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Research Article

EQUILIBRIUM, KINETIC AND THERMODYNAMICS STUDIES OF METHYLENE BLUE DYE FROM AQUEOUS SOLUTION BY USING NATURAL ADSORBENT

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ABSTRACT
The studies of adsorption were carried out in batch scale to estimate the different adsorption parameters concerning the efficiencies of dye removal from aqueous solutions. The data obtained from the adsorption of methylene blue on the natural waste material such as algae (dried form). The uptake equilibrium was increased and adsorption percentage was decreased with increasing the initial dye concentration for the adsorbent. The percentage adsorption of dye increases with increasing the adsorbent dosage. The percentage adsorption of dye decreases with increasing particle size. In this work, the effect of temperature on the equilibrium adsorption of Methylene Blue dye from aqueous solution using dried Algae was investigated. The percentage adsorption and dye uptake of dye increases with increasing the temperature of solution. Thermodynamic parameters, such as ΔG°, ΔH°, and ΔS° were calculated using adsorption equilibrium constant obtained from the Langmuir isotherm. The Langmuir isotherm for both the adsorbents proved to be the best adjustment of the experimental data than the Freundlich Isotherm. The results suggested that the Methylene Blue dye on dried Algae was a spontaneous and endothermic process.

Keywords: Methylene Blue, isotherm, adsorption, Algae.

1.0 INTRODUCTION
Dyes and pigments have been used in many industries for coloration purpose. Textile industry is one of the prominent polluters releasing high concentrated effluent in to the surrounding environment. Dyes and pigments have been used in many industries for coloration purpose. Textile industry is one of the prominent polluters releasing high concentrated effluent into the surrounding environment. Over $7x10^5$ tones and approximately 10,000 different types of dyeand pigment are produced worldwide annually and the volume is steadily increasing. Dyes contain carcinogenic materials which can poseserious hazards to aquatic life and endusers of the water. Dyes and pigments are widely used, mostly in the textiles, paper, plastics, leather, food and cosmetic industry to color products. The release of colour wastewater from these industries may present an eco-toxic hazard. Dyes are an important class of pollutants, and can even be identified by the human eye. Disposal of dyes in precious water resources must be avoided, however, and for that various treatment techniques like precipitation, ion exchange, chemical oxidation, and Adsorption have been used for the removal of toxic pollutant from, wastewater.

Methylene blue is a heterocyclic aromatic chemical compound with the molecular formula $C_{16}H_{18}N_3SCl$. It has many uses in a range of different fields, such as biology and chemistry. At room temperature it appears as a solid, odorless, dark green powder. So that it yields a blue solution when dissolved in water. The hydrated form has 3 molecules of water per molecule of methylene blue. Methylene blue was chosen for this study because of its known strong Adsorption onto solids. Methylene Blue is the most commonly used material for dying cotton, wood, and silk with molecular weight 373.9 corresponds to methylene blue hydro chlorine with three groups of water.

Removal of contaminants from industrial wastewaters, many conventional methods such asprecipitation, solvent extraction, filtration, ion exchange, biosorption and electrochemicaltreatment has been applied. These methods are either expensive or could not cope with highconcentration of contaminants. All these methods have significant disadvantages such asrequirements and production of toxic sludge, incomplete ion removal or other waste products that require further disposal. Hence, these processes do not suit the needs of developingcountries. Adsorption process has been a prominent method of treating aqueous effluent inindustrial processes for a variety of separation and purification purposes. This technique is also found to be highly efficient for the removal of colour in terms of initial cost, ease of operation, simplicity of design and insensitivity to toxic substances. Most of the absorbents were active in removal of dye from the dye effluent. In this project cheap and eco-friendly adsorbents have been studied to find an alternative substitution of above mentioned methods for the removal the removal of Methylene Blue dye from aqueous solution. The study of adsorption isotherms in water treatment is significant as it provides valuable insights into the application of design. An isotherm describes the relationship between the quantity adsorbed and that remaining in the solution at a fixed temperature at equilibrium. Adsorption thermodynamic parameters can be obtained from adsorption equilibrium constants with temperatures.

