



Thermodynamics and Equilibrium Studies on the Removal of Methyl Violet by *Ulva Lactuca* Algae

KEYWORDS

adsorption isotherm, batch process, kinetics, thermodynamic parameters

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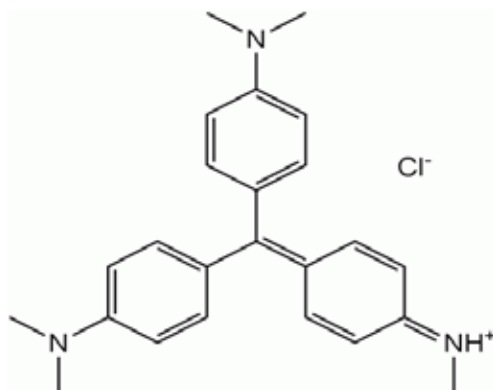
ABSTRACT Batch adsorption experiment was carried out using a novel adsorbent *Ulva lactuca* (UL) for the removal of Methyl violet (MV) from aqueous solution. Potential of UL for adsorption of MV was considered to be excellent. Effect of adsorbent dosage, concentration, and temperature was studied. Freundlich, Langmuir and Temkin isotherm models were used to test the equilibrium data. The best fitting isotherm models were found to be Langmuir. Thermodynamic analysis showed negative values of ΔG indicating adsorption was favourable and spontaneous, positive values of ΔH indicating endothermic physical adsorption and positive values of ΔS indicating increased disorder and randomness at the solid solution interface of MV with the adsorbent UL.

Introduction

Synthetic dyes are used in industrial processes, such as textile industries, paper printing and photography[1]. Waste effluent containing coloured compound causes serious environmental problems. Dyes can have acute effects on exposed organisms being dependent on the exposure time and dye concentrations. Dyes are inherently highly visible meaning that concentrations as low as 0.005 ppm capture the attention of both the public and the authorities[2]. Dye absorbs and reflects sunlight entering water and harmful to bacteria and hinder photosynthesis in aquatic plants [3]. Basic dyes have high intensity of colours and are highly visible even in a very low concentration[4]. Prolonged exposure of methyl violet can produce skin and eye damage. Activated carbon has been investigated for Adsorption of basic dyes[5], but its high cost limits its commercial application. In recent years, extensive research has been undertaken to develop alternative and economic adsorbents.

Among the biological materials, marine algae known as seaweeds, have been reported to have high metal binding capacities due to the presence of polysaccharides, proteins or lipid on the cell wall surface containing functional groups such as amino, hydroxyl, carboxyl and sulphate, which can act as binding sites for metals[6]. The green algae, *Ulva lactuca* and *Sargassum* are particularly useful in these respects because of its wide distribution and relatively simple structure. *Ulva lactuca* and *Saragassum* have sheet-like thallus structures which have two cells thicknesses, resulting relatively in large surface area having uniform and physiologically active cells[7]. *Ulva lactuca* is a widespread algae along the shores.

The objective of this work is to examine the efficiency of *Ulva Lactuca* biomass in removing Methyl Violet dye from aqueous solution under different conditions.



Molecular structure of Methyl violet Dye

Experimental Procedure

Ulva Lactuca were collected from the sand spit sea side near Mandapam coast, India. They were washed thoroughly with tap water. Then distilled water and dried in oven at 60 °C for overnight in order to remove moisture. The dry constant was grinding to obtain 100 micron mesh sizes and then it was used for adsorption studies.

The basic dye, Methyl Violet, was used without further purification. A stock solution of 1000 mg/dm³ was prepared by dissolving a weighed amount of Methyl Violet in 1000 ml distilled water. The experimental solution was prepared by diluting the stock solution with distilled water when necessary.

Biosorption Studies

Batch adsorption experiments were carried out in a mechanical stirrer at 150 rpm using 100mL shaking flasks containing 50mL of dye solution. Influence of each parameter (initial dye concentration, adsorbent dose and temperature) was evaluated by varying the parameter under evaluation, while all other parameters in the experiment were maintained constant. After stirring, the solutions were centrifuged to get clear supernatant and the dye concentration in the supernatant was calculated by measuring absorbance at 584nm (λ_{max}) with a systronic Spectrophotometer.

