



## Scavenging methyl orange dye from aqueous solution using an effective low-cost activated carbon prepared from delonix Regia seeds

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An increasing textile industry has exacerbated the serious problem of dealing with industrial effluent that contains toxic dye molecules. Despite the development of various techniques for adsorbing dyes in wastewater, many researchers have yet to expand a highly efficient technique for the revival of dye molecules from textile waste water. However, adsorption techniques using low cost, eco-friendly, effective adsorbents are extensively used due to their simplicity and good efficiency. A novel approach for the capture of dye molecules using a composite inexpensive activated carbon (AC) adsorbent synthesized from Gulmohar (GM) plant seeds has been proposed in this study. Prepared AC before and after adsorption of Methyl Orange (MO) has been characterized by SEM, EDX and FT-IR. Experimental adsorption data of chosen anionic dyes fits several kinetic and isotherm models. Kinetic studies reveal that a pseudo-second order is the mainly suitable model in the adsorption process. The equilibrium adsorption data of anionic dye show that the system followed the Langmuir adsorption isotherm. In addition, through thermodynamic calculations the negative value of  $\Delta G^\circ$  and negative value of  $\Delta H^\circ$  show that the adsorption is a spontaneous and exothermic process. All the above results conclude that the GMAC can be used as an effective adsorbent for removing dyes from wastewater.

**Keywords:** Activated carbon, Gulmohar (Delonix Regia), Isotherms, Methyl Orange

In recent days, due to rapid urbanization and industrialization water resources has been contaminated by several harmful chemicals which lead to serious water pollution problems<sup>1</sup>. Every day tons of sewage and pollutants are poured into the rivers and lakes. Carcinogenic and mutagenic effects of dyes are one of the important water pollutants which cause serious damage to animals, human beings and aquatic biota<sup>2</sup>. There are several methods available for the effective removal of dyes from aqueous solutions including: Adsorption, electrochemical precipitation, ion exchange, ultra filtration, catalytic reduction<sup>3</sup> and reverse osmosis. Among the various processes adsorption techniques have been recognized as technically and economically important<sup>4</sup>. Numerous dye adsorbents have been reported in recent days, the utilization of natural bio resources as adsorbents for removal of dye, has received special focus because of their low cost and renewable characteristic<sup>1</sup>. Enormous bioresources such as Aloe Vera leaves wastes<sup>5</sup>, sesame straw<sup>6</sup>, tamarind gum<sup>7</sup>, xanthan gum<sup>8</sup>, corn stalk<sup>9</sup>, fruit peels<sup>10</sup> and carexmyerianakunth<sup>11</sup> have also been studied as bio sorbents to remove various dyes from water.

However, the bio sorbents generally have drawbacks of low adsorption capacity, slow adsorption rate, and moderate adsorption selectivity, which limit their practical applications. Therefore, the developments of activated carbon possess high adsorption capacity, fast adsorption rate and adsorption selectivity remains greatly desired.

Gulmohar (Delonix Regia) plant is also known as flame tree. The objective of this study is to prepare a new adsorbent gulmohar seed activated carbon (GMAC) for the removal of anionic dye methyl orange (MO) from its aqueous solution. The effects of pH, temperature and initial dye concentration on dye adsorption using prepared activated carbon were investigated. The experimental data were analyzed using the Lagergren pseudo-first-order kinetic model and pseudo-second-order model. Thermodynamics parameters,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ , were also calculated.

### Experimental Section

#### Preparation of Adsorbent

Gulmohar (Delonix Regia) Activated Carbon (GMAC) was prepared from the GM plant seeds. The

thinly powdered seeds were put into a muffle furnace and heated at 450°C for 5 h. The carbonized sample was impregnated in 1:1 H<sub>2</sub>SO<sub>4</sub> solution for 12 h. The suspension was filtered and carbonized samples were washed several times with distilled water until the pH of the washings turn to neutral. Finally, the modified AC was dried in an electrical oven at 105°C for 12h. The modified AC was crushed to have a uniform particle size and utilized for the adsorption experiments and stored in a plastic container for further use<sup>12</sup>.

