.00077	132.40	0.991
		1.00				0.00191	73.58	0.993
		1.50				0.00242	54.51	0.997
		2.00				0.00540	42.91	0.996
		2.50				0.00822	34.76	0.999
303	200	2.0	40	150	7.00	0.00357	65.30	0.9990
			125			0.00127	61.70	0.9960
			230			0.00088	52.14	0.9967
			548			0.00056	42.92	0.9599
303	200	2.0	125	50	7.00	0.000775	68.85	0.9835
				100		0.001210	64.18	0.9945
				150		0.001272	61.70	0.9960
				200		0.001518	65.57	0.9973

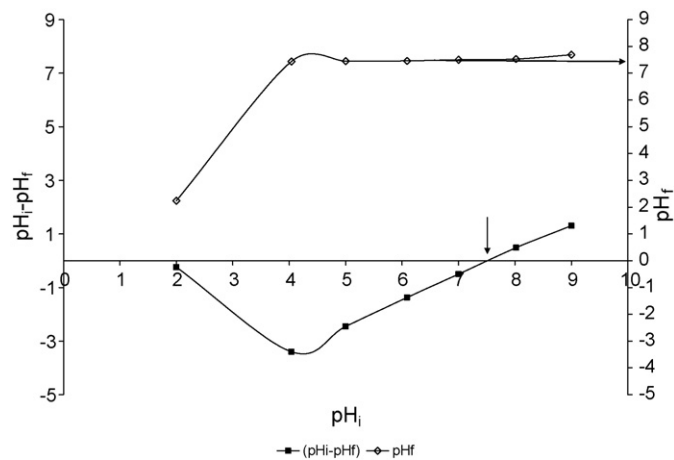


Fig. 2. pH_{zpc} of GUL.

$pH > pH_{zpc}$ ($=7.5$) the surface of the adsorbent gets more negatively charged by losing protons and therefore favors uptake of cationic dyes due to increased electrostatic force of attraction. Thus, MB adsorption onto GUL was favored at solution pH higher than 7.5 (pH_{zpc}). Meanwhile, at lower pH ($pH < pH_{zpc}$), the adsorbent surfaces become more positively charged by gaining protons. Therefore, dye cations were repelled and hence the equilibrium uptake was low. FTIR shown in Fig. 1 suggest that the adsorption of MB onto GUL may be due to electrostatic attraction between cationic dye molecules and negatively charged functional groups present on the surface of the adsorbents. Since the MB solution pH was close to 7.5, pH correction was not necessary for further experiments.

3.2. Effect of initial dye concentration

Initial dye concentration is one of the important factors that affect adsorption kinetics. Adsorption of MB onto GUL was, therefore, studied at different initial dye concentrations (50, 100, 150 and 200 mg/dm^3) at 303, 313 and 323 K in order to investigate the effects of initial dye concentration. Each 0.2 g of adsorbent (GUL) was added to 100 cm^3 of MB solutions ($C_0 = 50, 100, 150,$ and 200 mg/dm^3) taken in 500 cm^3 conical flask. Pseudo second order model fits the kinetic data well ($R^2 > 0.99$). Values of pseudo second order kinetic parameters K_2 and q_e along with coefficients of determination are given in Table 2. Increase in concentration enhances the interaction between the dye and adsorbent apart from providing necessary driving force to overcome the resistances to mass transfer of dye. Therefore, rate of adsorption and hence dye uptake increased with increase in dye concentration. The present findings were in good agreement with the earlier reports. Similar trends for q_e had been reported by Mane et al., [4], Ho and McKay [22], Hameed et al. [26], Ofomaja and Ho [27], Kumar and Porkodi [18], Vadivelan and Kumar [28] etc.

Values of K_2 were shown to decrease with the increase in concentration by the previous researchers for many dye adsorption systems. For example, adsorption of brilliant green onto bagasse flyash [4], adsorption of MB onto activated carbon produced from rattan sawdust [26] adsorption of Basic Blue 3 onto activated carbon prepared from rubber (*Hevea brasiliensis*) seed coat [29], adsorption of methyl violet onto sunflower (*Helianthus annuus* L.) seed hull (SSH) [15], adsorption of Basic Blue 69 onto Sphagnum moss peat [22], adsorption of MB onto nitric acid treated water-hyacinth [30] etc. Present findings are in good agreement with these observations. However, increasing trend of K_2 with increase in concentration had also been reported earlier for certain adsorption systems. Alkan et al. [31] had observed such a trend of K_2 while studying adsorption

of an anionic dye (reactive blue 221, RB221) onto sepiolite. Vadivelan and Kumar [28], Porkodi and Kumar [32] had also reported similar increasing trend for K_2 .

