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BIOSORPTION OF METHYLENE BLUE FROM WASTE WATER USING SCABIOSAPROLIFERA (CARMEL DAISY)

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INTRODUCTION

Many industries use synthetic dyes and pigments that may find their way into natural waterways [1].Reactive dyes, an anionic or cationic dye, are most commonly used due to their provision of bright colors, excellent color fastness, and easy application. However, many reactive dyes are toxic to organisms and may cause direct harm to aquatic life. Accumulation of these dyes in wastewater from industries such as textiles, paper, cosmetics, rubber, and plastics has been regarded as a significant source of water pollution [2].Discharge of colored wastewater without proper treatment can results in numerous problems such as chemical oxygen demand (COD) by the water body and an increase in toxicity. Currently, there are about 10,000 different commercial dyes and pigments exist and over $7x10^5$ tones of synthetic dyes are produced annually world-wide [3].Furthermore, dyes in Waste water are difficult to remove because they are stable to light, heat and oxidizing agents. In short, they are not easily degradable [4]. Moreover, their degradation products may be mutagenic and carcinogenic [5]. Many dyes may cause allergic dermatitis, skin irritation, dysfunction of kidney, liver, brain, reproductive and central nervous system[6]. Organic dyes are harmful to human beings, the need to remove color from wastewater effluents become environmentally important. It is rather difficult to treat dye effluents because of their synthetic origins and mainly aromatic structures, which are biologically non-degradable. Among several chemical and physical methods, adsorption process is one of the effective techniques that have been successfully employed for color removal from wastewater [7]. Numerous treatment processes are now available for effluent discharged from industrial processes containing dyes as:adsorption[8], chemical oxidation[9], electrolysis [10],biodegradation [11], and photo-catalysis[12]. Among all the physical treatments, adsorption process has been reported to be the most effective method for water decontamination [13]. The removal of methylene blue from wastewater needs great attention. In this present study, *scabiosaprolifera*(Carmel Daisy) has been utilized as an adsorbent for the removal of methylene blue from aqueous solutions. The sorption data have also been correlated with adsorption isotherms and kinetics of adsorption has been studied to determine the efficiency of an adsorption process.

The present research aims to remove methylene blue from aqueous solution using Carmel Daisy as bio-sorbent. Adsorption isotherm which includes Langmuir andFreundlich was used to correlate the adsorption data, kinetic and thermodynamic parameters were studied too.

1.MATERIALS AND METHODS

1.1. Preparation of Methylene Blue Solution

Methylene blue (MB) a basic cationic dye, ($C_{16}H_{18}ClN_3S.3H_2O$; M.W: 373.90), was supplied by UNI-CHEM and used as an adsorbate. Stock solution of 1000 ppm was prepared by dissolving an accurately measured weight in 1 L distilled water. The solutions for use in experiments were obtained by diluting the stock solution to the desired concentration.

1.2. Preparation and Characterization of Adsorbent

Carmel Daisy (CD) utilized in this work was collected fromHoula valley South Lebanon. The collected plants were carefully washedwith running water to remove impurities, and then they were washed with distilled water. The clean plant was dried at room temperature for 10 days then in an oven at 70 ^{o}C for 6 hours. The dried CD was grinded to a fine powder in a grinding mill to get a size of 0.25 mm. Fourier transformation infrared (FTIR) analysis using JASCO FT/IR-6300 spectrometer was applied to determine the surface functional groups interfering in the adsorption of MB, where the spectra was recorded in the range of 4000 to 400 cm^{-1}.