To determine the percentage of dye removal equation (1) is used:

$$\% \text{ removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

Where C_0 and C_e are the initial and equilibrium concentrations of dye (mg L^{-1}), respectively.

$$qe = (C_0 - C_e) \times \left(\frac{V}{m}\right) \quad (2)$$

The equilibrium solid phase concentration q_e (mg/g) was then calculated according to the following equation:

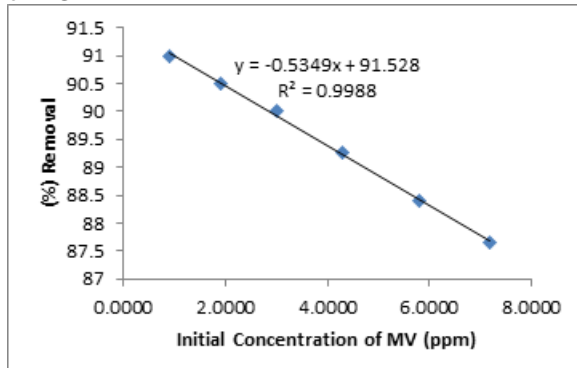
Where q_e (mg/g) is the amount of dye adsorbed by the biomass; V (mL), the initial volume of the dye solution; and m (g), the weight of the algae powder. All the experiments were repeated thrice and the mean values were calculated.

Results and discussion

Effect of initial dye concentration

The influence of dye concentration on the adsorption of the dye is shown in Fig. 1. When the dye concentration is increases from 10 ppm to 60 ppm, the percentage of dye adsorbed decreases from 91% to 87%. The results show that the % removal depends on the initial dye concentration.

Figure 1: Effect of Initial Concentration on the removal of MG

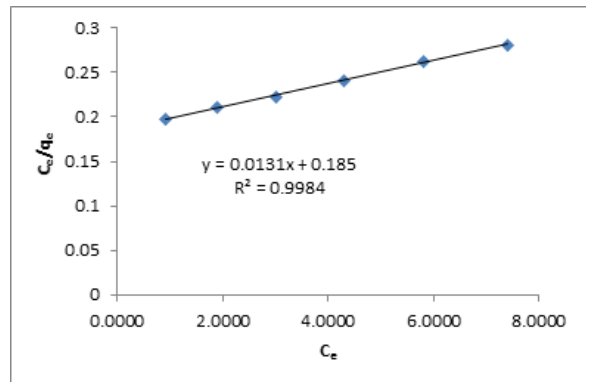


The adsorption isotherms

The Langmuir isotherm equation $C_e/q_e = q_m/b + C_e/q_m$ describes the relationship between C_e , and q_e . The Langmuir coefficient, q_m , is defined as the amount adsorbed to form a monolayer. A plot of C_e/q_e vs C_e gives a straight line with $1/q_m$ as slope and q_m/b as intercept from which both the Langmuir coefficients can be found. The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the equilibrium parameter, R_L .

$$R_L = 1/(1 + b C_0) \quad (3)$$

Figure 2: Langmuir isotherm for MV adsorption on UL



Where b (mg/l) is the Langmuir constant and C_0 (mg/l) is the initial dye concentration, with R_L values indicating the type of isotherm. The R_L value indicates the adsorption to be unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The R_L value obtained from the experimental data falls between zero and one, indicating favourable adsorption. The empirical isotherm equation given by Freundlich and useful in describing nonspecific adsorption is

$$q_e = K_f C_e^n \quad (4)$$

Where q_e and C_e have similar meaning as earlier with K_f and n being the Freundlich coefficients. When equation 4 is obeyed, the plot of $\log q_e$ vs $\log C_e$ yields a straight line and the both the Freundlich coefficients could be obtained from the slope and intercept of the plot.

Where K_f (L/g) is the Freundlich constant related to the adsorption capacity and n is the constant for intensity. The value of n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity and becomes more heterogeneous as its value gets closer to zero.

Temkin isotherms exhibit the effect of indirect interaction between adsorbate by adsorption isotherm.

$$q_e = (RT/b)\ln AC_e$$

$$q_e = B_1 \ln A + B_1 \ln C_e \quad (5)$$

Where $B_1 = RT/b$: T is the absolute temperature (K); R is the gas constant (8.314J/mol K); A is equilibrium binding; q_e is the amount of adsorbed dye on per unit weight of solid surface (mg/g); and C_e is the concentration of dye in aqueous solution at equilibrium. The value of B_1 and A have been calculated by slopes and intercepts of the plots, respectively, from graph q_e vs $\ln C_e$. b is related to the heat of adsorption. The adsorption coefficients and correlation coefficients obtained from the isotherm are given in Table 1. The comparison of maximum monolayer adsorption capacity of various basic dyes onto various adsorbents is shown in Table 2.

Table 1: Adsorption isotherm constant for adsorption of Methyl violet onto *Ulva lactuca* adsorbent.

Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
q_m	b	R^2	K_f	n	R^2	b_T	A_T	R^2
(mg/g)	(l/mg)		(mg/g)			(kJ/mol)	(dm ³ /mol)	
76.92	0.07	0.998	5.16	0.833	0.996	108.36	1.452	0.962

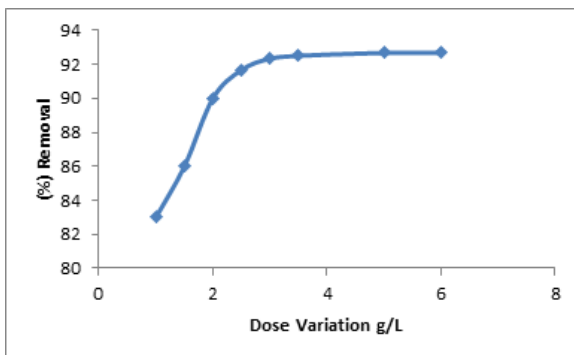
Table 2. Comparison of monolayer equilibrium capacity for basic dye onto other low-cost sorbents.

Dye	Adsorbent	adsorption capacity (mg/g)	references
Rhodamine-B	Orange peel	3.2	11
Methylene blue	Rice husk	40.58	10
Malachite green	Beaucaite	5.858	13
Neutral red	Peanut hull	87.72	14
Methylene blue	Peanut hull	68.03	14
Methylene blue	Raw Posidonia oceanica fibres	5.56	15
Basic violet 1	Sugarcane dust	50.40	16
Basic violet 10	Sugarcane dust	13.90	16
Methyl violet	<i>Ulva lactuca</i>	76.92	This study

Effect of adsorbent dose

Biosorbent dose is an important parameter influencing the sorption processes since it determines the sorption capacity of an adsorbent for a given initial concentration of the adsorbate under the operating conditions. The biosorption efficiency increased from 76 % to 92 % as the biosorbent dose increased from 1 to 6 g. The increase in the percentage of dye removal with biosorbent dosage could be attributed to an increase in the biosorbent surface area, augmenting the number of biosorption sites available for biosorption, as already reported[8].

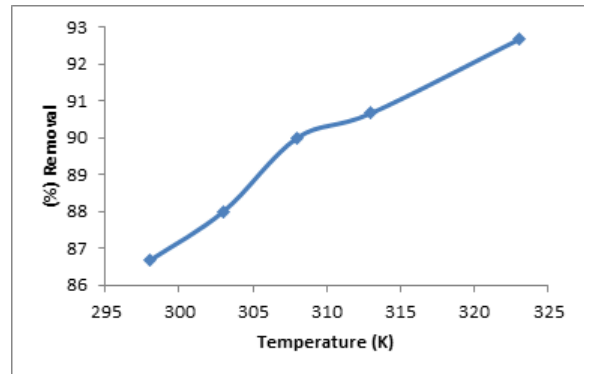
Figure 3: Effect of Dose on the removal of MB by UL



Effect of temperature

The effect of temperature on the sorption capacity of green seaweed was studied at 25, 30, 35, 40 and 50 °C and the results were shown in Fig. 6. The results show that the sorption capacity increased with temperature increase from 25 to 50 °C. Equilibrium uptake of the Methyl violet dye increases with increasing temperature suggesting that biosorption between *Ulva Lactuca* and Methyl violet dye was an endothermic process and the mechanism was mainly chemisorption.

Figure 4: Effect of Temperature on the removal of MB by UL



Thermodynamic Parameters

Spontaneity of a process can be determined by thermodynamic parameters such as enthalpy change (ΔH°), free energy change (ΔG°) and entropy change (ΔS°). A spontaneous process will show a decrease in ΔG° and ΔH° values with increasing temperature[9]. The temperatures used in the thermodynamic study were 298, 303, 308, 313 and 323 K. The thermodynamic parameters were calculated based on the following equations:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Where k is the equilibrium constant, R is the universal gas constant, and T is the temperature (K). ΔH° and ΔS° values are obtained from the slope and intercept of plot $\ln K$ against $1/T$. The negative value of ΔG° indicates the biosorption is favorable and spontaneous. The high positive values of ΔH° confirm the endothermic nature of adsorption process. The positive values of ΔS° indicate the increased disorder and randomness at the solid solution interface of MV with the adsorbent. The increase of adsorption capacity of the biosorbent at higher temperatures was due to enlargement of pore size and activation of adsorbent surface[10].

Table 3: Thermodynamic parameters

Temperature(K)	Thermodynamic parameters		
	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol/K)
298	-29.71	18.0	70.17
303	-33.21		
308	-36.72		
313	-40.23		
323	-47.25		

Conclusion

The present study shows that UL algae, can be used as biosorbent for removal of MV from aqueous solution. The amount of dye adsorbed was found to vary with biosorbent dosage, initial dye concentration, and temperature. The amount of dye uptake (mg/g) was found to increase with temperature, initial dye concentration, and biosorbent dosage. The thermodynamic analysis showed that, the negative value of ΔG° indicates the biosorption is favorable and spontaneous.

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