Removal of Methylene Blue Dye from Aqueous Solution by Adsorption Using Low Cost Adsorbent Obtained from *Andrographis paniculata* Leaves

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Abstract- The objective of this work is to study the removal of methylene blue dye from aqueous solution using low cost adsorbent obtained from the leaves of Andrographis *paniculata*. Batch adsorption studies were carried out by observing the effects of various experimental parameters, such as dye concentration, contact time, adsorbent dose, effect of temperature and pH. The data were fitted into the Langmuir and Freundlich adsorption isotherm equations. Thermodynamic parameters like change in free energy, enthalpy and entropy were calculated. The experimental data were fitted into the pseudo first model. Results indicate that *Andrographis paniculata* is a promising adsorbent for the removal of MB from an aqueous solution.

Index terms- Methylene blue, Isotherm models, Kinetics, Adsorbent, Thermodynamic Parameters.

I. INTRODUCTION

Industries such as leather, paper, plastics, textiles and rubber use lot of synthetic dyes in order to colour their products . As a result the effluents discharged from these industries contain these dyes[1]. The pollution caused by the discharge of untreated effluents from these industries is a major concern. The presence of very small amounts of colour in water is highly visible and undesirable[2]. Once the dyes enter the water it is no longer good and sometimes 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].

Generally biological aerobic wastewater systems are not successful for decolourization of majority of dyes[5]. Therefore colour removal was extensively studied with physio- chemical methods such as adsorption, coagulation, ultra-filtration, electro-chemical adsorption and photo oxidation[6] . Among these adsorption is one of the effective methods for removing dyes from waste water[7]. Granulated activated carbon (GAC) is commonly used for dye removal[8]. But these are expensive, so activated carbon, due to its effectiveness, is the most widely used adsorbent Recently, numerous approaches have been made for the development of cheaper and effective adsorbents[9].Many low-cost adsorbents including natural and waste materials from industry and agriculture, have been employed by several workers. 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]. In the present study we utilized the adsorbent obtained from the leaves of *Andrographis paniculata* for the removal of Methylene blue dye from the aqueous solution.

II.EXPERIMENTAL

Preparation of the adsorbate

Methylene blue dye (chemical formula- $C_{16}H_{18}ClN_3S$, Molecular weight-373.91and λmax 664nm) was obtained from Merck, India. 1000mg 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.

Preparation of adsorbent

Andrographis paniculata leaves was collected 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 soaked in con.H_2SO_4 (1:1,w/w), for a day, then filtered and dried. The charred mass was kept in a muffle furnace at 400^0C for 1 hour, it was taken out, ground well to fine powder and stored in vacuum desiccators. The Characteristics of the adsorbent is presented in the table-1

pH	6.9
Moisture Content, %	11.8
Ash Content, %	9.9
Volatile Matter, %	20.8
Water Soluble matter, %	0.40
Acid Soluble Matter, %	0.92
Bulk Density, g/mL	0.43
Specific Gravity	0.91
Porosity, %	49.8
BET Surface Area, m^2/g	478.529
Fixed Carbon, %	45.2

Table-1 Characteristics of the adsorbent

Adsorption studies

Adsorption experiments were carried out in 250ml Erlenmeyer flasks. A known weight of *Andrographis paniculata adsorbent was* added to 50ml of the dye solutions with an intial concentration of 10mg/l to 50mg/l. Flasks were shaken in an orbitary shaker with a speed of 120 rpm 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.

% MB dye removal$= Ci - Ce/Ci * 100$

Where Ci = initial concentration(mg/l),Ce = equilibrium concentration(mg/l)

The adsorption capacity Qe (mg/g), is obtained from the following equation

$$Qe = (Ci - Ce)V/M$$

Where, Q_e = adsorbent capacity(mg/g),C_i= initial MG concentration (mg/l),V = 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 decreases. Hence the pH of the medium was maintained at 6 for further studies.