1.3. Experimental Methods

Batch experiments to study the capacity of CD to remove MB from solution were carried out using a series of Erlenmeyer flask of 50 ml capacity where 25 ml of MB were mixed with 0.25 g of the adsorbent. The experiments were prepared to study the effect of initial MB concentration, pH, contact time, adsorbent dose and temperature on adsorption of MB from its solution. All the adsorption experiments were carried out at room temperature and the original pH of the solution except where the effect of temperature and pH was being investigated. The initial pH was adjusted with(0.1 M) HNO_3 or(0.1 M) NaOH solutions. At the end of each adsorption experiment, the adsorbent was removed by filtration through a (0.45 μm) filter paper, and the dye concentration at equivalence was analyzed using a UV-visible spectrophotometer by monitoring the absorbance changes at λ_{max}= 665 nm. The dye removal efficiency (R) and the amount of dye adsorbed per unit mass of adsorbent at time t (q_t, $mg.g^{-1}$) and at equilibrium (q_e, $mg.g^{-1}$), were calculated using the following equations:

$R\,(\%) = [(C_0 - C_e)/C_0]*100$

$q_t = [(C_0 - C_t)/m]*V$

$q_e = [(C_0 - C_e)/m]*V$

C_0($mg.L^{-1}$): initialdye concentration

C_t ($mg.L^{-1}$): dye concentration at time *t*

C_e($mg.L^{-1}$): equilibriumdye concentration

q_e($mg.g^{-1}$): amount of dye adsorbed onto the adsorbent at equilibrium

q_t($mg.g^{-1}$): amount of dye adsorbed onto the adsorbent at time t

V (L): volume of the dye solution

m(g): mass of the adsorbent

1.4. Adsorption Isotherm

Adsorption isotherm is basically important to describe how solutes interact with adsorbates, and is critical in optimizing the use of adsorbents[14].

1.4.1.Langmuir Isotherm

It is based on the assumption that it predicts monolayer coverage of the adsorbate on the outer surface of the adsorbent. This model also suggests that there is no lateral interaction between the sorbed molecules[14]. Linear form of Langmuir isotherm is:

$1/q_e=1/bq_mC_e + 1/q_m$

C_e ($mg.L^{-1}$): equilibrium dye concentration

q_e($mg.g^{-1}$): amount of dye adsorbed onto adsorbent at equilibrium

q_m ($mg.g^{-1}$): maximum monolayer capacity of the adsorbent

b ($L.mg^{-1}$): Langmuir isotherm constant

1.4.2.Freundlich Isotherm

It is based on multilayer adsorption on heterogeneous surface[14]. The linear form of Freundlich isotherm is:

$lnq_e = lnK_F + (1/n)lnC_e$

K_F(L.mg^{-1}): Freundlich constant indicating adsorption capacity

n: adsorption intensity

2. RESULTS AND DISCUSSION

2.1. Characterization of CD

The infrared of CD is shown in Fig. 1. The intense broad peak (1) around3300 cm^{-1} corresponds to the stretching vibration of amino and hydroxyl groups. Peak (2) at ~2900 cm^{-1} can be referred to C-H stretching vibrations. Peak (3) at 1740 cm^{-1} is attributed to carboxyl group and that at 1600 cm^{-1}(4) corresponds to C=C stretching vibration. Peak (5) at 1500 cm^{-1} is referred to N-H bending mode, and peaks (6, 8 & 9) at ~1450, 1350 & 1250 cm^{-1} respectively are attributed to C-H bending vibrations. The intense peak (10) at 1100 cm^{-1} reveals the stretching vibration of C-O.

2.2. Effect of Mb Concentration

To investigate the effects of the MB concentration on the adsorption capacity, the process was carried out with initial MB concentration between 100 and 400 mg.L^{-1} while keeping the other four parameters constant. As can be seen from Fig. 2 (a), there is a general increase in adsorption capacity of MB with the increasing concentration.

An increase in the initial MB concentration from 100 to 400 mg.L^{-1}, leads to an increase in the adsorption capacity of CD as well from 9.54 to 37.65 mg.g^{-1} respectively, and this can be attributed to an increase in the driving force for the mass transfer between the aqueous phases and the solid phase [15].

2.3. Effect of Temperature

Temperature is an important factor that can affect the adsorption process. The effect of temperature on MB adsorption is shown in Fig.2(b). A decrease in the efficiency of removal of the dye from 95.4 to 95.1 % as the temperature increases from 25 to 45 ºC can be seen, revealing that the adsorption of MB on CD is of an exothermic nature, and lower temperature favors the adsorption.