3.3. Effect of adsorbent dosage

The effect of adsorbent dosage on the removal of MB was studied for an initial dye concentration of 100 mg/dm^3 , by varying the dosage from 0.5 to 2.5 g/dm^3 , keeping all other parameters constant (30 °C, 125 μm , 200 RPM, pH 7.5). Second order rate constants and equilibrium dye uptakes predicted by Ho's second order model are presented in Table 2. Percentage dye removal increased with increase in dosage. Higher uptake was obtained when the dosage was low. Specific dye uptake decreased from 132.4 to 34.76 mg/g when the adsorbent dosage was increased from 0.5 to 2.5 g/dm^3 . This is due to the fact that the active sites could be effectively utilized when the dosage was low (i.e., low adsorbent/adsorbate ratio). When the adsorbent dosage is higher (high adsorbent/adsorbate ratio) it is more likely that a significant portion of the available active sites remain uncovered, leading to lower specific uptake. Values of K_2 increased with increase in adsorbent dosage in the present study. The present observations are in good agreement with the previous findings. Bhattacharya and Sharma [8], Yeddou and Bensmaili [33], Ho and Ofomaja [34] etc., had shown similar trends for q_e while studying different adsorbent-adsorbate systems. Yeddou and Bensmaili [33], Ho and Ofomaja [34] had got similar trends for K_2 . However, Ho and McKay [35] observed, while studying adsorption of Basic Red 22 onto bagasse pith, that value of K_2 decreased with increase in adsorbent dosage initially and then increased.

3.4. Effect of particle size

Effect of particle size on adsorption of MB was studied by conducting batch studies with different size particles. Initial dye concentration, solution temperature, agitation speed and adsorbent dosage were maintained at 200 mg/dm^3 , 303 K, 150 RPM and 2 g/dm^3 . Second order rate constant decreased with increase in particle size. Pseudo second order model parameters for adsorption of MB onto GUL are presented in Table 2. The specific dye uptake increased from 42.92 to 65.30 mg/g when particles size was decreased from 548 to 40 μm . Meanwhile, second order rate constant increased from 0.00056 to 0.00357 $g\ mg^{-1}\ min^{-1}$ when particle size was decreased from 548 to 40 μm .

3.5. Effect of agitation speed

Effect of agitation was studied at constant temperature, pH, dosage, initial concentration and particle size (303 K, 7.5, 2 mg/dm^3 , 200 mg/dm^3 and 125 μm). Effects of agitation speed on pseudo second order model parameters for adsorption of MB onto GUL are presented in Table 2. Since equilibrium condition is not affected by the agitation speed, equilibrium dye uptake was nearly constant. However, second order rate constant increased from 0.00078 to 0.00152 $g\ mg^{-1}\ min^{-1}$ when RPM was increased from 50 to 200. This can be attributed to the fact that increase in agitation speed favored the rate by decreasing the mass transfer resistances.

3.6. Equilibrium analysis

Fig. 3 shows the comparison of predicted and experimental equilibrium data. Langmuir isotherm was found to best fit the experimental data with low χ^2 and high R^2 values as indicated in Table 3. Monolayer adsorption capacity of GUL was found to be 186.22 mg/g . Table 4 shows the comparison of monolayer capacity

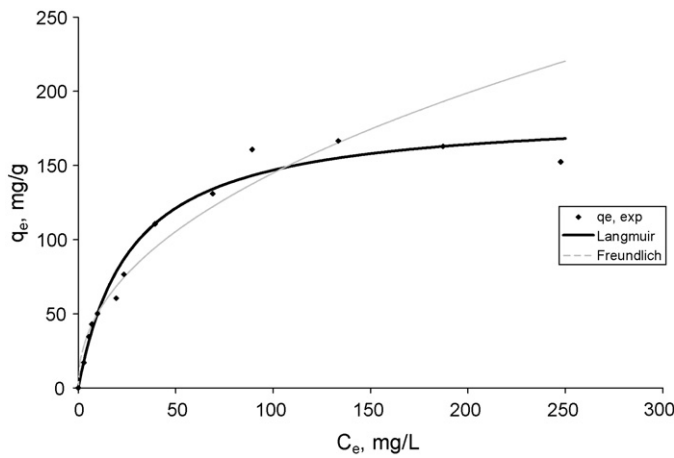


Fig. 3. Equilibrium plot.

