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REMOVAL OF METHYLENE BLUE DYE FROM AQUEOUS SOLUTION BY ADSORPTION USING LOW COST ADSORBENT OBTAINED FROM *centella asiatica* LEAVES

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

Index terms- Methylene blue , Isotherm models, 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]. Over 10^5 commercial available dyes exist and more than $7x10^5$ tonnes are produced every year. As a result approximately$7x10^4$ tonnes of dyes are released into the water bodies every year. The pollution caused by the discharge of untreated effluents from these industries is a major concern. The presence of colour in water is highly visible and undesirabale[2]as it reduces sunlight penetration into the water, thus affecting aquatic plants leading to a disturbance of the ecosystem. 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 various 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 its high cost limits its use. 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 *Centella asiatica* 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. 1000 mg of Methylene blue was dissolved in one litre of double distilled water to get the stock solution. Desired concentration of the dye solution was obtained from the stock solution by dilution.

Preparation of adsorbent

Centella asiatica leaves was collected locally and washed with tape water several times to remove soil dust and finally washed with DD water. It was then 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	6.5
Moisture Content, %	13.5
Ash Content, %	10.2
Volatile Matter, %	21.3
Water Soluble matter, %	0.45
Acid Soluble Matter, %	0.89
Porosity, %	48.1
Micropore volume cm^3/g	0.194194
Average pore width ^0A	28.2065
BET Surface Area, m^2/g	604.27

Table-1 Characteristics of the adsorbent

Adsorption studies

Adsorption experiments were carried out in 250ml Erlenmeyer flasks. A known weight of *centella asiatica 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.

$$\%\ Dye\ \text{Re}moval = \frac{(C_0 - C_e)}{C_0}\ X\ 100$$

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

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

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

Where, Q_e = adsorbent capacity(mg/g),C_i= initial MB 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 influence of pH of the solution on the removal of the dye was studied with an initial dye concentration of 10mg/l, adsorbent dosage of 100mg, contact time 90min, temperature 303K and 120 rpm and varying the pH of the solution from 2 to 10.The pH of the working solution was controlled by adding 1NHCl or 1NNaOH solution. The results are presented in the fig-1. As the pH of the solution increased the percentage of the adsorption also increased and reaches the maximum at pH-6 and thereafter no appreciable change was observed. At low pH the dye is protonated and the surface of the adsorbent is positively charged which reduces the adsorption of the cationic form of the dye. In addition to that, the H^+ ions also compete with the dye for the available vacant sites of the adsorbent. With increase in the pH of the medium the positive charge on the adsorbent surface decreases which facilitates the adsorption of the dye molecules. Maximum adsorption was observed at pH -6. Hence the pH of the medium was maintained at 6 for further studies.

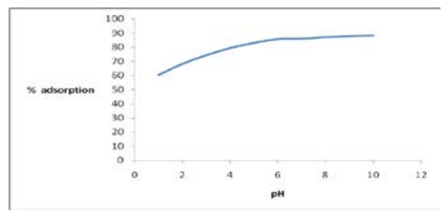

Fig:1 Effect of pH on the adsorption of MB on to the adsorbent

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].

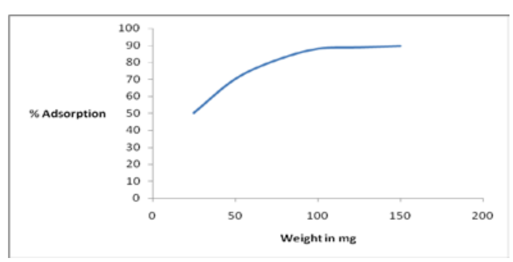

Fig:2 Effect of adsorbent dose on the adsorption of MB on to the adsorbent

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, keeping the other parameters constant, the the percentage removal of MB dye decreased from 83% to 46 %. As the initial concentration is increased the ratio of the number of vacant sites on the adsorbent to the dye molecules decreases. This leads to a decrease in the percentage of adsorption of the dye.