2.0 Experimental Procedure

2.1 Preparation of adsorbent

After collecting the algae from nearby sources, it is cleaned by washing with water and dried in the atmosphere. After drying it is separated into various sizes by using BSS sieves.

2.2 Preparation of Methylene Blue solution

Stock solution of Methylene Blue concentration (1000mg/L) was prepared by diluting 1 g of Methylene Blue powder in a 1000ml of distilled water. Later it was diluted to get the test solutions of concentrations 0.02 to 0.1 g/L.

2.3 Effect of Contact Time

To study the effect of contact time 0.5 g of 137.5 µm average particle size adsorbent is taken 30 ml of aqueous solution of initial methylene blue concentration 0.02 g/L, at known pH 6.8 and the shaking was provided for 35 minutes. The experiment was repeated for different time intervals like 1,2,3,4,5,6,7,8,9,10,15,20,25,30,35 minutes at constant agitation speed. After each interval of time the sample was filtered and analyzed to determine optimum contact time. The data obtained from the Adsorption of methylene blue on to dried algae showed that a contact time of 25 minutes was sufficient to achieve equilibrium and the Adsorption did not change significantly with further increase in contact time.

2.4 Effect of Initial Concentration

To study the effect of methylene blue concentration 0.5 grams of Adsorbent is added to 30 ml of stock solution of methylene blue concentration 0.02 g/L and is kept shaking for optimum time then the procedure is repeated at pH 6.8 with 30 ml of stock solution with different initial concentrations 20, 40, 60, 80,100mg/L keeping the agitation speed and room temperature constant then the sample was filtered and analyzed for methylene blue concentration.

2.5 Effect of Adsorbent Dosage

The effect of Adsorbent Dosage on the amount of methylene blue Adsorbed was obtained by agitating 30 ml of methylene blue solution of 0.02 g/L separately with 0.5, 1, 2, 3, 4 grams of Adsorbent at room temperature for optimum shaking time at constant agitation speed, maintaining the pH 6.8. The filtered solution of methylene blue was analyzed with the help of colorimeter to know the percentage Adsorption.

2.6 Effect of Average Particle Size

To study the effect of average particle size 30 ml of 20 g/L stock solution was added to 0.5 grams of known average particle size of adsorbent i.e., above 120 BSS; and it was kept until optimum time. The sample was filtered and analyzed for concentration of methylene blue. This experiment was repeated at constant agitation speed and room temperature with different particle sizes of Adsorbent from 137.5 µm to 302.5 µm mesh size.

2.7 Effect of pH

To determine the effect of pH the stock solutions of concentration 0.1 g/L with pH 6.7, acid was added in order to reduce pH value 2, 4, 6, and base was added to increase the pH up to 10. The acid used was freshly prepared hydrochloric acid and base was sodium hydroxide. After setting the pH of the ranges 2, 4, 6, 8, 10, 50 ml stock solution was pipette out in to each flask and 0.5 grams of dried algae was added to it and allowed to undergo shaking for optimum time then the sample was analyzed for the percentage Absorption.

2.8 Adsorption Isotherms

The Adsorbent Isotherms indicate how the Adsorption molecules distribute between the liquid phase and the solid phase when the Adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose. Adsorption isotherm is basically to describe how solute interacts with adsorbents. The application of the isotherm equation is compared by judging the correlation coefficients R^2. Isotherms are calculated under existing conditions. These isotherms are useful for estimating the total amount of adsorbent needed to adsorb a required amount of Adsorbate from solution.

Langmuir Isotherm:

$$(C_{eq}/q_{eq}) = (1/bq_{max}) + (1/q_{max})C_{eq}$$

Freundlich Isotherm: $\log q_{eq} = \log K_f + n \log C_{eq}$

Where, q_{eq} is the amount adsorbed per unit weight of adsorbents at equilibrium. C_{eq} is the equilibrium concentration of the Adsorbate (mg/L). q_{max} is equal to $q_{eq}$for a complete monolayer. n is the Freundlich constant. While b is the Langmuir constant and K_f is the Freundlich constant related to the Adsorption capacity.