Table 3 Isotherm data for adsorption of MB onto GUL.

Langmuir		Freundlich	
K_L ($\text{dm}^3 \text{mg}^{-1}$)	0.037	K_F (mg/g) (dm^3/mg) ^{1/n}	17.55
q_{max} (mg/g)	186.22	n	0.458
R^2	0.9675	R^2	0.8726
χ^2	8.53	χ^2	15.20

of GUL with that of other low cost adsorbents. From the comparison it is clear that adsorption capacity of GUL, to remove basic dye, is much higher than that of many other low cost adsorbents.

4. Multiple regression models

Though conventional one–one analyses are widely adapted to identify optimum operating conditions, in most of the real problems, the process variables do have combined effects. Thus, multivariate analysis is quite useful to elucidate the interactive and combined effects. In the present section the experimental data were analyzed to elucidate possible interactive effect of the process variables on the dependent. Thus, functional relationships between the independent process variables concentration–dosage ratio (C/D), particle diameter, agitation speed, and temperature and the dependent variables namely pseudo second order rate constant and equilibrium dye uptake were investigated. In order to do this, the analysis was done with coded values of the variables. The variables X_i were coded as x_i according to the following relationship:

$$x_i = \frac{X_i - X_o}{\delta X} \quad (4)$$

Table 4 Comparison of reported adsorption capacities of various adsorbents for methylene blue.

Adsorbent	q_{max} (mg/g)
Neem leaf	8.76–19.61 [8]
Fallen phoenix leaves	80.9–89.7 [10]
Untreated guava leaves	295 [12]
<i>Paspalum notatum</i>	31 [18]
Activated carbon prepared from rattan sawdust	294.11 [26]
Rice husk	40.58 [28]
GUL	186.24, present study

Table 5 Pseudo second order rate constants for the adsorption of MB onto GUL.

C/D	d_p (μm)	RPS (s^{-1})	$1/T$ (K^{-1})	$\ln K_{2\text{mol}}$
0.025	125	3.33	3.30E–03	7.58
0.050	125	3.33	3.30E–03	6.90
0.075	125	3.33	3.30E–03	6.10
0.100	125	3.33	3.30E–03	5.66
0.025	125	3.33	3.19E–03	7.56
0.050	125	3.33	3.19E–03	7.05
0.075	125	3.33	3.19E–03	6.10
0.100	125	3.33	3.19E–03	5.86
0.025	125	3.33	3.10E–03	7.82
0.050	125	3.33	3.10E–03	7.69
0.075	125	3.33	3.10E–03	6.80
0.100	125	3.33	3.10E–03	7.29
0.100	40	2.50	3.30E–03	7.04
0.100	125	2.50	3.30E–03	6.01
0.100	230	2.50	3.30E–03	5.64
0.100	548	2.50	3.30E–03	5.19
0.100	40	3.33	3.30E–03	7.44
0.100	125	3.33	3.30E–03	6.19
0.100	230	3.33	3.30E–03	5.27
0.100	548	3.33	3.30E–03	5.04
0.100	40	1.67	3.30E–03	6.88
0.100	125	1.67	3.30E–03	5.96
0.100	230	1.67	3.30E–03	5.04
0.100	40	0.83	3.30E–03	6.86
0.100	125	0.83	3.30E–03	5.51
0.100	230	0.83	3.30E–03	4.26

Table 6 Multiple regression coefficients t - and p -values for $\ln K_{2\text{mol}}$ (adsorption on MB onto GUL).