#### Preparation of Adsorbate

A calculated quantity of 1g of Methyl Orange dye was taken and dissolved in one litre of distilled water to get stock solution. For experiment purpose the dye solution of desired concentration was obtained by appropriate dilution from stock solution. Double distilled water was used throughout the adsorption experiments.

#### Characterization of adsorbent

Prepared adsorbent was characterized by FT-IR spectrometer (Bruker ALPHA T). The FT-IR study was conducted on the frequency range 400-4000 cm<sup>-1</sup>. The surface morphology of adsorbent was analyzed by scanning electron microscopy using SEM (Hitachi S-3400N)<sup>13</sup>.

#### Batch mode experiments

Batch mode experiments were conducted using temperature controlled orbital shaker with a constant speed of 200 rpm using 250 mL conical flasks containing 60 mL of dye solutions. After shaking up the flasks for predetermined time intervals, samples were removed from the flasks and the adsorbents were separated from the solution by centrifugation (REMI make) at 2000 rpm for 15 min. The absorbance of the supernatant solution was measured using UV-Visible Spectrophotometer to determine the dye concentration. The amount of adsorbent, adsorbed at equilibrium condition,  $q_e$  (mg/g) was calculated using the following equation<sup>14</sup>:

$$q_e = \frac{(C_o - C_e)V}{W} \quad \dots(1)$$

Where,  $C_o$ - is the initial dye concentration (mg/L),  $C_e$ - is the dye concentration at equilibrium(mg/L),  $V$  - is the volume of the dye solution(litre), and  $W$  - is the mass of AC (gram).

The percentage removal of dye was calculated by the following equation<sup>15</sup>,

$$\% \text{ Removal} = \frac{(C_o - C_t)}{C_o} \times 100 \quad \dots(2)$$

Where,  $C_o$ - is the initial dye concentration(mg/L) and  $C_t$  - is the concentration of dye at particular time(mg/L).

## Results and Discussion

#### Characterization with SEM and FTIR

SEM images of GMAC are shown in Fig.1. It can be concluded from SEM images that porous structure was formed because of most of the organic volatiles were evolved, leaving behind the ruptured surface of activated carbon with a huge number of pores.

#### Functional groups of GMAC

FTIR spectra of GMAC before and after adsorption of Methyl orange are shown in Fig. 2.

The intense sharp peak at 3737 cm<sup>-1</sup> is largely due to stretching vibration of -OH group. So the AC still carries surface residual -OH group. Presence of trace amount of water is also evident by its bending vibrations close to 1632 cm<sup>-1</sup>. The peak at 3458 cm<sup>-1</sup>

