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Removal of Methylene Blue from aqueous solution by *Cynodon dactylon* leaf powder

KEYWORDS: adsorption isotherm, batch process, exothermic nature, thermodynamic parameters.

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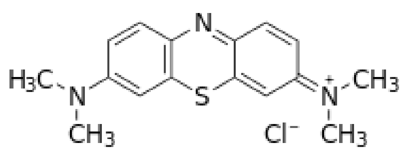
ABSTRACT *In this study, we reported the removal of Methylene Blue (MB) by Cynodon dactylon leaf powder (CDLP) using batch technique. Adsorption studies are conducted in different initial dye concentrations, adsorbent doses and temperature. The removal of MB is increases with decrease in concentration of dye. The experimental data were analysed by Langmuir, Freundlich and Temkin models. The adsorption capacity (Qo) of CDLP was found to be 24.57 mg/g. From the effect of temperature, thermodynamic parameters such as the free energy change (ΔGo), enthalpy change (ΔHo) and entropy change (ΔSo) were determined.*

1. Introduction

Dyeing process is a major source of contamination responsible for the environmental pollution. Many dyes have toxic as well as carcinogenic, mutagenic and teratogenic effects [1] on aquatic life and to human [2]. Therefore, decolourisation of dyes is an important aspect of wastewater before discharge. Various physical and chemical methods such as coagulation, floatation, chemical oxidation, solvent extraction, precipitation, flocculation etc., have been attempted in order to remove colour from wastewater. But they have not meant very successful because dyes are stable to light and oxidizing agents and they involve high operational cost and aerobic digestion [3], [4]. Adsorption has been tried and found a better technique [5] compared to other methods of wastewater treatment in terms of cost, simplicity of design and operation, availability, effectiveness and their insensitivity to toxic substances.

Adsorption of dyes onto granulated activated carbon (GAC) or powdered activated carbon is a common practice [6]-[8]. However, the technology for manufacturing good quality of activated carbon is still extremely cost – prohibitive and the regeneration or disposal of the carbon is often problematic. Numerous novel materials have been developed as adsorbents in recent years particularly from various plant materials with the objective of replacing activated carbon with cheaper, more effective and recyclable alternatives. Such low cost adsorbents have been used for treatment of various pollutants in wastewater [9]. Biosorbents collected from biological sources such as pineapple stem [10], banana peel [11] coir pith [12], Orange peel [13], guava leaf powder [14] etc., have been shown to give satisfactory results in removal of commercial dyes from aqueous solution.

The present work is a non-conventional; adsorbent developed from a well-known bio resource the leaves of Cynodon dactylon, to remove Methylene Blue from aqueous medium. Actually, it is an easily available plant species. Cynodon dactylon (Family poaceae) is a vital ingredient in various ayurvedic preparations [15]. Methylene Blue is a cationic dye and its structure is given as follows.



Structure of Methylene Blue

2. Experimental procedure

Fresh leaves of Cynodon dactylon were collected and washed with distilled water. They were shade dried for 15 days. They were then crushed in a grinder to obtain CDLP powder. This fraction was again thoroughly washed with double distilled water to remove dust and other impurities and dried at 100°C. It was stored in a well-closed container free from environmental climatic changes until use. Methylene blue (Merck) was used without further purification. All solutions were made in double distilled water.

Adsorption experiments were carried out in a batch process using aqueous solution of MB by varying the initial concentration of dye, initial pH, temperature, adsorbent dosage and contact time. In each experiment, accurately weighed CDLP was added to 50 ml of aqueous dye solution in a 250 ml conical flask and the mixture was agitated in a thermostatic mechanical shaker for a given period at a constant temperature. The samples were withdrawn at a regular interval of contact time and centrifuged (Remi Research centrifuge). The dye concentration was determined using UV-Visible spectrophotometer (Systronic Spectrophotometer -104) at 650 nm. The equilibrium solid-phase concentration q_e (mg/g) was calculated according to the following relation:

$q_e = (C_i - C_e)$ ´ V/ m--------------- (1)

where q_e is the amount of dye adsorbed by CDLP;

C_i and C_e (ppm) are the initial and the equilibrium liquid phase concentration dye solution

V is the initial volume of dye solution (l)

m is the weight of the adsorbent (g)

3. Results and Discussion

3.1. Effect of dose and the initial concentration of the dye

To examine the effect of adsorbent mass on percentage removal of MB, a series of experiments were performed keeping the contact time constant and varying both the amount of adsorbent and dye concentration at constant temperature. The result indicated that the percentage removal of dye increases with an increase of CDLP. This may be explained by the effect of adsorbent mass on porosity of the adsorbent suspension. In general, these might have been affected by changes in a number of physical properties of the solid-liquid suspensions including their viscosity. A similar observation is observed in adsorption of MB on Neem Leaf powder [9].