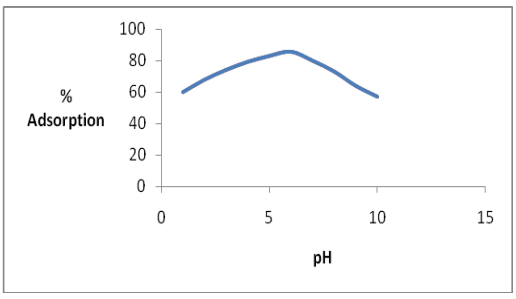

Fig:1 Effect of pH on the adsorption of MB on to the adsorbent

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 10mg/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].

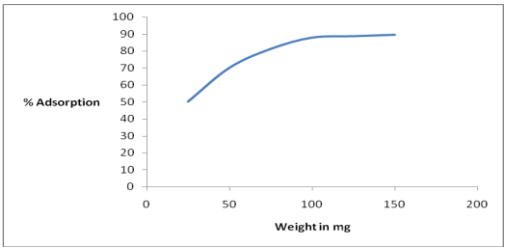

Fig:2 Effect of adsorbent dose on the adsorption of MB on to the adsorbent

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 10mg/l to 50mg/l, the percentage removal of MB dye decreased from 85% to 55%. As the initial concentration is increased the ratio of the number of vacant sites on the adsorbent to the dye molecules decreases.

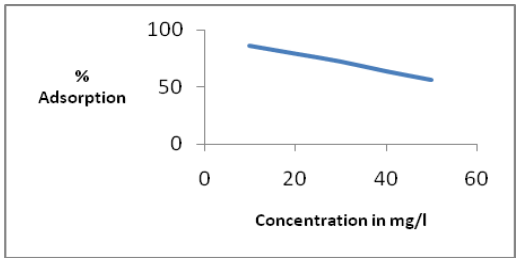

Fig:3 Effect of dye concentration on the adsorption of MB on to the adsorbent

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.

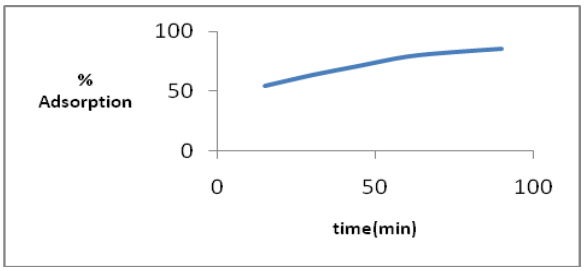

Fig:4 Effect of contact time on the adsorption of MB on to the adsorbent

IV. ADSORPTION ISOTHERMS

Langmuir Adsorption Isotherm

In our study Langmuir and Freundlich isotherms were utilized to describe the adsorption of methylene blue on to the adsorbent. 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-2.

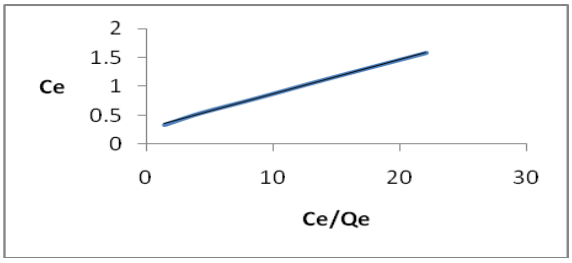

Fig:5 Langmuir isotherm for the adsorption of MB on to the adsorbent

Qo(mg/g)	b	R^2
16.6666	0.2264	0.999

Table -2.Langmuir constants

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 0.3063. 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

$$\log Qe = \log K_f + 1/n \log Ce$$

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 were calculated from slope and intercept respectively (fig-6). The values of K_f and n are given in table-3. The value of linear regression co-efficient (R^2) was found to be 0.963.This indicates that the adsorption process follows Langmuir adsorption isotherm more than Freundlich adsorption isotherm.