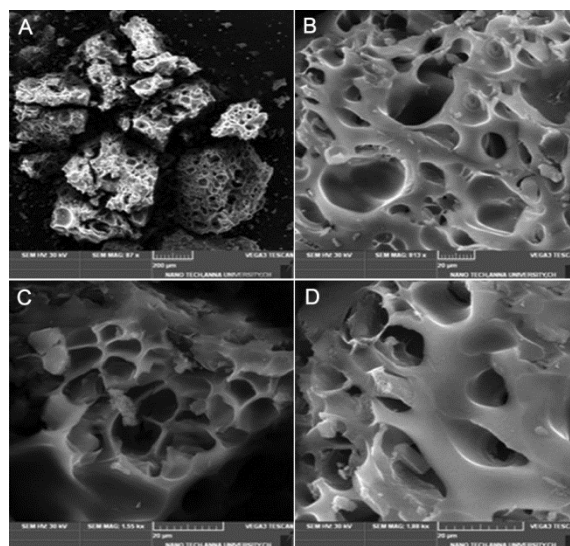


Fig. 1(A-D) — SEM images of GMAC

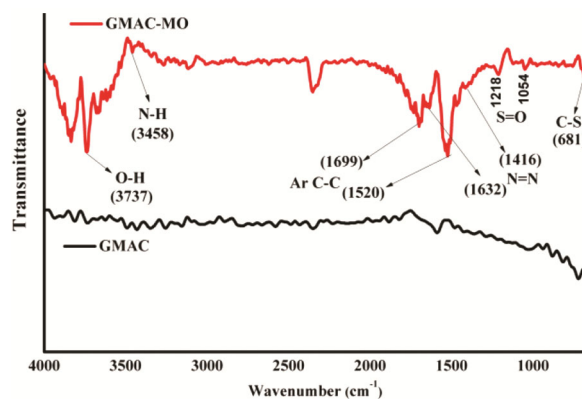


Fig. 2 — FT-IR spectra of GMAC-MO and GMAC

corresponds to N-H stretching vibration. The aromatic ring skeletal vibration of methyl orange occurred at 1699 and 1520  $\text{cm}^{-1}$ . The C-S stretching vibration observed at 681  $\text{cm}^{-1}$ .

### Adsorption studies

#### Effect of pH

The pH is one of the important factor controlling the adsorption of dye onto activated carbon. Surface properties of the adsorbent influenced by solution pH. With increasing pH values adsorption of methyl orange on AC increases. This is due to the electrostatic interaction of anionic dye with the positively charged surface<sup>16</sup>.

The effect of initial pH on adsorption of methyl orange was studied from pH 2.0-10 at  $25 \pm 0.5^\circ\text{C}$ , with 60 mg/L dye concentration and adsorbent dosage of 0.5 g and contact time of 60 min. The maximum adsorption of the methyl orange is obtained at pH 4.0 is shown in Fig. 3A. Result depicts that pH significantly affects the extent of adsorption of dye over the adsorbent.

#### Effect of adsorbent dose

The adsorption of methyl orange dye onto GMAC was studied by changing the quantity of adsorbent range (0.1 to 1)g with the dye concentration of 60 mg/L, at room temperature and pH of 4 shown in Fig. 3B. It was seen that with increasing adsorbent dosage from 0.1 to 1g, the percentage of dye removal was increased. The increase in the adsorption with the increase in adsorbent dosage can be attributed to the increased GMAC surface area and the availability of more adsorption sites. For the removal of dye the adsorption density of dyes decreased with the increase in adsorbent dosage.

#### Effect of initial dye concentration

The effect of dye concentration on adsorption of the methyl orange onto GMAC was investigated in the concentration range 60–100 mg /L at pH 4.0 and  $25^\circ\text{C}$ . The results are shown in Fig. 3C. When initial concentrations of dyes was increased from 60 to 90

mg, the percentage of removal decreased from 97.5% to 93% .

The adsorption is rapid in the initial stage, and then slow, because a large number of vacant surface sites of activated carbon were available for adsorption in the initial stage. Therefore the remaining vacant surface were tedious to occupy because of the high repulsive forces between themethyl orange dye molecules on the GMAC and the bulk phase<sup>17</sup>.

#### Effect of temperature and adsorption isotherms

Temperature has a notable effect on the adsorption capacity of chosen adsorbents. In this work, adsorption studies were conducted at three different temperatures is shown in Fig. 3D.

Using GMAC adsorbent, the percentage removal of methyl orange at  $25^\circ\text{C}$  was 97.86%. Further increase of temperature from  $25^\circ\text{C}$  to  $45^\circ\text{C}$  adsorptive removal of methyl orange was 94.25%. So, an increase of temperature decreases the removal of methyl orange. The optimum temperature was found to be  $25^\circ\text{C}$ .

#### Adsorption isotherms

Adsorption isotherm is significant for understanding the adsorption process. It intimates the relationship between the amount of a solute adsorbed at constant temperature and its concentration in the equilibrium solution. In this work, two typical isotherm models, such as Langmuir and Freundlich isotherm<sup>18</sup> are selected to describe the equilibrium adsorption.

#### Langmuir isotherms

There are two types of equations for linear form of Langmuir Isotherm.