Table 1: Effect of initial dye concentration on the removal of MB by CDLP at 303K
Amount of CDLP = 2 g/L; pH = 7.0.

Ci (mg/L)	C_e (mg/L)	% removal of MB	Amount adsorbed (mg/g)
15	0.50	96.7	7.25
20	0.90	95.5	9.55
25	1.90	92.4	11.6
30	3.60	88.0	13.2
40	5.50	86.3	17.2
50	7.40	85.2	21.3

Table 2: The effect of dose on the removal of MB by CDLP.
[MB] = 20 mg/L, temperature 303 K and pH = 7.0.

Dose (g/l)	C_e (mg/L)	% removal of MB	Amount adsorbed (mg/g)
1.0	3.9	80.5	16.1
1.5	2.0	90.0	12.0
2.0	1.3	93.5	9.35
2.5	0.90	95.5	7.64
3.0	0.80	96.0	6.40
3.5	0.60	97.0	5.54
5.0	0.20	99.0	3.96
6.0	0.00	100	3.33

3.2. Adsorption isotherm studies

Freundlich isotherm (equation 2) is widely used to explain adsorption on a surface having heterogeneous energy distribution. The Langmuir adsorption isotherm (equation 3) is strictly applicable to mono layer chemisorptions. The Temkin isotherm (equation 4) can be expressed in its linear form.

$$q_e = K_F C_e^{1/n} \quad \text{------------------ (2)}$$

K_F and n are indicators of adsorption capacity and adsorption intensity respectively.

$$\frac{1}{qe} = \frac{1}{q_m K_l C_e} + \frac{1}{q_m} \quad \text{-----------------(3)}$$

By plotting $1/q_e$ *versus* $1/C_e$ the Langmuir constant can be obtained.

$$q_e = B_T \ln A_T + B_T \ln C_e \quad \text{---------------(4)}$$

Where $B_T = RT/b_T$, T is the absolute temperature in Kelvin and R is universal gas constant, 8.314 J/mol/K . The contant b_T is related to the heat of adsorption [16].

CDLP is found to have a relatively large adsorption capacity of 24.7 mg/g and this indicates that it could be considered a promising material for the removal of basic dye from aqueous solution.

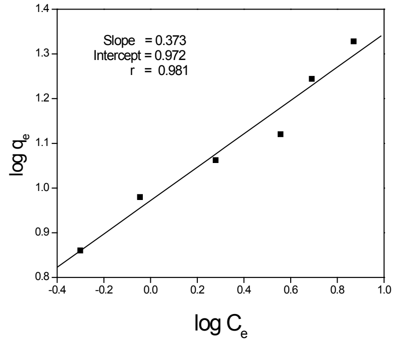


Fig. 1. Freundlich adsorption isotherm for the removal of MB by CDLP

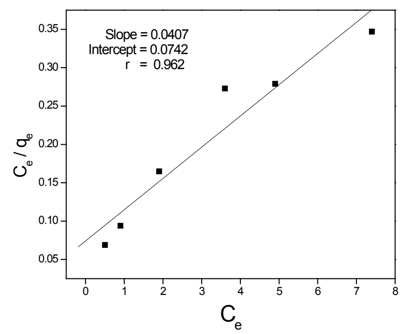


Fig. 2. Langmuir adsorption isotherm for the removal of MB by CDLP

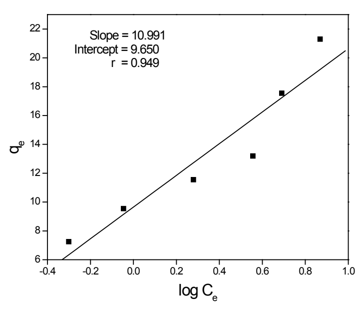


Fig. 3. Temkin adsorption isotherm for the removal of MB by CDLP

Table: 3 Langmuir, Freundlich and Temkin isotherm constants and correlation coefficients for adsorption of MB onto CDLP.