Term	Coefficient	SE coefficient	T	p
Constant	5.20	0.287	18.131	0.000
C/D	–0.69	0.100	–6.882	0.000
d_p	–1.04	0.122	–8.556	0.000
RPS	0.31	0.100	3.118	0.006
$1/T$	–0.37	0.093	–3.944	0.001
$(C/D)^2$	0.29	0.177	1.638	0.120
d_p^2	1.29	0.192	6.723	0.000

A quadratic equation of the following form was used to describe the behavior of the system.

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \quad (5)$$

In the present study the model coefficients were determined using MINITAB 14.

4.1. Regression for pseudo second order rate constant

The values of the process variables and experimental kinetic parameters obtained for the adsorption of MB onto GUL are given in Table 5. Student’s t -test was employed to determine whether calculated effects were significantly different from zero. By comparing the calculated t -values with the table values, statistically insignificant effects were identified. p -Values are the smallest level

Table 7 Analysis of variance for $\ln K_{2\text{mol}}$ (adsorption of MB onto GUL).

Source	D.F.	Seq. SS	Adj. SS	Adj. MS	F	p
Regression	8	22.22	22.22	2.78	33.44	0.000
Linear	4	16.96	17.23	4.31	51.87	0.000
Square	4	5.26	5.26	1.32	15.85	0.000
Residual error	17	1.41	1.41	0.08		
Lack-of-fit	16	1.28	1.28	0.08	0.58	0.791
Pure error	1	0.14	0.14	0.14		
Total	25	23.63				

of significance leading to rejection of null hypothesis. Therefore, at 95% confidence limits those terms with p -values greater than 0.05 were considered to be statistically not significant and were eliminated from the proposed model. Thus, after elimination of

the insignificant terms multiple regression was repeated for the reduced model and the regression coefficients were determined. These values are presented in Table 6. Table 7 presents the analysis of variance for the reduced model. Sum of squares were used to

