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Research Article

ADSORPTION OF METHYLENE BLUE USING LOW COST ADSORBENT OBTAINED FROM *ADHATODA ZEYLANICA* LEAVES

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ABSTRACT

This work deals with the removal of methylene blue dye from aqueous solution using low cost adsorbent obtained from the leaves of *Adhatoda zeylanica.* Adsorption isotherm of the methylene blue (MB) on the activated carbon was determined and correlated with common isotherm equations. The equilibrium data for methylene blue adsorption well fitted to the Langmuir equation. Thermodynamic parameters like change in free energy, enthalpy and entropy were calculated. Results revealed that *Adhatoda zeylanica* is a promising adsorbent for the removal of MB from an aqueous solution.

Keywords: Methylene blue , Isotherm models, Adsorbent, Thermodynamic Parameters.

I. INTRODUCTION

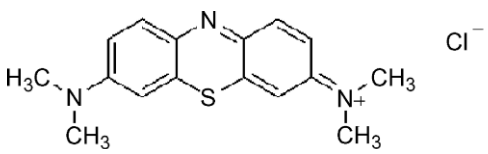
Many industries such as leather, paper, plastics, textiles and rubber use dyes extensively to colour their final products. Such use of dyes frequently leads to environmental problems in the form of colored wastewater. As a result the effluents discharged from these industries contain these dyes[1]. Discharge of such colored effluents imparts color to the receiving water bodies. Color inhibits light penetration, reduces photosynthetic activity and affects the growth of biota. The presence of even traces of dyes in water is highly visible and undesirable[2]. Once the dyes enter the water it is very difficult to treat as the dyes have a synthetic origin and a complex molecular structure, which makes them more stable and difficult to be biodegraded[3,4]. Activated carbon as an adsorbent has been widely investigated for the adsorption of dyes[5-9] but the high-cost involved in its preparation greatly limits its commercial application.

Many low-cost adsorbents including natural and waste materials from industry and agriculture, have been employed by several workers for the removal of dyes from waste waters. Some of these include Bagasse pith[10], Maizecob[11], Coconut shell[12], Chitosan[13], Peat[14], Biomass[15], Orange peel[16], Papaya seed[17], Tamarind fruit sheel[18], Pumpkin seed hull[19]. The objective of this work is to explore the potential of *Adhatoda zeylanica* leaves as an adsorbent in the removal of the basic dye, methylene blue, from aqueous solutions.

II. EXPERIMENTAL

Preparation of the adsorbate

Appropriate quantity of Methylene blue was dissolved in one litre of distilled water to get the stock solution. Desired concentration of the dye solution was obtained from the stock solution by dilution. The MB was chosen in this study because of its known strong adsorption onto solids. The maximum wavelength of this dye is 668 nm. The structure of MB is shown as below.



Preparation of adsorbent

Adhatoda zeylanica leaves was collected from the local market and washed with tape water several times to remove soil dust and finally washed with DD water. It is dried in sun shade. The dried leaves were powdered and impregnated with 50% H_2SO_4 for 24 h and then filtered and the resulting chemical loaded *Adhatoda zeylanica leaves* was placed in a furnace and heated to 850 ^{0}C for 30 min After the cooling, the activated carbon was repeatedly washed with deionized water and dried at 105 ^{0}C. The carbonized material was ground well to fine powder,stored in vacuum desiccators and used for adsorption experiments.

Adsorption studies

Adsorption experiments were carried out in 250ml Erlenmeyer flasks. A known weight of adsorbent obtained from *Adhatoda zeylanica* leaves *was* added to 50ml of the dye solutions with an initial concentration of 20mg/l to 1000mg/l. Flasks were agitated in a shaker at room temperature for 90min. The solution was then filtered at preset time intervals and the residual dye concentration was measured spectrophotometrically. The percentage of MB dye removal was calculated by using the following equation.

$$\%\ Dye\ Removal = \frac{(C_0 - C_e)}{C_0}\ X\ 100$$

Where C_o is the initial concentration (mg/l),C_e is the equilibrium concentration(mg/l)
The adsorption capacity Q_e (mg/g), is obtained from the following equation

$$q_e = (C_0 - C_e)\frac{V}{M}$$

Where, q_e is the adsorbent capacity(mg/g), C_o is the initial concentration (mg/l) C_i is the initial MG concentration (mg/l), V is the volume of the solution(l), M = mass of the adsorbent (g).