Langmuir type-1 isotherm model can be written as

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L C_e} \quad \dots(3)$$

Where,  $q_e$  is the amount of adsorbate adsorbed at equilibrium time (mg/g),  $C_e$  is the equilibrium concentration of adsorbate in solution (mg/L),  $q_m$  is the theoretical maximum saturated monolayer

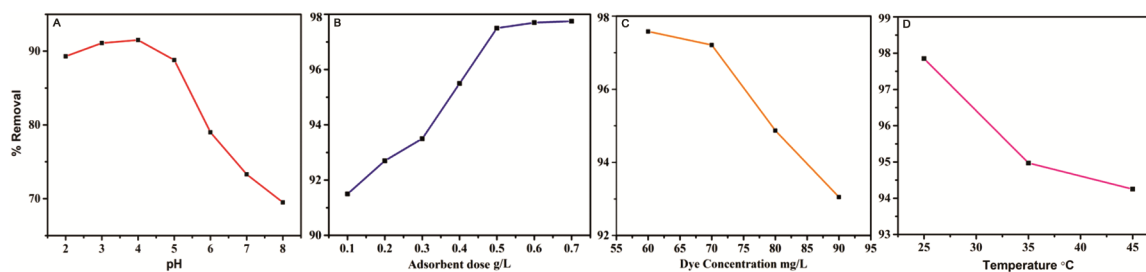


Fig. 3 — (a) Effect of pH; (b) Effect of adsorbent dose; (c) Effect of Initial dye concentration and (d) Effect of temperature

adsorption capacity (mg/g) of the adsorbent and  $K_L$  is the isotherm constant for Langmuir ( $L \text{ mg}^{-1}$ ). By plotting  $C_e/q_e$  vs.  $C_e$ , the  $q_m$  and  $K_L$  values can be calculated from slope and intercept of the plot.

Langmuir type-2 isotherm model used in the present study can be written as

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \quad \dots(4)$$

In this form  $q_m$  and  $K_L$  are determined from the slope and intercept value from the plot of  $1/q_e$  vs.  $1/C_e$ .

An additional equilibrium parameter, ( $R_L$ ) can be calculated from Langmuir plot as per the following relation

$$R_L = 1/1 + K_L C_0 \quad \dots(5)$$

$R_L$  value gives the characteristics or type of the Langmuir isotherm<sup>19</sup>.

Where  $C_0$  is the initial methyl orange concentration ( $\text{mg L}^{-1}$ ) and  $K_L$  ( $L \text{ mg}^{-1}$ ) is the Langmuir constant. The values of  $RL$  suggest types of the isotherm which

can be irreversible ( $RL = 0$ ), favourable ( $0 < RL < 1$ ), linear ( $RL = 1$ ) or unfavourable ( $RL > 1$ ).

#### Freundlich isotherms

The linear form of Freundlich isotherm model can be represented as,

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \dots(6)$$

$K_F$  is Freundlich constant ( $(\text{mg/g})(1/\text{mg})^{(1/n)}$ ) and  $n$  is the heterogeneity factor. The  $K_F$  value represents the adsorption capacity; while  $1/n$  value is associated to the adsorption intensity. A plot of  $\log q_e$  versus  $\log C_e$ , gives a straight line.  $K_F$  and  $1/n$  can be determined from the intercept and the slope of the plot respectively. Freundlich Isotherm implies adsorption on a heterogeneous surface with different binding energy. The exponent  $1/n$  is usually less than 1.0 because sites with the highest binding energies are utilized first, followed by weaker sites, and so on.

Langmuir and Freundlich isotherm plots are shown in Fig. 4A & 4B and Table 1.