3.0 RESULTS AND DISCUSSIONS

3.1 Effect of Contact Time

The present study has shown that for algae, the percentage of dye removal was high. The Adsorption data for the uptake of methylene blue verses contact time at initial concentration 0.02g/L was shown. It indicated that the Adsorption of methylene blue increases with increase in contact time. The amount of dye uptake was found to occur in the first rapid phase (25 minutes) and their after the sorption rate was found to be constant. This is due to an increased number of vacant sites available at the initial stage and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases.

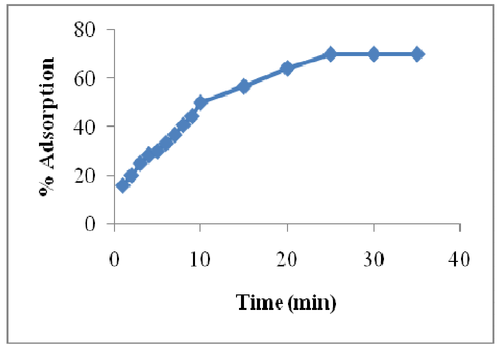

Fig. 1: Effect of Contact Time

Effect of Contact Time on % Adsorption of Methylene Blue on to dried algae was studied over a shaking speed of 180 rpm and time of 35 minutes using 0.5 grams of algae, 30 ml of 20 ppm of individual Methylene Blue solution concentration at pH 6.8, temperature 30°C. The data obtained from the Adsorption of Methylene Blue on to algae, showed that a constant time of 25 minutes was sufficient to achieve equilibrium and Adsorption did not change significantly with further increase of time.

3.2 Effect of Initial Concentration

The study has shown that the percentage of dye removal was 70% high at initial concentration 20 ppm at a shaking speed of 180 rpm and time 25 minutes. The lowest dye removal 58.6% was observed for concentration of 100 ppm. This indicates that an increase in the dye concentration had caused the decrease in the percentage of dye removal, even though the amount of dye being adsorbed is increased. This is due to increase in the driving force of the concentration gradient as an increase in the initial dye concentration and decrease in percentage Adsorption may be attributed to a lack of sufficient surface area to accommodate much more adsorbate available in the solution.

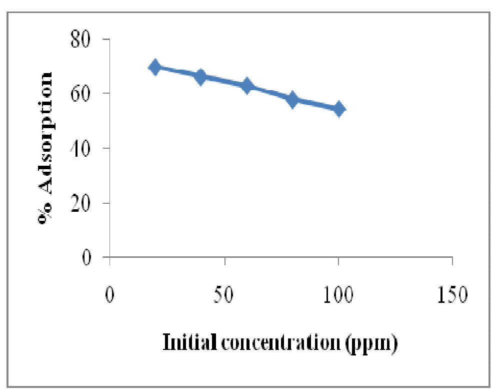

Fig. 2: Effect of concentration of MB

At lower concentrations almost all the adsorbate present in the solution could interact with the binding sites and thus percentageadsorption higher than those higher at initial concentrations. At higher concentrations and lower Adsorption sites yield is due to the saturation of Adsorption of sites.

3.3 Effect of Adsorbent Dosage

From the Figure 3, it was observed that, the amount of the dye adsorbed varied with varying adsorbent mass. The optical density decreased for an increase in adsorbent mass from 0.5 to 4.0 grams, where as percentage color removal increased from 70 to 83 with an increase in adsorbent mass. The decrease in the optical density with increasing adsorbent mass is due to the split in the flux or the concentration gradient between solute concentration in the solution and the solute concentration in the surface of the adsorbent. The increase in the percentage of dye removal is due to increase in the surface area and availability of Adsorption site with increase in the Adsorbent dosage.