2.4. Effect of Contact Time

The effect of time has also been studied over an interval of 5 to 120 minutes. As shown in Fig. 2(c)the efficiency of removal increases with the contact time to reach an optimum of more than (95%) after 60 min. MB is rapidly removed within the first 5 min of contact then the rate gradually becomes slower as the equilibrium is attained. This is due to the availability of high number of adsorption vacant sites on the surface of CD at the initial stage of adsorption. However, the remaining vacant sites are less available for adsorption as time lapses because of the repulsive forces between the adsorbed and the free molecules [16].

2.5. Effect of pH

The pH of the initial solution is one of the most important factors influencing the adsorption of dyes on an adsorbent [17]. Fig. 2(d) shows the effect of initial pH on the % of MB removed. With pH increasing from 3 to 4, the % removed increases from 96.17 to 96.87 % respectively. Further increase in the pH leads to a drop in the % removed to reach a minimum of 95.7% at pH = 9. Generally, the dissolved cationic dye is positively charged in aqueous solution. At low pH, the surface of the adsorbent gathers positive charges by adsorbing H^+ ions, which prevents the adsorption of cationic dye onto the adsorbent surface due to electrostatic repulsion and the competition between H^+ ions and the cationic dye for the adsorption sites [15]. If electrostatic attraction was the only mechanism for MB adsorption, the % removed should have increased with the increase in pH. However, the experimental data from this study did not follow this prediction, revealing that electrostatic interaction was not the only mechanism for MB dye adsorption in the present system. It seems that the phenomenon of dye removal by CD is carried out by several sorption processes (adsorption, ion exchange, hydrogen bonding, chelation for example). Similar observation was previously reported for MB sorption on wheat bran [18].

2.6. Effect of Adsorbent Dose

The effect of CD dose on MB adsorption is shown in Fig. 2(e). With increasing the adsorbent dose from 0.1 to 0.7 g, the % of MB removed increased from 94 to 97.74 %, but the adsorption capacity (q_e) for CD decreased from 23.5 to 3.4 $mg.g^{-1}$ respectively. This phenomenon can be referred to the increase in the unsaturated adsorption sites coming along with the high surface area. High number of unsaturated adsorption sites occurs with higher adsorbent dose favoring the adsorption[17].

2.7. Adsorption Isotherms

2.7.1. Langmuir Isotherm: The maximum monolayer capacity $q_m$and Langmuir isotherm constant *b* can be calculated from the intercept and slope, respectively. The values are listed in Table 1. The linear plot of $1/q_e$ versus $1/C_e$ with a correlation coefficient $R^2 = 0.999$ shows that the studied process obeys Langumir adsorption isotherm. Moreover, q_{max} calculated from Langmuir isotherm was greater than the experimental values. Therefore the Langmuir model does not describe the adsorption of MB on CD. Similar results were reported by Tingguo Y. and Lijuan W. [19].

2.7.2.Freundlich Isotherm

The adsorption capacity *n* and Freundlich constant K_F can be calculated from the slope and intercept, respectively. And the values are listed in Table 1 as well. The plot of ln q_e versus ln C_e showed linearity with $R^2 = 0.999$ indicating that this process is consistent with Freundlich adsorption isotherm.

The time data up to 120 min was tested for the following two kinetic models:

Pseudo-first-order rate equation of Lagergren

$log(q_e-q_t) = logq_e – k1/2.303 * t$

Pseudo-second-order rate equation

$t/q_t = 1/k_2q_e^2 + 1/q_e * t$

k_1(L.min^{-1}): adsorption rate constant for 1st order kinetic

k_2 (g.mg^{-1}.min): rate constant of pseudo-second-order adsorption

Two kinetic models were studied; their parameters and correlation coefficients of MB were calculated from Fig. 5&6 and listed in Table 2. From Fig. 5it is observed that for the first order kinetic model $R^2 = 0.949$ and the adsorption capacity is much lower than that obtained experimentally. On the other hand, R^2 for the second model is 1 showed in Fig. 6, and the values obtained are comparable with the experimental values. This observation suggests the applicability of the second kinetic model on the adsorption process in this study.

