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Adsorption Isotherms and Thermodynamics Study for Methyl Violet Dye Removal from Aqueous Solution using Water Hyacinth as an Adsorbent

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Abstract : The adsorption behaviour of Methyl Violet from aqueous solution onto aWater Hyacinth was examined as a function of parameters such as initial methyl violet concentration, contact time, particle size, pH and temperature. The Langmuir and Freundlich adsorption isotherms were applied to describe the equilibrium isotherms. The Langmuir monolayer adsorption capacity of Water Hyacinth was estimated at 6.67mg/g. The values of the energy, enthalpy and entropy of activation were 3.197kJ/mol, 5.269 kJ/mol and4.078 kJ/mol, respectively, at pH 2.
Keywords :-Methyl Violet, pH, Temperature, Contact time.

Introduction

Textile industries include most polluting sectors in terms of wastewater generation and their capacity of release. Dyes are moderately arising as a class of anthropogenic organic compounds; those are containing aromatic cyclic rings which produce hydrophilic nature when contact with water. So, these kinds of dyestuff are difficult to treat (1). The releases of highly coloured wastewater into the environment either toxic or carcinogenic and that pose a potential health hazard to all forms of life (2). Even the very low concentration of the dye i.e. less than 1 mg/L in the wastewater is affected and requires to be removed before the wastewater can be released into the environment(3).

Various physical and chemical techniques like oxidations (4), coagulation and flocculation (5), adsorption (6),ion-exchange (7) etc. were established for dyes removal from wastewater. Adsorption is commonly used to intensify the dyestuffs on an adsorbent before chemical or biological treatment (8). Some of the cost effective adsorbents that are evaluated for the dye adsorption operations are rice husk (9), sawdust (10), coconut husk (11), corncob (12), peat (13), Adsorption is a surface occurrence wherein matter adheres to the surface of the other has been examined for colour removal using immobilized aquatic weeds (14).Water Hyacinth removed nutrients and heavy metals from wastewater (15). Recently, utilization of adsorbent (Water Hyacinth)in the removal of methyl violet dye from wastewater was studied (16). The aim of this study is to analysis the capacity of Water Hyacinth and it revived derivative to adsorbmethyl violet dye. The rate of dye adsorption process was analysed including the influence of the different parameters like contact time, pH, concentration of dye, temperature, sieve size and dosage of the adsorbents. Simple equilibrium data for both Langmuir and Freundlich isotherms and thermodynamics analysis were found.

Experimental

Adsorbent Preparation

The water hyacinth used in this study were accumulated then take into the laboratory rubbing with water to remove clay and other foreign materials from surrounding them and slice into pieces. The slice material would drying by under the shadow for 15 days and after put in at 80°C temperature for 1 Hour in a hot air convection oven. The material would grinding into a powder form and would allowing to pass through a (300-150) µ, (150-75) µ and passed from 75 µ sieve sizes. After that the material sealed in plastic bags, and stored in desiccators (17).

Materials and methods

Methyl violet is used as dye that are mainly member of organic compounds. The colour of the dye can be changed, considering on the number of attached methyl groups. Its main use is as a purple dye fortextiles.Methyl violetis also uses in medical purposes. It is used as a pH indicator. The IUPAC name of dye is [4-[bis[4-(dimethylamino) phenyl]methylidene]cyclohexa-2,5-dien-1-ylidene]dimethylazanium;chloride (chemical formula:$C_{25}H_{30}ClN_3$; molecular weight: 407.9788 g/mol) [18] was used as shown in fig. (1).

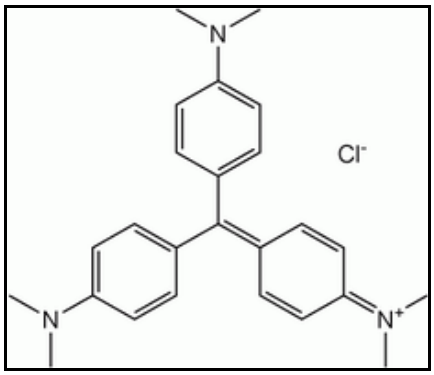

Fig. (1) Methyl violet dye structure

Preparation of dye solution

Methyl violet is used without any purification. A required amount of dye dissolved in 500 ml distilled water solution, this solution is our stock solution.

Effect of Contact Time

The variation in amount percent removal at any time (q_t) of dye with the time is shown in figure 2. The equilibrium concentrations was found in 120 minutes, further that in the adsorption process do not predicted more amount of active sites which do not allow further adsorption to take place[19].