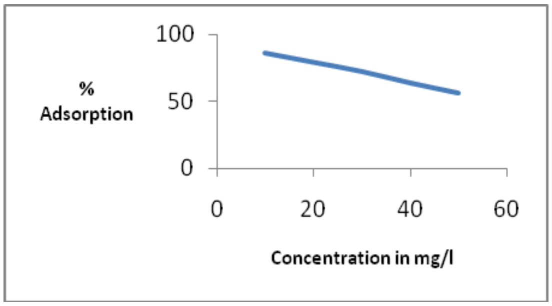

Fig:3 Effect of dye concentration on the adsorption of MB on to the adsorbent

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 later increases in a slow and gradual manner till it reaches the equilibrium state. Maximum adsorption was found to be at 90min. This is because the intial stage is film diffusion which is very rapid followed by pore diffusion which is a slow process. Therefore, 90min shaking time was found to be appropriate for the maximum adsorption and was maintained in all subsequent experiments.

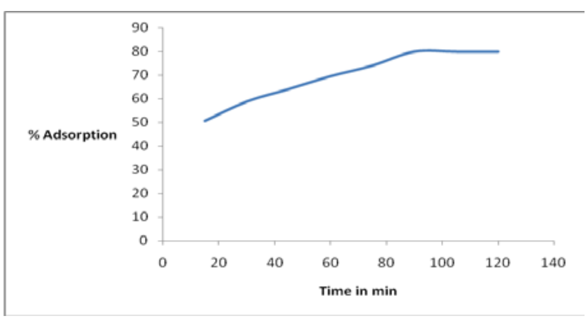

Fig:4 Effect of contact time on the adsorption of MB on to the adsorbent

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.

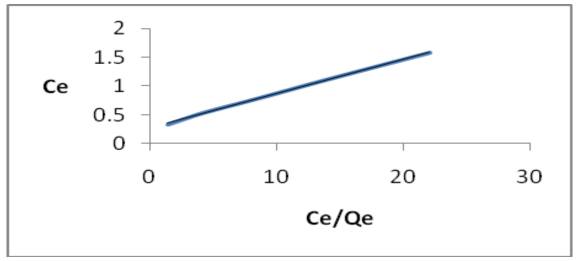

Fig:5 Langmuir isotherm for the adsorption of MB on to the adsorbent

Qo(mg/g)	b	R^2
13.5135	0.2710	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 – initial 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 MB concentration is 0.2695. 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

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

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 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.

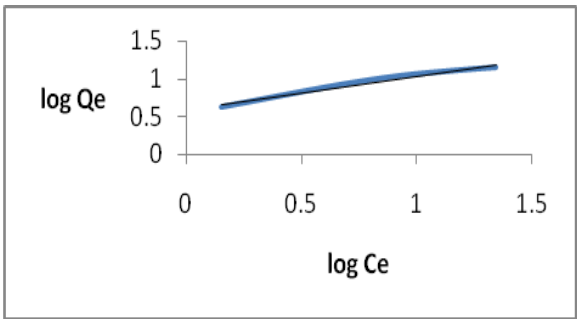

Fig:6 . Freundlich isotherm for the adsorption of MB on to the adsorbent

n	K_f(mg/g)	R^2
2.6178	3.7325	0.941

Table-3 Freundlich constants

The value of n lies between 2 and 10 indicating 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 $\Delta G^{o,}$ 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 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-4.

Conc.of MG dye (mg/l)	$-\Delta G^o$ (KJ/mol)				ΔH^o (KJ/mol)	ΔS^o (J/k/mol)
	30^0 C	40^0 C	50^0 C	60^0 C		
10	3.993	4.315	4.614	5.107	6.912	35.88
20	2.828	3.203	3.557	3.995	8.742	38.14
30	1.779	2.180	2.531	2.935	9.684	37.83
40	0.602	1.024	1.368	1.780	1.780	38.42
50	0.307	0.230	0.377	0.840	1.107	35.67

Table-4 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 positive 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 by the adsorbent obtained from *Centella asiatica* was studied with various parameters like effect of pH, adsorbent dose, dye concentration, contact time and temperature It was concluded that maximum adsorption of MB from aqueous solutions occurred at pH 6. The experimental data were correlated well by the Langmuir adsorption isotherm. 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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