III. RESULTS AND DISCUSSION

Effect of pH

The pH is an important controlling parameter in the adsorption process. The interaction between dye molecule and adsorbent is basically a combined result of the charges on dye molecules and the surface of the adsorbent[20]. The percentage of dye adsorption was determined by varying the pH of the solution, fixing the other parameters constant and the results are given in fig-1. The pH of the working solution was controlled by adding 1NHCl or 1NNaOH solution. As the pH of the solution increased the percentage of the adsorption also increased and reaches the maximum at pH-6 and thereafter it remains almost unchanged. Hence the pH of the medium was maintained at 6 for further studies.

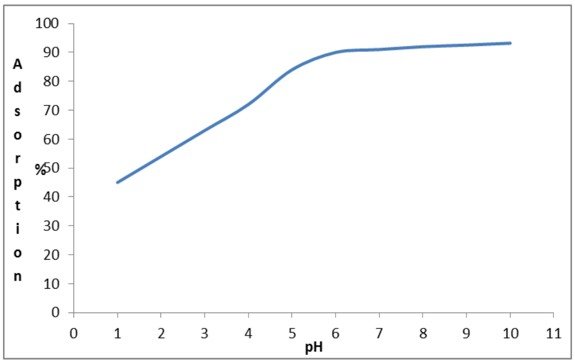


Fig. 1: Effect of pH on the adsorption of MB on to the adsorbent

Effect of adsorbent dose

Effect of adsorbent dose on the removal of Methylene blue dye from aqueous solution was investigated by varying adsorbent dose from 25mg to 150mg for 20mg/l of dye concentration, keeping the other parameters constant, and the results are presented in the fig-2. As the adsorbent dose increases, the MB dye removal also increases and reaches the maximum at 100mg of adsorbent dosage thereafter there was no appreciable increase in the percentage of dye removal. Therefore the adsorbent dosage was maintained at 100mg for further studies. The increase in the dye removal with an increase in the adsorbent dosage can be attributed to increased carbon surface area and the availability of more adsorption sites. This is an agreement with already reported[21].

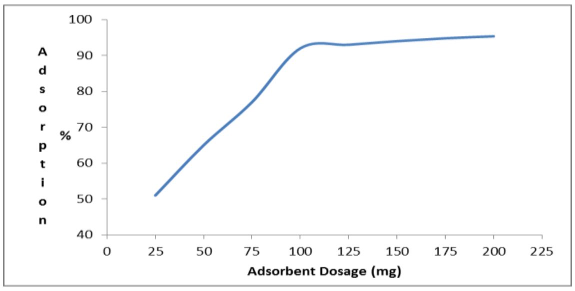


Fig. 2: Effect of adsorbent dose on the adsorption of MB on to the adsorbent

Effect of dye concentration

The effect of initial dye concentration on the removal of MB dye is illustrated in fig-3. When the initial MB dye concentration increased from 20mg/l to 100mg/l, the percentage removal of MB dye decreased from 91.64 % to 74.20 %. As the initial concentration is increased the ratio of the number of vacant sites on the adsorbent to the dye molecules decreases.