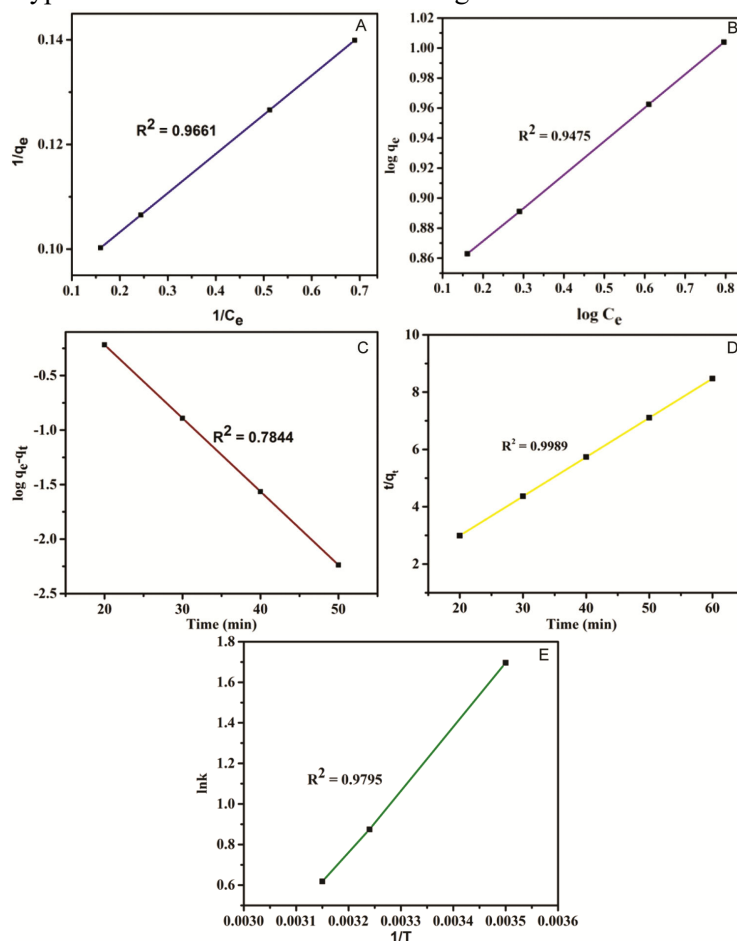


Fig. 4 — (A) Langmuir Isotherm plots; (B) Freundlich Isotherm plots; (C) Pseudo First Order plot; (D) Pseudo Second Order plot and (E) Thermodynamic plots

All the correlation coefficient, R<sup>2</sup> values and the constants obtained from the two

Isotherm models are summarized in Table 1. Based on the results, Langmuir isotherm model very closely fitted the experimental data with better correlation coefficients than that of Freundlich model. And the RL values are lying in the range 0-1 which indicates that the Langmuir isotherm model was favourable for adsorption of methyl orange onto AC.

**Adsorption kinetics**

Adsorption kinetics is important because it controls the efficiency of the adsorption process, rate of methyl orange dye uptake on GMAC and equilibrium time. The adsorption capacity of activated carbon at different temperature (298, 308, and 318 K) was investigated and the kinetic data were modeled using Lagergren pseudo-first-order and pseudo-second-order.

**Lagergren pseudo-first-order kinetics model**

Lagergren rate equation for the pseudo-first-order kinetic model was expressed as follows<sup>20,21</sup>:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad \dots(7)$$

where q<sub>e</sub> and q<sub>t</sub> are the amounts of methyl orange adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k<sub>1</sub> (1 min<sup>-1</sup>) is the pseudo-first-order rate constant. The experimental and calculated values of k<sub>1</sub>, q<sub>e</sub> and correlation coefficient are summarized in Table 2 and Fig. 4C.

Table 1 — Langmuir and Freundlich Isotherm Parameters

Isotherm	Parameters	MO
Langmuir	q <sub>m</sub> (mg/g)	11.36
	K <sub>L</sub> (L/mg)	1.1895
	R <sub>L</sub>	0.0092
	R <sup>2</sup>	0.966
Freundlich	n	4.50
	K <sub>F</sub>	6.6988
	R <sup>2</sup>	0.947