Thermodynamic Parameters

The adsorption mechanism may be determined through the thermodynamic quantities as the change in free energy (ΔG^0), enthalpy of adsorption(ΔH^0), and entropy (ΔS^0). Thermodynamic parameters of the adsorption of MB on the surface of CD were determined at five various temperatures and initial dye concentration of 100 $mg.L^{-1}$ using the following equations.

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

Where T is the temperature in Kelvin, R is the gas constant (8.314×10^{-3} kJ/mol K), and K_c is the distribution coefficient determined as: $K_c = q_e/C_e$

ΔH^0 and ΔS^0 are determined from Van't Hoff equation:

$\log K_c = \Delta S^0/2.303R - \Delta H^0/2.303RT$

ΔH^0 and ΔS^0 were calculated from the slope and intercept of the plot between $\log K_c$ and 1/T. their values are given in Table 3 below. The negative value of ΔH^0 confirms the exothermic nature of the adsorption of MB on CD surface. The positive ΔS^0 value reflects the change occurring. And the negative value of ΔG^0 reveals the spontaneity of the adsorption process.

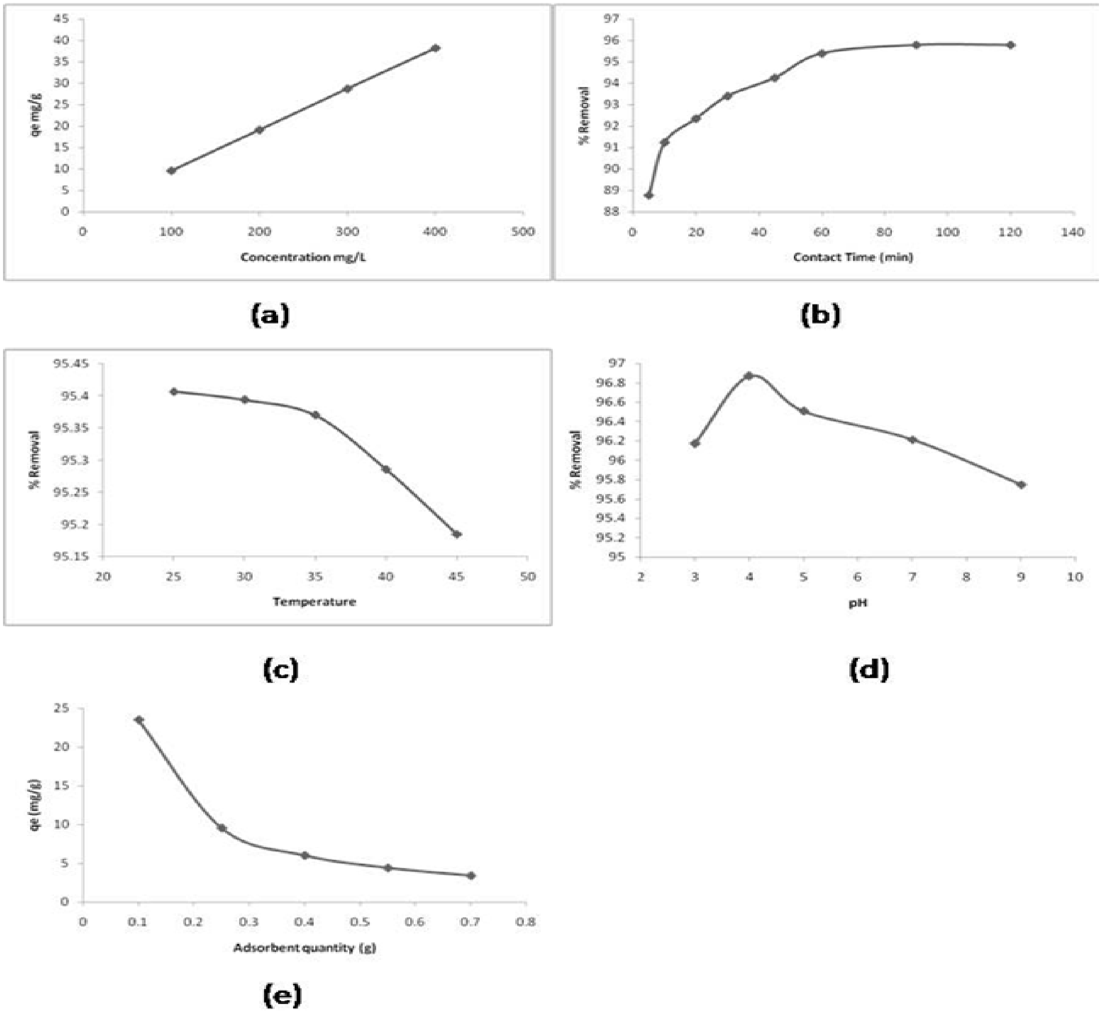

Figure 1: Effect of (a) Concentration, (b) time, (c) Temperature, (d) pH and (e) dose on adsorption of MB