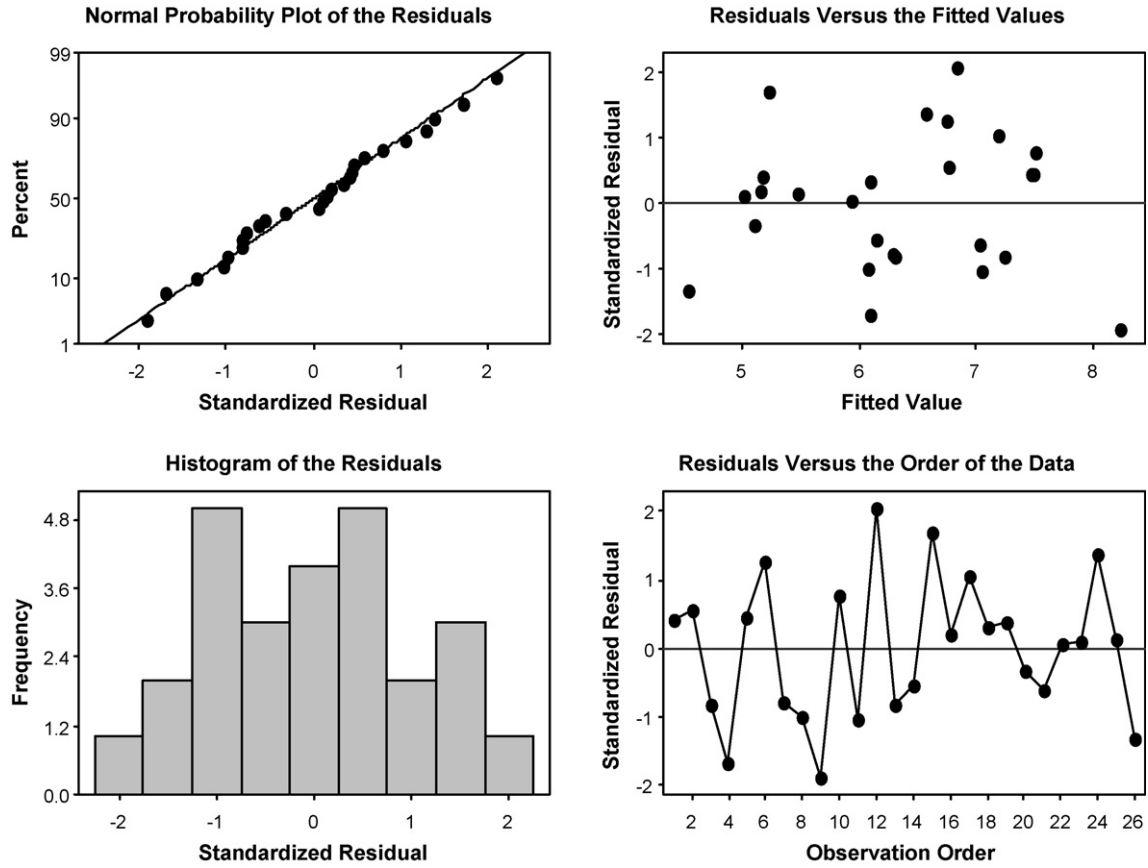


Fig. 4. Residuals plots for $\ln K_{2mol}$ for adsorption of MB onto GUL.

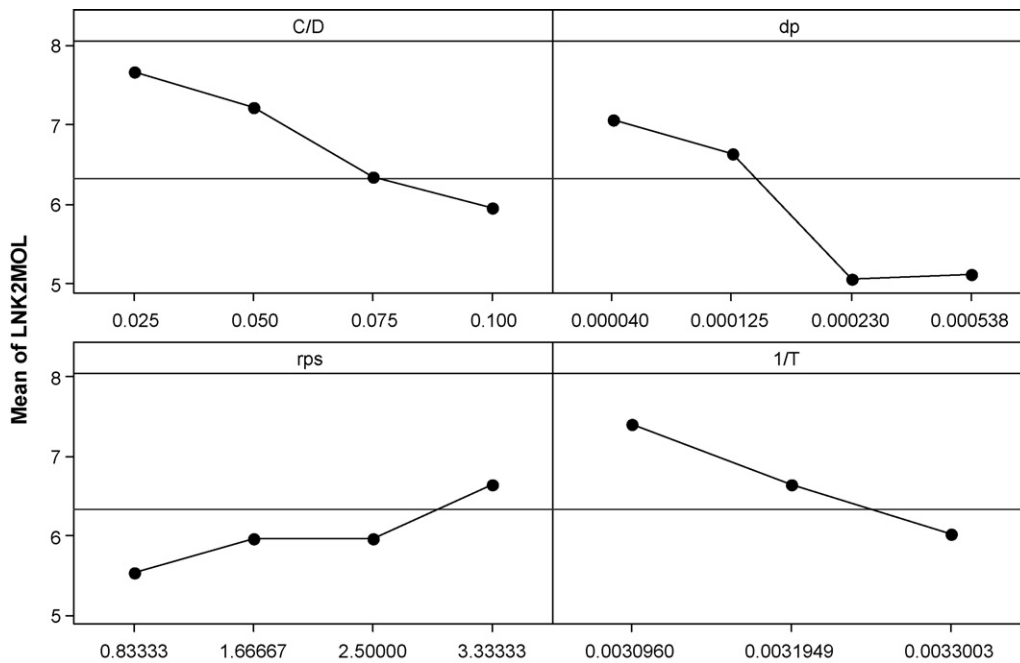


Fig. 5. Main effects plots for $\ln K_{2mol}$ for adsorption of MB onto GUL.