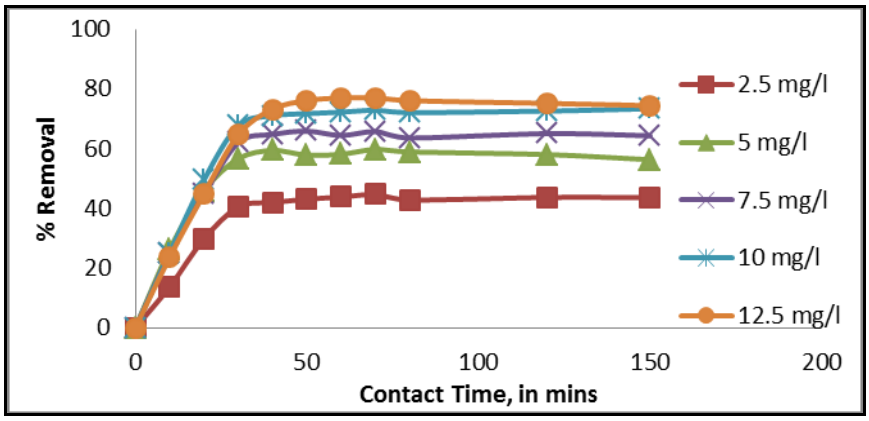

Fig. (2) Effect of Contact Time

Effect of pH

The pH of the wastewater solution is a significant parameter in the adsorption process of dyes. The effect of solution pH on methyl violet dye adsorption was analysed at the pH ranges of 2–12and the results are shown in Fig. 3. The sorption of methyl violet was found to be maximum at the initial pH 2 and it decreased up to pH 12. At alkaline pH, lower adsorption of methyl violet might be due to the presence of excess OH^- ions competing with the cation groups on the dye for adsorption sites. A similar result was reported for methylene blue previously [20].

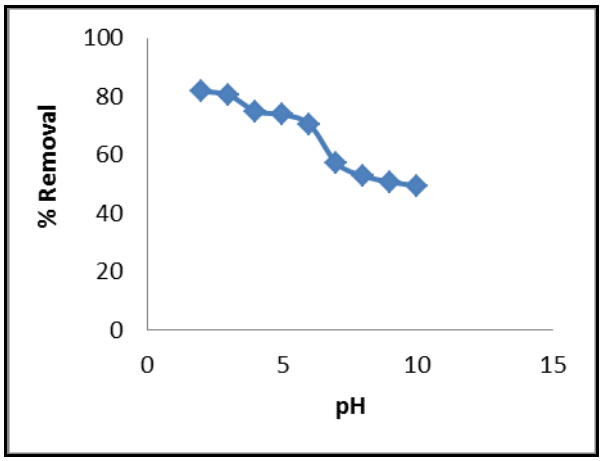

Fig. (3) Effect of pH

Adsorption isotherm

Langmuir isotherm(21) is represented by the following equation below:

$$C_e/q_e = 1/q_{max} K_L + (1/q_{max}) C_e$$

Where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration (mg/l) and q_{max} and K_L are the Langmuir isotherm constants related to free energy. The above equation can be linearised to get the maximum capacity, q_{max} by plotting a graph of C_e/q_e Vs C_e .

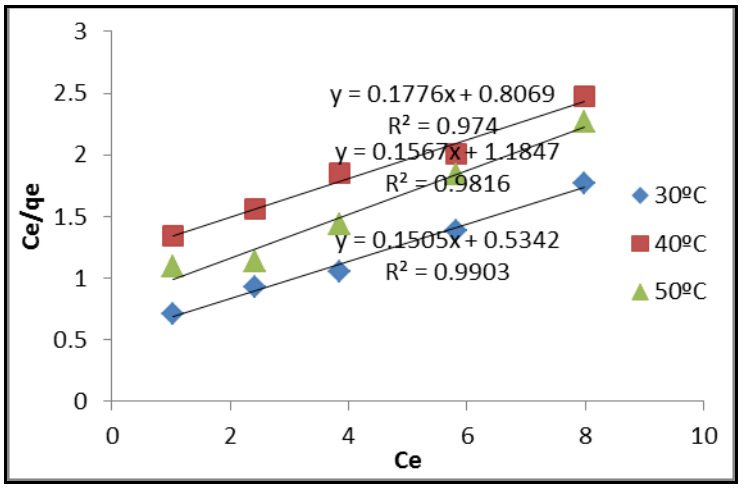

Fig. (4) Langmuir Adsorption Isotherm

The important characteristics of the Langmuir isotherm can be indicated in terms of a unitless equilibrium parameter (R_L), which is expressed by:

$R_L = 1/(1 + K_L C_o)$

where K_L is the Langmuir constant and C_o the initial dye concentration (mg/l). The value of R_L indicates the nature of the isotherm to be either favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$),unfavourable ($R_L > 1$), linear ($R_L = 1$). The value of R_L for temperatures30°C, 40°C and 50°Cwere found to be 0.587, 0.752 and 0.645 respectively, confirmed that the treated water hyacinthis favourable for adsorption of the methyl violet dye under conditions used in this study.