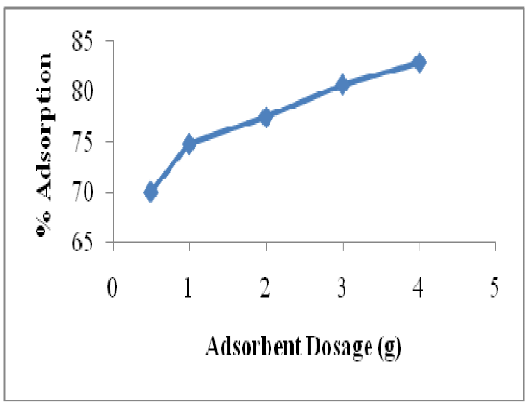

Fig. 3: Effect of dosage on to Removal of MB

3.4 Effect of Average Particle Size

The variation of the rate of Adsorption of the substance with different particle size of adsorbent is another factor influencing the rate of Adsorption. The present work was carried out at particle sizes 302.5, 230, 195, 165, 137.5μm,(BSS mesh sizes) and Adsorption of dye was monitored. Maximum Adsorption about 70% can be achieved at a particle size 137.5μm. This indicates that as the particle size increases the Adsorption rate decreases. High Adsorption with the smaller particle size is due to availability of more specific surface area on the Adsorbent.

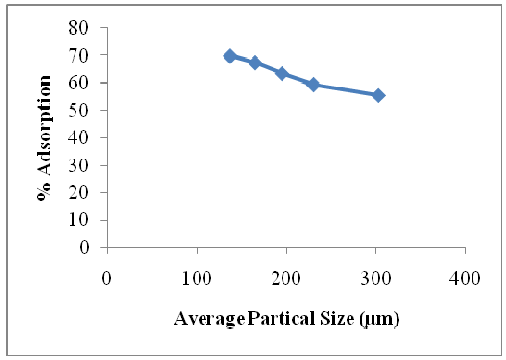

Fig. 4: Effect of Average Particle size on Removal of MB

3.5 Effect of pH

The study has shown that the percentage of dye removal was 70% high at initial concentration 0.02 g/L at a shaking speed of 180 rpm and time 25 minutes. The lowest dye removal 55.60 % was observed for concentration of 0.1 g/L.

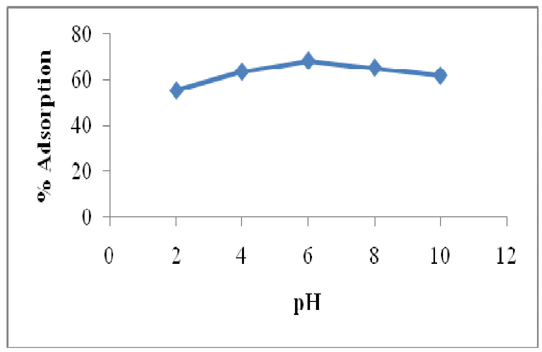

Fig. 5: Effect of pH on removal of MB

The effect of pH on the percentage of the Methylene Blue is shown in Figure 5under various other fixed operating conditions. The initial pH of Adsorption medium is one of the most important parameters affecting the Adsorption process. It can be seen here that the percentage of dye removal was increased from 57.5 to 67.5 with an increase in the pH from 2 to 6, but there observed a decrease in dye removal from 67.5 to 62.0 the pH 6 to10. As expected, the adsorbent surface acidity and basicity are strong functions of pH of solutions. In this case the adsorbent surface acidity and adsorbent surface basicity might be responsible for such behavior in Adsorption and such surface properties can be expressed by the following equations;

$$\text{Adsorbent-OH} \xrightarrow{\quad} \text{Adsorbent-O}^- + H^+ \quad \textbf{(a)}$$

$$\text{Adsorbent-O}^- + H^+ \xrightarrow{\quad} \text{Adsorbent-}H_2^+ \quad \textbf{(b)}$$

Equation (a) represents adsorbent surface basicity at higher pH. While equation (b) is represents adsorbent surface acidity at lower pH. Methylene Blue being an anionic dye, adsorbed onto the adsorbent surface effectually at lower pH values since the adsorbent surface attained at lower pH as per equation (b). As a result Adsorption of Methylene Blue on dried algae was better at pH 6 to 7.