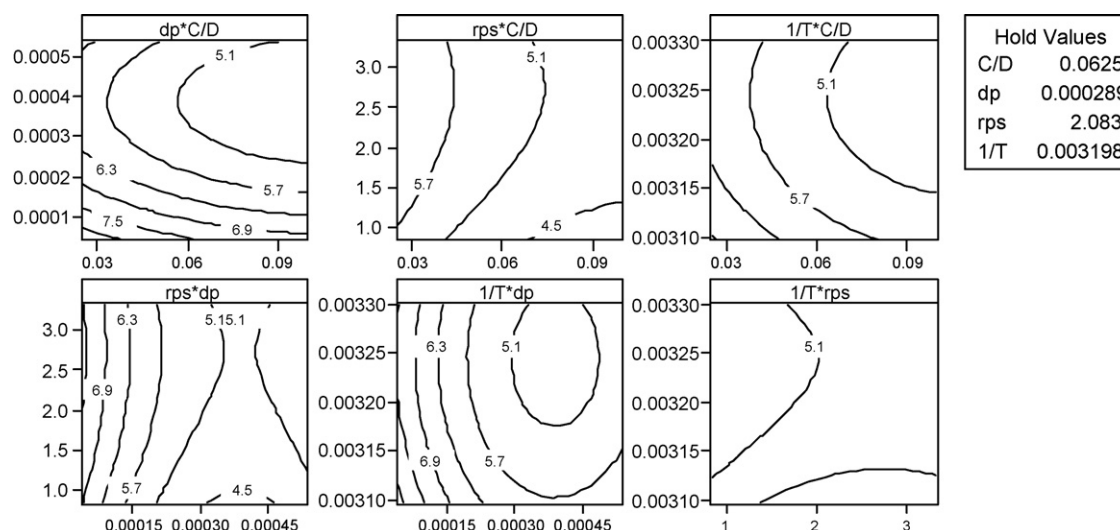


Fig. 6. Contour plots for $\ln K_{2mol}$ for adsorption of MB onto GUL.

calculate F ratio as followed:

$$F = \frac{\text{sum of adjusted mean square}}{\text{sum of adjusted residual error}} \quad (6)$$

Factors having $F_{calc} > F_{table}$ are statistically significant. Here, Table 7 shows that all the effects included in the reduced model were statistically significant. Also, calculated F -value of lack-of-fit was very low. This confirmed that the factors eliminated from the full quadratic model did not have statistical significance. In addition, in order to check the adequacy of the model to explain the system, the residual distribution was examined. Residual distribution plots are shown in Fig. 4. Normal distribution of the residuals and the bell shaped histogram confirmed the adequacy of the model. High R^2 (0.94) indicated that the model was able to predict 94% of the total variation in the response variable (K_{2mol}) about average values for MB adsorption onto GUL. Substituting the coefficients in the regression model following empirical correlation was obtained to predict $\ln K_{2mol}$ for the adsorption of MB onto GUL (in coded units):

$$\ln K_{2mol} = 5.2 - 0.69 \left(\frac{C}{D} \right) - 1.04d_p + 0.31RPS - 0.37 \left(\frac{1}{T} \right) + 0.29 \left(\frac{C}{D} \right)^2 + 1.29d_p^2 \quad (7)$$

Main effects plot (Fig. 5) was in good agreement with the observations earlier recorded in Sections 3.2–3.5. The contour plot (Fig. 6) revealed combined effects of the process variables on the rate constants.

4.2. Regression for equilibrium uptake

The experimental data for equilibrium uptake are presented in Table 8 for the adsorption of MB onto GUL. Here, since agitation speed does not affect the equilibrium conditions, agitation speed was not included in the regression model. Regression analysis was performed to predict the equilibrium uptake in terms of selected process variables as mentioned in the previous section (Section 4.1). Statistically significant effects were identified by Student's t -test and ANOVA test. Regression was repeated after eliminating statistically insignificant factors from the quadratic model. The regression coefficients and their standard errors are presented in Table 9 for the reduced model. ANOVA is shown in Table 10. Values of the statistical parameters t , p and F confirmed the statistical significance of the factors in the reduced model. As the next step, residual analysis was

Table 8

Experimental and predicted values of equilibrium specific uptake for the adsorption of MB onto GUL.

Sr. no.	C/D	d_p (m)	$1/T$ (K^{-1})	$q_{e,exp}$ (mg/g)	$q_{e,pre}$ (mg/g)
1	0.025	0.000125	0.0033	0.0213	0.0198
2	0.050	0.000125	0.0033	0.0422	0.0407
3	0.075	0.000125	0.0033	0.0607	0.0561
4	0.025	0.000125	0.0032	0.0184	0.0198
5	0.050	0.000125	0.0032	0.0340	0.0407
6	0.075	0.000125	0.0032	0.0535	0.0561
7	0.100	0.000125	0.0032	0.0673	0.0661
8	0.025	0.000125	0.0031	0.0222	0.0198
9	0.050	0.000125	0.0031	0.0388	0.0407
10	0.075	0.000125	0.0031	0.0612	0.0561
11	0.100	0.000125	0.0031	0.0681	0.0661
12	0.100	0.000040	0.0033	0.0653	0.0652
13	0.100	0.000125	0.0033	0.0617	0.0661
14	0.100	0.000548	0.0033	0.0429	0.0434
15	0.100	0.000040	0.0033	0.0617	0.0652
16	0.100	0.000125	0.0033	0.0656	0.0661
17	0.100	0.000230	0.0033	0.0594	0.0645
18	0.100	0.000548	0.0033	0.0514	0.0434
19	0.100	0.000040	0.0033	0.0667	0.0652
20	0.100	0.000125	0.0033	0.0642	0.0661
21	0.100	0.000230	0.0033	0.0688	0.0645
22	0.100	0.000040	0.0033	0.0665	0.0652
23	0.100	0.000125	0.0033	0.0689	0.0661
24	0.100	0.000548	0.0033	0.0359	0.0434