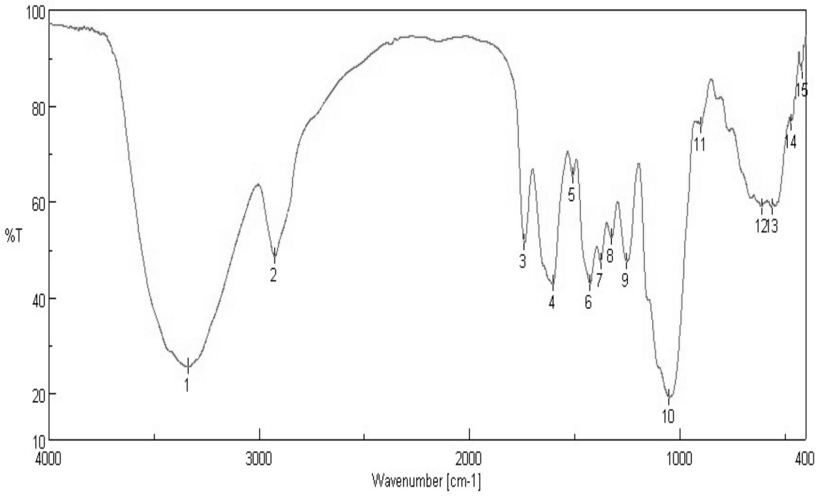

Figure 2: IR spectrum of CD

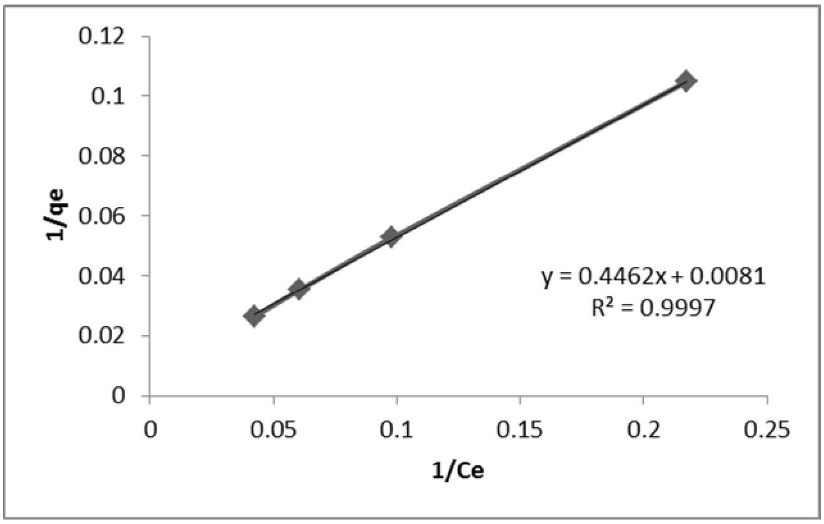

Figure 3: Langumir isotherm using CD

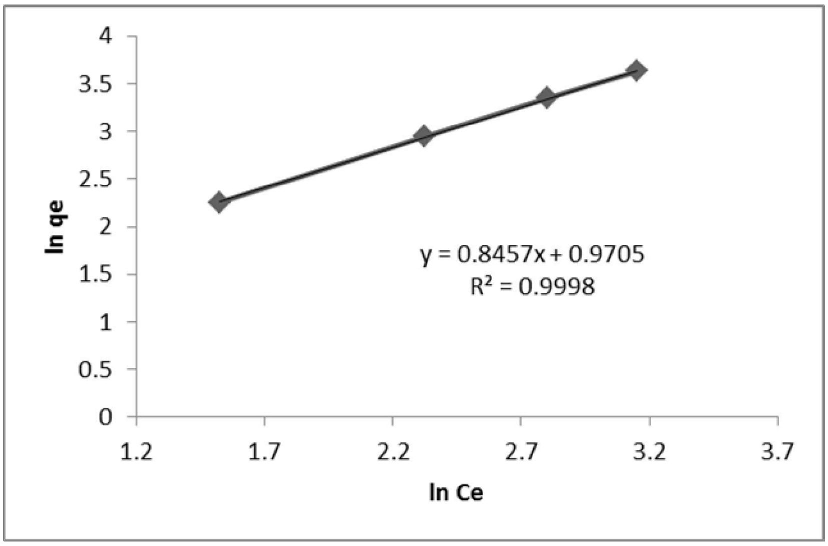

Figure 4: Freundlich Isotherm Using CD

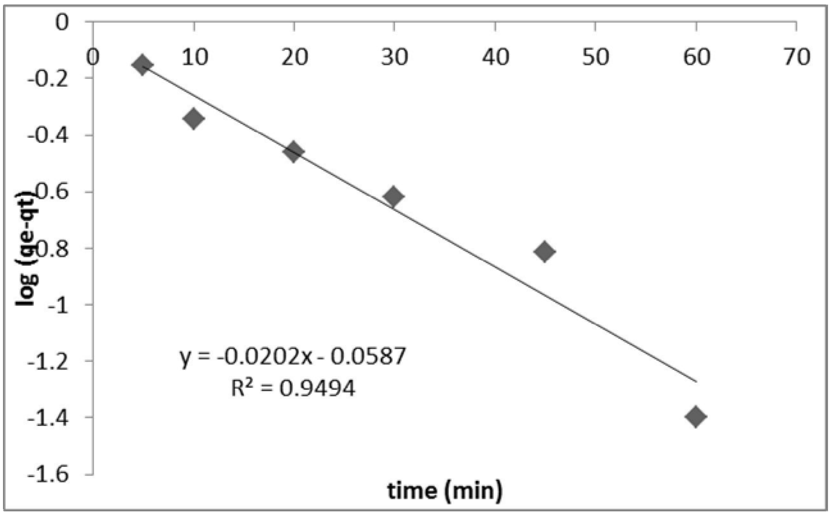

Figure 5: Pseudo first order kinetic plot of MB adsorption on CD

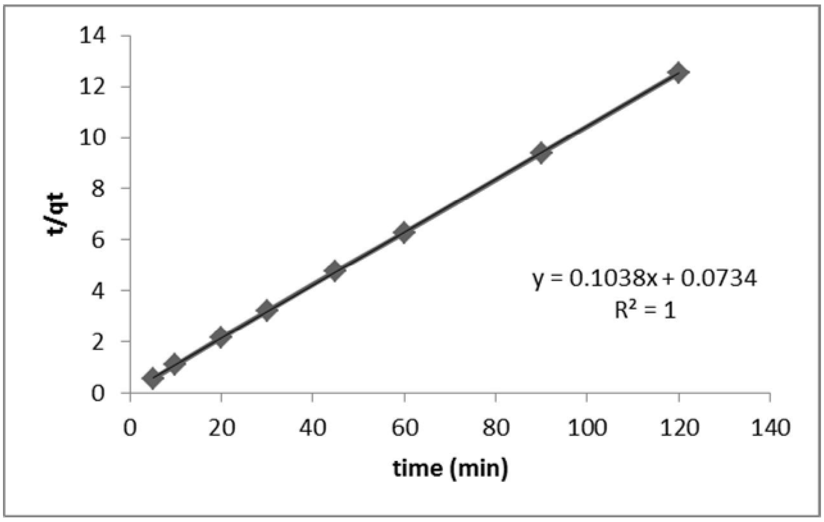

Figure 6: Pseudo second order kinetic plot of MB adsorption on CD

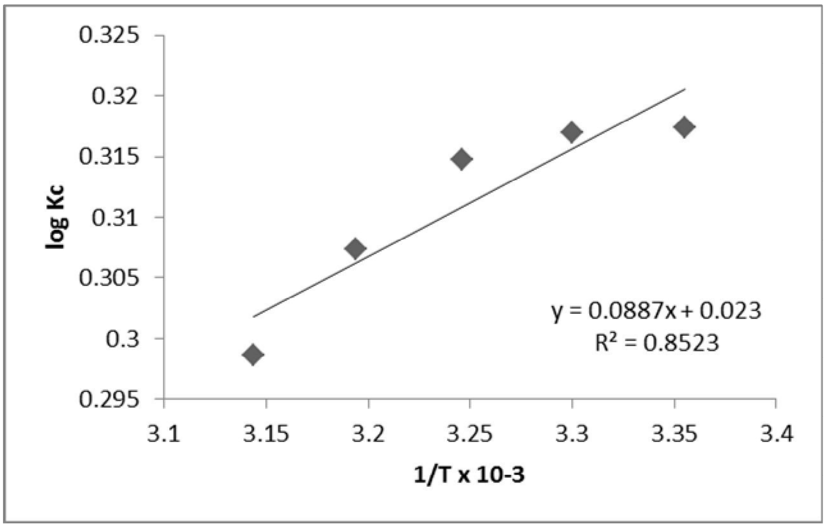

Figure 7: Van’t Hoff plots

Table 1: Equilibrium constatns for MB adsorption on CD

Langmuir	q_{max}	b	R^2
	125	0.0179	0.999
Freundlich	n	K_F	R^2