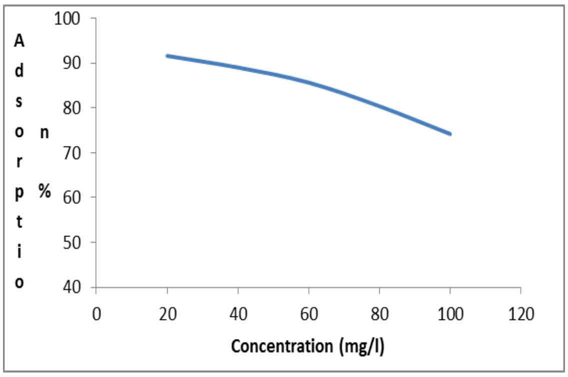


Fig. 3: Effect of dye concentration on the adsorption of MB on to the adsorbent

Effect of contact time

The effect of contact time on the removal of the dye is shown in fig-4. It is observed that initially the percentage removal of dye increases rapidly and reaches the maximum at 90min. Thereafter, there was no appreciable change in the adsorption percentage, Therefore, 90min shaking time was found to be appropriate for the maximum adsorption and was maintained in all subsequent experiments.

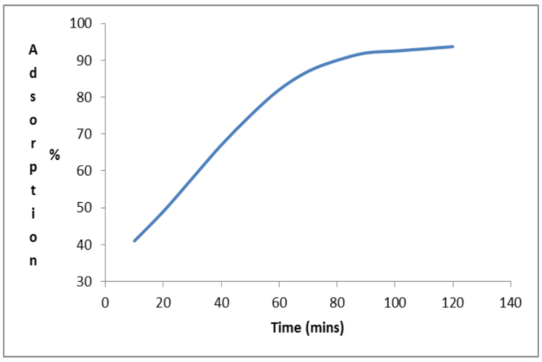


Fig. 4: Effect of contact time on the adsorption of MB on to the adsorbent

IV. ADSORPTION ISOTHERMS

Langmuir Adsorption Isotherm

The Langmuir model assumes monolayer surface coverage, equal availability of adsorption sites and no interaction among the adsorbed dye molecules. The linear form of Langmuir equation[22] is expressed as follows

$$\frac{Ce}{Qe} = \frac{Ce}{Q_0} + \frac{1}{Q_0 b}$$

The values of Q_0 and b were calculated from the slope and intercept of the linear plots of C_e/Q_e verses C_e. Langmuir adsorption isotherm is presented in fig-5. Higher value of correlation co-efficient (R^2-0.999) indicates that the experimental data fits well with the Langmuir equation.The values of Q_0 and b are given in Table-1.

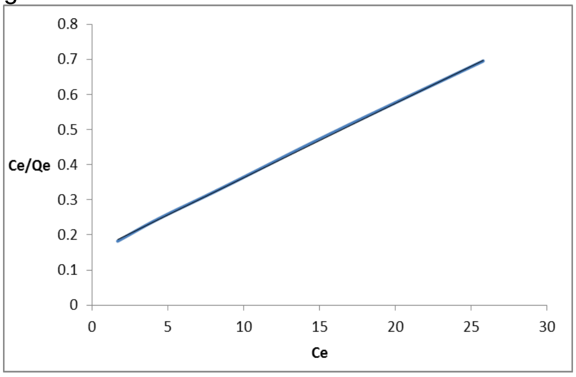


Fig. 5: Langmuir isotherm for the adsorption of MB on to the adsorbent

Table 1: Langmuir constants

Qo(mg/g)	b	R^2
47.1678	0.1403	0.9997

The essential characteristics of the Langmuir adsorption isotherm is expressed by a dimensionless constant called separation factor. This value indicates whether the adsorption is favorable or not.

R_L is defined by the following equation

R_L = 1/ (1+bCo)

Where,R_L _ dimensionless separation factor[23], Ci – intial concentration , b – Langmuir constant (Lmg-[1]),The parameter $R_L$indicates the type of the isotherm.

Values of R_L	Types of isotherms
$R_L>1$	Unfavourable
$R_L = 1$	Linear
$0<R_L<1$	Favourable
$R_L = 0$	Irrevisible

The R_L value obtained using the above equation for 10mg/l MG concentration is 0.2627. This R_L value lies between 0 and 1 indicating the favourability of the adsorption.