Table 9

Estimated regression coefficients for q_e (adsorption of MB onto GUL).

	Coefficient	SE coefficient	T	p
Constant	0.045	0.00266	17.047	0.000
C/D	0.023	0.00133	17.462	0.000
d_p	-0.011	0.001533	-7.121	0.000
$(C/D)^2$	-0.153	0.061321	-2.495	0.022
d_p^2	-0.008	0.00314	-2.585	0.018

Table 10

ANOVA for q_e (adsorption of MB onto GUL).

Source	D.F.	Seq. SS	Adj. SS	Adj. MS	F	p
Regression	4	0.005952	0.005952	0.001488	85.19	0.000
Linear	2	0.005691	0.000953	0.000476	27.27	0.000
Square	2	0.000262	0.000262	0.000131	7.49	0.004
Residual error	19	0.000332	0.000332	0.000017		
Lack-of-fit	2	0.000036	0.000036	0.000018	1.04	0.375
Pure error	17	0.000296	0.000296	0.000017		
Total	23	0.006284				

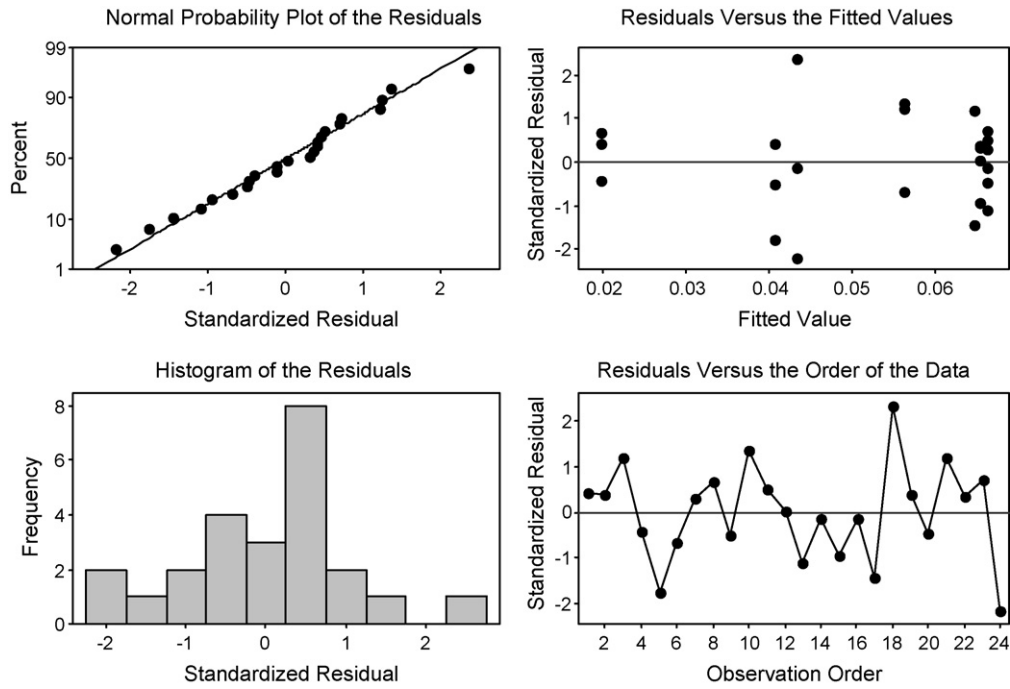


Fig. 7. Residuals plots for q_e for adsorption of MB onto GUL.