Langmuir isotherm	Freundlich isotherm	Temkin isotherm
Q_o = 24.7 mg/g b = 0.546 r = 0.962 R_L = 0.066	K_f = 9.375 L/g n = 2.68 r = 0.981	A_T = 2.404 B_T = 10.991 b_T = 229.2 r = 0.949

Table 4: Comparison of adsorption capacity of various adsorbents for Methylene Blue

Adsorbent	Q_o (mgg^{-1})	Temperature (K)	Reference
Activated carbon from Coconut coir	15.59	303	[17]
Wheat shell	16.56	303	[18]
Tartaric acid modified wheat Bran	25.18	303	[19]
Banana peel	20.80	303	[20]
Neem leaf powder	8.76– 19.6	303	[9]
Beer brewery Waste	4.92	303	[21]
Sugarcane dust	3.75	303	[22]
Date stones	12.8	303	[23]
Fly ash	13.4	303	[8]
Orange peel	18.6	303	[20]
Clay	6.30	303	[24]
CDLP	24.7	303	This study

3.3. Effect of temperature and Thermodynamic parameters

The effect of temperature on the removal of MB by CDLP is carried out at different temperatures. This indicated that the extend of adsorption decreases as the temperature increases (Fig. 10). Therefore, in our study MB adsorption on CDLP is an exothermic process. The thermodynamic parameters for the removal of MB by CDLP were calculated using the following basic thermodynamic equations.

$DG^o = - RT \ln K_c$ ------------- (5)

$\ln K_c = DS^o/R - DH^o/RT$ ------------- (6)

where R is the universal gas constant, 8.314 J/mol/K; and T, the absolute temperature (K); and DH°, DG° & DS° are the changes in enthalpy (J/mol), Gibb's free energy (J/mol) and entropy (J/K/mol) respectively. The negative value of DS° (- 83.88 J/K/mol) interprets the decreased randomness at the solid-liquid interface.

Table 5: Thermodynamic parameters for the removal of MB by CDLP.

Temperature (K)	q_e (mg/g)	k_c (S^{-1})	DG (kJ/mol)	DH (kJ/mol)	DS (J/K/mol)
303	9.55	21.2	−3.34		
313	9.35	14.4	−3.01		
318	9.15	10.8	−2.73	−3.76	−83.88
323	8.95	8.52	−2.50		
333	8.80	7.33	−2.40		

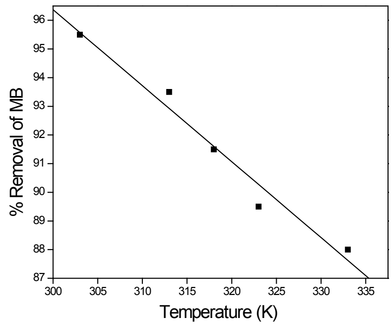


Fig. 4. Effect of Temperature for the removal of MB by CDLP

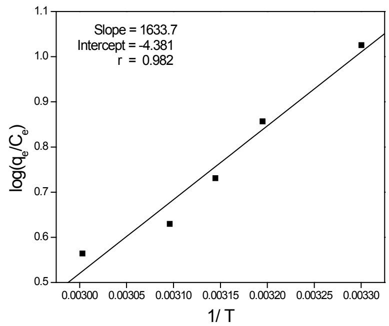


Fig. 5. van't Hoff plot for the removal of MB by CDLP

4. Conclusion

The present investigation shows that CDLP is an effective adsorbent for the removal of MB from aqueous solution. From the kinetics studies it is observed that

Freundlich, and Langmuir isotherm, Temkin models are found to be linear, indicating the applicability of classical adsorption isotherm in this system.

the exothermic nature of the process.

the data reported may be very useful for designing an economically cheap treatment process using batch process for the accumulation of MB in aqueous solution.

adsorption capacity of various adsorbent in MB removal was compared with CDLP.

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