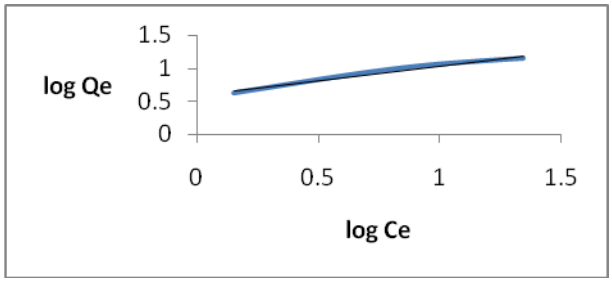

Fig:6 . Freundlich isotherm for the adsorption of MB on to the adsorbent

n	K_f(mg/g)	R^2
2.3094	3.9445	0.923

Table-3 Freundlich constants

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

V. KINETIC STUDY

Pseudo First Order Model

The linear form of Pseudo first order kinetic equation[25] is given as,

$$\log (q_e - qt) = \log q_e - (k_1/2.303)t$$

Where q_e is the amount of dye adsorbed at equilibrium. k_1 is the first order rate constant.

A plot of log (q_e-qt) verses t(min) gives a straight line fig.7 From the slope $k_1$and from the intercept q_e were determined.. These values are presented in the table-4.

q_e	k_1	R^2
13.9315	0.0207	0.999

Table-4 Pseudo First order kinetic parameters

The value of R^2 indicates that the first order kinetics was followed by MB adsorption.

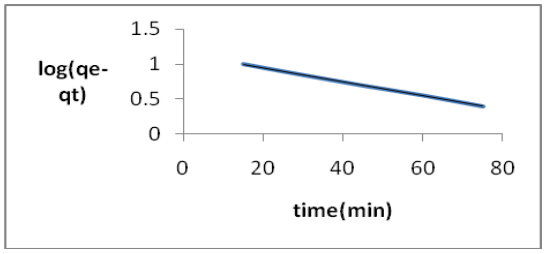

Fig:7. Pseudo first order kinetics for the adsorption of MB on to the adsorbent

Pseudo Second Order Model

The linear form of pseudo second order kinetic equation[26] is

$$t/qt = 1/k_2qe^2 + t/qe$$

Where k_2 is the rate constant of second order adsorption. The qe and k_2 can be determined from the slope and intercept of a linear plot of t/qt verses t shown in fig-8. These values are presented in the table-5.

Qe	k_2	R^2
25.6410	0.0004	0.8450

Table-5 Pseudo Second order kinetic parameters

The result shows that first order kinetics is more favored than second order kinetics.

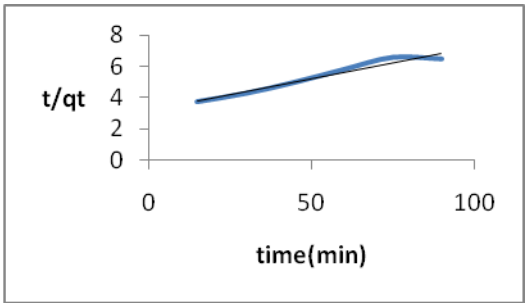

Fig:8. Pseudo second order kinetics for the adsorption of MB on to the adsorbent.

VI. 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 $\Delta G^{o,}$ 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 MG onto the adsorbent were calculated using the following equations.

$$K_0 = C_{solid} / C_{liquid}$$

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

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

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-6.

Conc.of MG dye (mg/l)	-ΔG^o (KJ/mol)				ΔH^o (KJ/mol)	ΔS^o (J/k/mol)
	30^0 C	40^0 C	50^0 C	60^0 C		
10	4.531	4.896	5.275	5.589	6.188	35.38
20	3.328	3.598	4.452	4.901	13.416	54.93
30	2.378	2.544	3.189	3.773	12.051	47.19
40	1.388	1.606	2.236	2.624	11.624	42.67
50	0.586	0.678	1.330	1.754	11.834	40.59

Table-6 Thermodynamic parameters for the adsorption of MB on to the adsorbent.

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.

VII. CONCLUSION

The adsorption of methylene blue from aqueous solution was studied with various parameters like contact time, pH, intial concentration, adsorbent dose and temperature. It was concluded that maximum adsorption of MB from aqueous solutions occurred at pH6. Kinetic and isotherm studies revealed that *Andrographis paniculata* leaves can be effectively employed for the adsorption of MB. The experimental data were correlated well by the Langmuir adsorption isotherm. The adsorption process was well described by pseudo first order kinetics. The result of this study indicates that this adsorbent can be successfully utilized for the removal of MB from aqueous solution.

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