Table 2 — Kinetic parameters

Type of Kinetics	Parameters	MO
Pseudo First Order	q <sub>e</sub> (exp)	7.04
	K <sub>1</sub> (ad)	0.1312
	q <sub>e</sub> (cal)	3.3728
	R <sup>2</sup>	0.784
	K <sub>2</sub>	0.0074
Pseudo Second Order	q <sub>e</sub> (cal)	7.22
	R <sup>2</sup>	0.998

**Pseudo-second-order kinetic model**

The linear form of pseudo-second-order kinetic model was expressed as follows<sup>22</sup>.

$$t/qt = 1/k_2 q_e^2 + t/q_e \quad \dots(8)$$

Where k<sub>2</sub> is the rate constant of the pseudo second order adsorption (g/mg/min). The plot of t/qt vs t gives a linear relationship, from which q<sub>e</sub> and k<sub>2</sub> can be determined from the slope and intercept of the plot. Pseudo second parameter values are listed in Table 2 and shown in Fig. 4D.

Besides the correlation coefficient R<sup>2</sup> value of pseudo-second-order kinetic model was greater than pseudo-first-order kinetic model. Since calculated correlation coefficient is closer to unity for pseudo-second-order kinetic model. It should be noted that the calculated q<sub>e</sub> values of pseudo-second-order kinetic model were very close to the experimental q<sub>e</sub> values. This indicates the applicability of pseudo-second-order kinetic model rather than pseudo-first-order kinetic model to narrate the adsorption of methyl orange on the GMAC. Hence the adsorption process was controlled by chemisorption.

**Thermodynamic Modelling Studies**

In order to characterize the adsorption process, three thermodynamic parameters must be used. The parameters are standard Gibbs free energy ΔG°, standard enthalpy ΔH° and standard entropy ΔS°. ΔH° and ΔS° can be calculated from the below equation

$$\ln K_L = \frac{\Delta S^\circ}{R} + \frac{\Delta H^\circ}{RT} \quad \dots(9)$$

Where T (K) is the absolute solution temperature, R (8.314J/mol K) is the universal gas constant and K<sub>L</sub> (L/mg) is the Langmuir isotherm constant.

Standard Gibbs free energy ΔG° can be determined using the formula given below

$$\Delta G^\circ = -RT \ln K_L \quad \dots(10)$$

Batch adsorption studies were carried out at varying temperatures from 298K, 308K and 318K with optimum dye concentration are investigated and graphically shown in Fig. 4E and listed in Table 3.

The thermodynamic parameters<sup>23</sup>, Gibbs free energy ΔG°, enthalpy ΔH° and entropy ΔS° were determined at different temperatures (298K, 308K and 318K). The values of ΔH° and ΔS° were calculated from the slope and intercept of Van't Hoff plots ln k vs 1/T respectively. From the observations the negative free energy change (ΔG°) implies that the adsorption process is feasible and spontaneous. The negative value of ΔH° indicates the nature of the

Table 3 — Thermodynamic parameters

T (K)	$\Delta G^\circ$ (KJ/mol)	$\Delta H^\circ$ (KJ/mol)	$\Delta S^\circ$ (J/mol/k)
298	-4.2111		
308	-2.0992	-56.50	-166.17
318	-1.7885		

adsorption process is exothermic nature. From the value of  $\Delta H^\circ$  indicates that Van der Waals interaction, hydrophobic interaction may contribute to the adsorption process in addition to electrostatic attraction. The value of entropy was negative  $\Delta S^\circ$  due to decreased randomness at the solid-solution interface during adsorption of methyl orange GMAC.

### Conclusion

In this research the cheap adsorbent such as Activated carbon is produced from GM plant seeds through chemical activation.

Sulphuric acid has been used as an activating agent. The modified AC using sulphuric acid was utilized for the investigation of removal of anionic dye namely methyl orange. The characteristic of prepared activated carbon is found to be suitable for adsorption of methyl orange from aqueous solution. Kinetic data fitted by the pseudo second order kinetics. Results of isotherm model conclude high monolayer adsorption capacities. Finally the utilization of GM seeds as a precursor for novel activated carbon also represents an eco-friendly alternative material for the disposal of methyl orange rich aqueous solution.

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