	1.183	2.637	0.999

Table 2: Kinetic parameters for adsorption of MB on CD

Pseudo 1st order	k_1	**qe**	R^2
	0.460	0.87	0.949
Pseudo 2nd order	k_2	**qe**	R^2
	0.145	9.70	0.999

Table 3: Thermodynamic parameters for adsorption of MB on CD

T	$Log\ K_c$	$\Delta H^0 \times 10^{-3}$ (kJ.mol^{-1})	$\Delta S^0 \times 10^{-4}$ (kJ.mol^{-1}.K^{-1})	ΔG^0 (kJ mol^{-1})
298	0.3174	-1.685	4.403	-1.810
303	0.317	-1.685	4.403	-1.838
308	0.3147	-1.685	4.403	-1.855
313	0.3074	-1.685	4.403	-1.842
318	0.2986	-1.685	4.403	-1.818

3. CONCLUSION

In the present study, *scabiosaprolifera* (Carmel Daisy) a natural growing plant in Houlavaly was used as a Bio-sorbent for the removal of Methylene Blue from waste water and to study its adsorption behavior. Kinetic study of MB showed that it followed pseudo-second-order kinetic model. The maximum loading capacity was found to be 37.65 mn.g^{-1}. The adsorption data showed a better fit to Freundlich than to Langumir isotherms. The adsorption process was found to be spontaneous and of exothermic nature under the studied conditions. This study provided a natural occurring, low cost, and environmentally friendly adsorbent for the treatment especially the removal of MB.

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