3.6 Langmuir Isotherm

Isotherms assume monolayer Adsorption onto a surface containing finite number of Adsorption sites of uniform strategies of Adsorption with no transmigration of Adsorbate in the plane of surface. The linear form of Langmuir Isotherm equation is given as;

$(C_{eq}/q_{eq}) = (1/bq_{max}) + (1/ q_{max})C_{eq}$

Where q_{max} and b are Langmuir constants related to Adsorption capacity and rate of Adsorption respectively. A plot of C_{eq}/q_{eq} versus $1/C_{eq}$ for Methylene Blue to Adsorption onto dried algaeis presented in the figure. The Langmuir constants b = 0.025and q_{max} = 5.675 are obtained from the graph. The R^2 value of 0.989 indicated that the Adsorption data of Methylene Blue onto dried best fitted the Langmuir isotherm model.

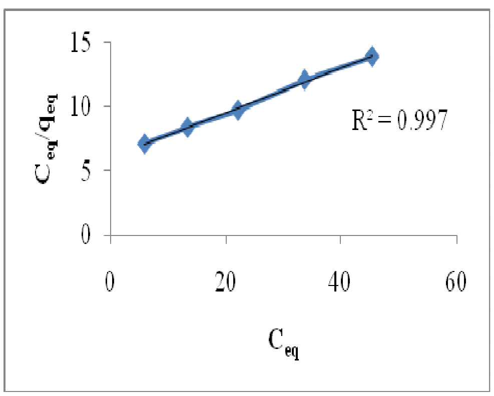

Fig. 6: Langmuir Adsorption isotherm at 0.5 g /30 ml of Adsorbate concentration

3.7 Freundlich Isotherm

Unlike Langmuir Isotherm Freundlich isotherm assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage, the linearized form of Freundlich isotherm can be written as:

$$\log q_{eq} = \log K_f + n \log C_{eq}$$

Where, K_f and n are Freundlich constants with n giving an indication of how favorable the Adsorption process. K_f can be defined as the Adsorption of distribution coefficient and represents the quality of dye adsorbed onto dried algaefor unit equilibrium concentration. The slope n ranging between 0 and 1 is a measure of Adsorption intensity or surface heterogeneity becoming more heterogeneous as its value coming closer to zero. From the Figure 7, we can getthe slope n =0.6524 and intercept K_f =0.2552 & R^2 = 0.989.

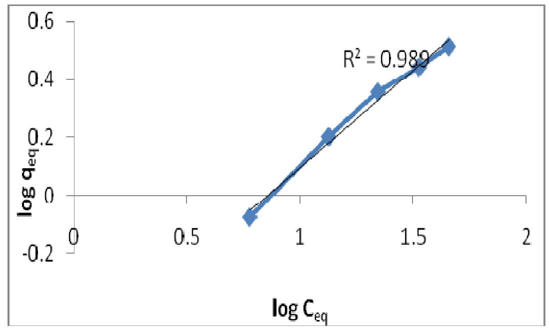

Fig. 7: Freundlich Adsorption isotherm at 0.5 gm/30 ml of adsorbent

Table 1: Equilibrium constants for Adsorption of MB

Isotherm	Constants	
Langmuir	b	0.025
	q_{max}	5.675
	R^2	0.989
Freundlich	K_f	0.2552
	n	0.6524
	R^2	0.989

The effect of isotherm can be used to predict whether a sorption system is favourable or unfavourable in batch process. Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor of equilibrium parameter K_R which is defined by the $K_R = 1/ (1+bC_i)$

Table 2: Comparison of different adsorbent percent Adsorption with sawdust Adsorption capacity on Methylene Blue removal

Types o adsorbent	% Adsorption
Activated carbon (coconut shell	75
Activated carbon (fruit peel)	73
Activated Carbon (palm kernel shell)	71
Dried Algae (Present study)	72
Mesoporous material MCM-41	50
Pistachio shell	44
Zeolite material	40

From the above table it is clear that percentage Adsorption of Methylene Blue from aqueous solution having concentration 0.02 g/L on WTP is more than that compared to different adsorbents (Coconut shell, Archassapota, Sugarcane Baggase, Tamarind Nut Shell) Adsorption capacity after undergoing a constant shaking of 25 minutes. So we carried out the whole Adsorption process with alge as

Adsorbent for highest concentration of Methylene Blue removal from aqueous solutions.