Freundlich Adsorption Isotherm

The Freundlich isotherm considers multilayer adsorption with interactions among the adsorbed molecules. The linear form of the Freundlich equation[24] is as follows

$$\log Qe = \log K_F + \frac{1}{n} \log Ce$$

Where Qe, amount of dye adsorbed (mg/g), K_F, (adsorption capacity) and n, (adsorption intensity). By ploting logQe Vs logCe, the values of n and K_F were calculated from slope and intercept respectively (fig-6). The values of K_F and n are given in table-2. The value of linear regression co-efficient (R^2) was found to be 0.9728.This indicates that the adsorption process follows Langmuir adsorption isotherm more than Freundlich adsorption isotherm.

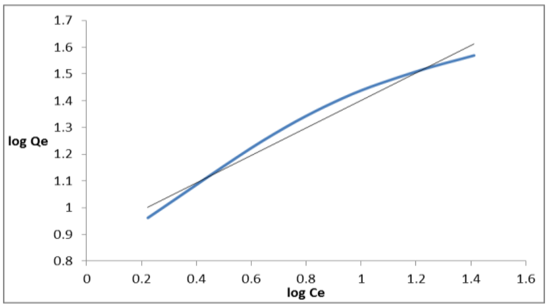


Fig. 6: Freundlich isotherm for the adsorption of MB on to the adsorbent

Table 2: Freundlich constants

n	K_f(mg/g)	R^2
1.9486	7.7197	0.9728

The value of n lies between 1 and 10 indicating the favourable adsorption.

V. THERMODYNAMIC PARAMETERS

Thermodynamic studies related to the adsorption process is essential to conclude whether a process will occur spontaneously or not, The fundamental criteria for spontaneity is the standard Gibbs free energy change $\Delta G^{0,}$ if the ΔG^o value is negative, the reaction will occur spontaneously. The thermodynamic parameters, standard free energy (ΔG^o), change in Standard enthalpy(ΔH^o) and change in Standard entropy(ΔS^o) for the adsorption of MB onto the adsorbent were calculated using the following equations.

$$K_0 = \frac{C_{solid}}{C_{liquid}}$$

$$\Delta G^0 = -RT \ln K_0$$

$$\log K_0 = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT}$$

Where Ci is the concentration of the dye at equilibrium and Ce is the amount of dye adsorbed on the adsorbent

The values of ΔG^o (KJ/mol), ΔH^o(KJ/mol) and ΔS^o (J/K/mol) can be obtained from the slope and intercept of a linear plot of log K_o verses 1/T and are presented in table-3.

The negative values of ΔG^o indicates that the adsorption process is spontaneous and highly favorable. The positive values of ΔS^o indicates the increased randomness at the solid solution interface. The values of ΔH^o indicates that the adsorption process is endothermic and physical in nature.

VI. CONCLUSION

The adsorption of methylene blue from aqueous solution was studied with various parameters like contact time, pH, initial concentration, and adsorbent dose. The present investigation showed that the adsorption process was fast, and it reached equilibrium in 90 min of contact, . The adsorption studies indicate that Langmuir model is better obeyed. Thermodynamic parameters (ΔG^o , ΔH^o , and ΔS^o) suggest that adsorption process is endothermic and spontaneous.. The result of this study indicates that this adsorbent can be successfully utilized for the removal of MB from aqueous solution.

Table 3: Thermodynamic parameters for the adsorption of MB on to the adsorbent

Conc.of MG (mg/l)	-ΔG^o (KJ/mol)				ΔH^o (KJ/mol)	ΔS^o (J/k/mol)
	35^0 C	45^0 C	55^0 C	65^0 C		
20	6.1317	6.5930	7.0088	7.5803	8.5488	47.6113
40	5.3629	5.8069	6.2029	6.7581	8.7579	45.7980
60	4.5812	5.0097	5.4161	54.9296	9.1446	44.5247
80	3.6158	4.0300	4.3901	4.9202	9.5582	42.7191
100	2.7054	3.1133	3.6129	3.9875	9.5180	39.9505

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