Table (1): The values of parameters of Langmuir equation

Langmuir Adsorption Isotherms Data				
Temperature, in °C	q_{max}	K_L	R_L	R^2
30°C	6.67	0.281	0.587	0.990
40°C	6.41	0.132	0.752	0.981
50°C	5.65	0.219	0.645	0.974

Freundlich isotherm (22)

$$q_e = K_f C_e^{\frac{1}{n}}$$

On rearranging this equation, we get

log q_e **= log** K_f **+1/n log** C_e

A graph between log q_e vs log C_e yields an intercept log K_f and straight line with a slope of 1/n.

where K_f and 1/n are freundlich isotherm constants related to amount of adsorption and intensity of adsorption respectively.

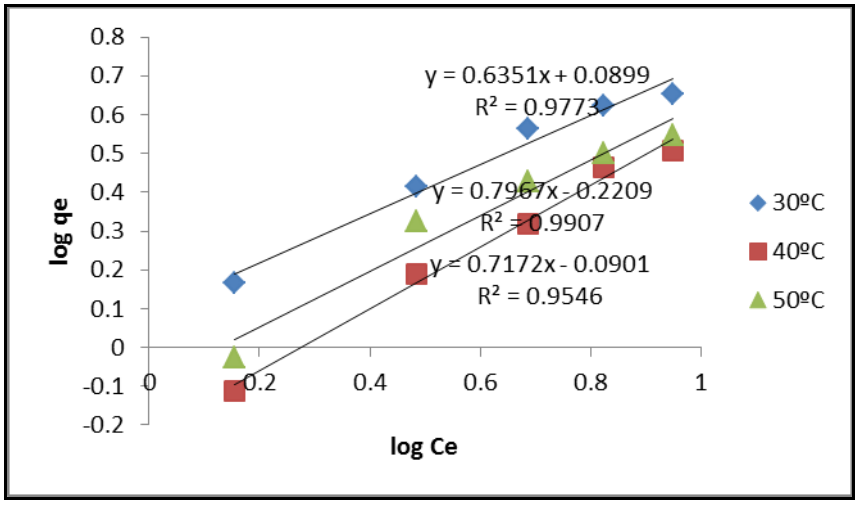

Fig. (5) Freundlich Adsorption Isotherm

Table 2: The values of parameters and correlation coefficient of Freundlich equation

Temperature, in °C	K_f	1/n	R^2
30°C	0.089	0.635	0.977
40°C	0.813	0.717	0.954
50°C	0.603	0.796	0.990

The Langmuir and Freundlich adsorption isotherms of methyl violet on water hyacinth are shown in figures4 and 5. Tables1 and 2 give the values of parameters and correlation coefficient of the Langmuir and Freundlich equations. The experimental results indicated that the adsorption isotherms of methyl violet adsorption on water hyacinth followed both Langmuir and Freundlich models.

It can be seen that the Langmuir isotherm fits the yield better than Freundlich isotherm. The homogeneous nature of the treated with water hyacinth, i.e. each dye molecule per water hyacinth adsorption has equal adsorption energy (23).This is also confirmed by the high value of R^2in case of Langmuir.

Thermodynamics of adsorption

The thermodynamic parameters such as alteration in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of adsorption were found using the following equations (24) :

$\Delta G^\circ = -RT \ln K$
$\Delta H^\circ = R(T_2T_1)/(T_2 - T_1) \ln (K_2/K_1)$
$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T$

where R is the gas constant K, K_1 and K_2 the Langmuir constants corresponding to the temperatures 303K, 313K and 323K and T is the solution temperature in Kelvin. The negative values of ΔG° indicate the degree of energy of the adsorption process. The positive values of ΔH° show that the adsorption is endothermic; the explanation for this being displacement of greater than one water molecules separately methyl violet ions for their adsorption, which gives result in the endothermic capacity of the adsorption process. The assured worth of ΔS° suggests reproduced randomness at the solid/solution interface completely the adsorption of water hyacinth towards methyl violet dye. Also the positive ΔS° value corresponds to an increase in the degree of freedom of the adsorbed dye. The values of thermodynamic parameters were given in Table (3).

Table (3): Thermodynamic parameters for the adsorption of methyl violet by water hyacinth

Temperature (K)	$-\Delta G^\circ$ (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})
303	3.197		
313	5.269	42.553	0.129
323	4.078		

Conclusion

The Langmuir and Freundlich isotherm parameters indicated that the adsorption of methyl violet dye on water hyacinth was favourable. Thermodynamic parameters were determined. Positive ΔH° value obtained confirms that the process is endothermic. ΔG° indicates degree of energy of the adsorption process of methyl violet dye on water hyacinth.

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