Table 3: Langmuir isotherm parameters obtained using the non-linear method for the adsorption of Methylene Blue dye onto Algae at various temperatures

T (K)	r^2	K_a	ΔG° ((kJ/mol)
295	0.989	0.422	-110
305	0.976	0.576	-135
315	0.983	0.690	-159

4.0 Thermodynamic Studies

The changes occurring during adsorption process can be explained by the three main important thermodynamic parameters enthalpy of adsorption (ΔH), entropy of adsorption (ΔS) and Gibbs free energy (ΔG) due to transfer of unit mole of solute from solution to the solid - liquid interface. The Vanthoff's equation is log(qe/Ce) = - ΔH/(2.303RT) + ΔS/(2.303R) ΔH and ΔS values are calculated from the plots between log (q_e/C_e) and (1/T). From the plot Slope = ΔH/2.303R and Intercept = ΔS/ 2.303R Gibbs free energy (ΔG) is related to enthalpy (ΔH) and entropy (ΔS) of adsorption as ΔG = ΔH - T (ΔS). The positive value of enthalpy indicates that the adsorption process is endothermic in nature. The value of entropy above zero confirms the irreversibility of the adsorption process. The negative value of Gibbs free energy shows the reaction as spontaneous. The adsorption equilibrium constant, K_a, obtained from the non-linear method was analyzed. A plot of $\Delta G°$ versus temperature, T, will be linear and the values of $\Delta H°$ and $\Delta S°$ are determined from the slope and intercept of the plot. The parameter $\Delta G°$ for the adsorption process using the K_a from the Langmuir isotherm is shown in Table 3. The values of $\Delta G°$ calculated using the $K_a$was negative for the adsorption of Methylene Blue dye onto dried Algae at all temperatures. The negative values confirm the feasibility of the process and the spontaneous nature of the adsorption. The values of $\Delta G°$ were found to decrease -110to -159 kJ/mol using the equilibrium constant, K_a. The decrease in the negative value of $\Delta G°$ with an increase in temperature indicates that the adsorption process of Methylene Blue dye onto dried Algae becomes more favourable at higher temperatures. The values of $\Delta H°$ and $\Delta S°$ calculated from the above equation relationships were found as 35.5 kJ/mol and 12.41 J/mol K, respectively. The value of $\Delta H°$ was positive, indicating that the adsorption process was endothermic. The positive value of $\Delta S°$ reflects the affinity of the algae for the Methylene Blue dye and suggests some structural changes in adsorbate and adsorbent. In addition, the positive value of $\Delta S°$ shows the increasing randomness at the solid/liquid interface during the sorption of Methylene Blue dye onto algae. The endothermic and spontaneous adsorption has also been reported for the system of basic dyes on treefern , Bentonite , Mansonia wood, sawdust and wheat shell.

4.0 CONCLUSIONS

Analytically discussed and the following conclusions could be drawn from the studies of Methylene Blue dye from Aqueous Solution by using natural adsorbent.The Adsorption performance is strongly affected by parameters such as initial concentration, pH, adsorbent dosage and adsorbent particlesize. The data obtained from the Adsorption of Methylene Blue on to algae showed that a contact time of 25 minutes was sufficient to achieve equilibrium. Itwas observed that 72 percentage Adsorption of Methylene Blue decreases with increase in the initial concentration of aqueous solution, It was observed that percentage Adsorption of Methylene Blue decreases with increasing particle size of algae. The amount of adsorbate adsorbed increases with the increasing of adsorbent dose. In this work, the effect of temperature on the equilibrium adsorption of Methylene Blue dye from aqueous solution using dried Algae was investigated. The percentage adsorption and dye uptake of dye increases with increasing the temperature of solution. Thermodynamic parameters, such as ΔG°, ΔH°, and $\Delta S°$ were calculated using adsorption equilibrium constant obtained from the Langmuir isotherm. The Langmuir isotherm for both the adsorbents proved to be the best adjustment of the experimental data than the Freundlich Isotherm. The results suggested that the Methylene Blue dye on dried Algae was a spontaneous and endothermic process.The positive value of $\Delta S°$ shows that increasing randomness at the solid/liquid interface during the adsorption of Methylene Blue dye onto dried Algae.

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