performed. Residual plots (Fig. 7) confirmed the normal distribution of residuals and hence the adequacy of the model. Substituting the coefficients in the regression model following empirical correlation was obtained to predict q_e for the adsorption of MB onto GUL (in coded units):

$$q_e = 0.045 + 0.023 \left(\frac{C}{D}\right) - 0.011d_p - 0.153\left(\frac{C}{D}\right)^2 - 0.008d_p^2 \quad (8)$$

Value of R^2 (0.9470) indicated that 94.7% of the total variation in q_e could be explained by the regression. For adsorption of MB onto GUL only C/D ratio had significant effect on q_e . While Fig. 8 illustrates the individual effects of the factors, Fig. 9 demonstrates the existence of interaction between particle size and C/D ratio.

Both these Eqs. (7) and (8) can be used to predict the concentration decay curve within the experimental range. Multiple regression analysis illustrates the interaction between the individual factors, which is not possible in conventional analysis.

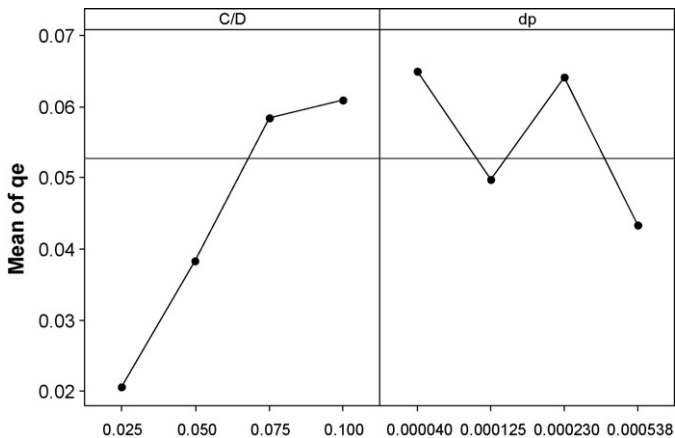


Fig. 8. Main effects plots for q_e for adsorption of MB onto GUL.

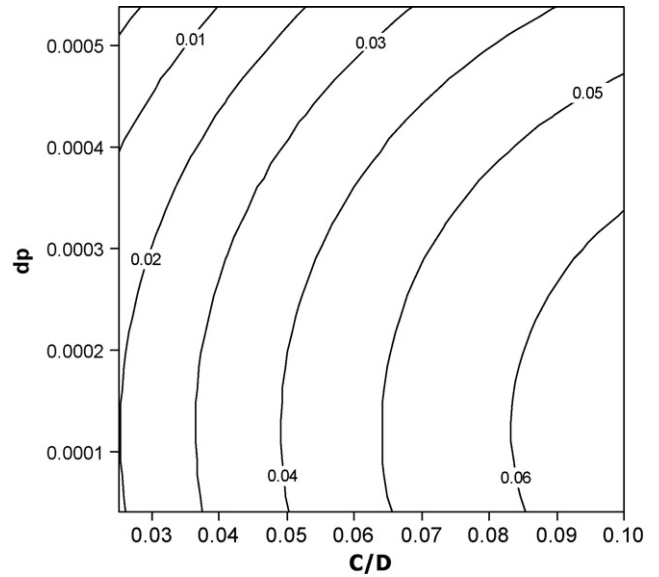


Fig. 9. Contour plots for q_e for adsorption of MB onto GUL.

5. Conclusion

In the present investigation it has been clearly shown that gul-mohar plant leaf powder could be effectively used as a low cost adsorbent for the removal dyes from aqueous effluents. Excellent adsorption potential of GUL had been revealed by its high Langmuir monolayer capacity which was found to be 186.22 mg/g. Adsorption of MB onto GUL followed pseudo second order kinetics. Increase in pH and concentration and decrease in adsorbent dosage resulted in increase in equilibrium dye uptake. Apart from individual effects, process variables also had combined effects on pseudo second order constant and equilibrium dye uptake. These relations could be explained by using suitable quadratic models. In the present study proposed models for second order rate constant and equilibrium

dye uptake could predict the rate constants closely with high R^2 values of 94 and 94.7%, respectively.

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