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Research Article

ADSORPTION OF MALACHITE GREEN USING LOW COST ADSORBENT OBTAINED FROM *ADHATODA ZEYLANICA* LEAVES

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ABSTRACT

In this paper, the adsorption of malachite green dye onto the adsorbent obtained from the leaves of Adhatoda zeylanica was investigated. The effect of operational parameters such as adsorbent dosage, dye concentration, pH and contact time on the removal of the dye was studied. Equilibrium isotherms were analyzed using Langmuir and Freundlich adsorption models. The results indicated that isotherm data of malachite green dye adsorption followed Langmuir isotherm model. Thermodynamic parameters of dye adsorption were obtained. Thermodynamic studies revealed that the adsorption processes is spontaneous and endothermic in nature.

Keywords: Malachite green , Isotherm models, Adsorbent, Thermodynamic Parameters.

I. INTRODUCTION

Textile industries which employ different dyes for colouring their products generate large amounts of coloured wastewater. Discharging of the untreated or partly treated waste water leads to many environmental problems. Presence of wastewater in water bodies can cause grave harm to aquatic life by hindering photosynthetic process due to the reduction in light penetration. It also leads to increasing toxicity and chemical oxygen demand[1]. Though malachite green (MG), finds application in the dyeing of silk, leather, plastics and paper can be harmful to humans and animals by direct contact of inhalation and ingestion[2]. Effects such as carcinogenesis, muta- genesis, teratogenesis, respiratory toxicity and reduced fertility in humans have been reported[3].

Because of its complicated chemical structure it is highly resistant to be boidegraded and pose serious environment problems. Various techniques have been proposed for dye removal which include aerobic and anaerobic microbial degradation, coagulation and chemical oxidation, membrane separation process, electrochemical, filtration and reverse osmosis[4-6].

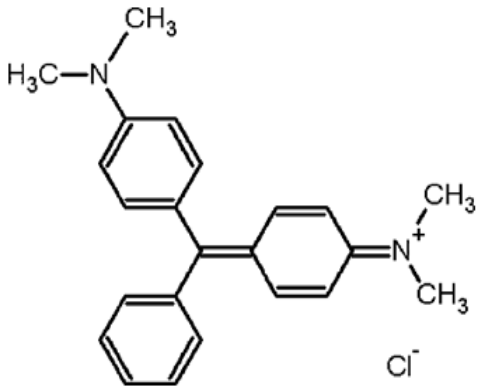
However, all these methods were not successful in removing color from wastewater completely. Adsorption is the simplest process for dye removal and activated carbon is the most effective adsorbent. However, high cost involved in the production and regeneration makes it uneconomical[7-9].

Many low-cost adsorbents including natural and waste materials from industry and agriculture, have been employed by several workers for the removal of dyes from waste waters. Some of these include Bagasse pith[10], Maizecob[11], Coconut shell[12], Chitosan[13], Peat[14], Biomass[15], Orange peel[16], Papaya seed[17], Tamarind fruit sheel[18], Pumpkin seed hull[19]. The objective of this work is to explore the potential of *Adhatoda zeylanica* leaves as an adsorbent in the removal of malachite green, from aqueous solutions.

II. EXPERIMENTAL

Preparation of the adsorbate

Malachite green dye stock solution (500 mg L^{-1}) was prepared by dissolving accurately weighed quantity of the dye in double distilled water.. Desired concentration of the dye solution was obtained from the stock solution by dilution. The structure of MG is shown as below.



Preparation of adsorbent

Adhatoda zeylanica leaves was collected from the local market, washed with tap water several times to remove soil dust and finally washed with DD water. It is dried in sun shade. The dried leaves were powdered and impregnated with 50% H_2SO_4 for 24 h and then filtered and the resulting chemical loaded *Adhatoda zeylanica leaves* was placed in a furnace and heated to 850 ^{0}C for 30 min After the cooling, the activated carbon was repeatedly washed with deionized water and dried at 105 ^{0}C. The carbonized material was ground well to fine powder,stored in vacuum desiccators and used for adsorption experiments.

Adsorption studies

Adsorption experiments were carried out in 250ml Erlenmeyer flasks. A known weight of adsorbent obtained from *Adhatoda zeylanica* leaves *was* added to 50ml of the dye solutions with an initial concentration of 20mg/l to 1000mg/l. Flasks were agitated in a shaker at room temperature for 90min. The solution was then filtered at preset time intervals and the residual dye concentration was measured spectrophotometrically. The percentage of MG dye removal was calculated by using the following equation.

$$\%\ Dye\ \mathrm{Re}moval = \frac{(C_0 - C_e)}{C_0}\ X\ 100$$

Where C_o is the initial concentration (mg/l),C_e is the equilibrium concentration(mg/l)

The adsorption capacity Q_e (mg/g), is obtained from the following equation

$$q_e = (C_0 - C_e)\frac{V}{M}$$

Where, q_e is the adsorbent capacity(mg/g), C_o is the initial concentration (mg/l) C_i is the initial MG concentration (mg/l), V is the volume of the solution(l), M = mass of the adsorbent (g).

III. RESULTS AND DISCUSSION

Effect of pH

In dye adsorption, the pH of an aqueous solution is an important parameter as it affects the surface charge of the adsorbent material and the degree of ionization of the dye molecule[20]. The effect of pH on adsorption of MG onto adsorbent was investigated in the pH range of 2.0–10.0. Percentage removal of the dye molecule as a function of pH is shown in Fig. 1. The removal of MG was found to increase with the increase in pH of the dye solution, appreciably up to pH 6.5. Between pH 6.5 and 10 the dye removal was insignificant. Hence, this pH was used for further studies. As MG is a cationic dye, it exists in aqueous solution in the form of positively charged ions. At low pH values, the protonation of the functional groups present on the adsorbent surface occurs easily, and thereby hamper the approach of positively charged dye cations to the surface of the adsorbent leading to low adsorption of dye in acidic solution. When the pH of the solution increased, deprotonation of the functional groups on the adsorbent surface occurs resulting in an increase in the negative charge density on the adsorbent surface and facilitate the adsorption of the dye cations. The increase in percentage of dye removal at higher pH values may also be attributed to the decline in the number of of H^+ ions which compete with dye cations for vaccant sites on the adsorbent surface. With increasing pH, this competition decreases and dye cations replace H^+ ions adsorbed to

the adsorbent surface leading to increased dye uptake. Similar observation has been reported already[21].

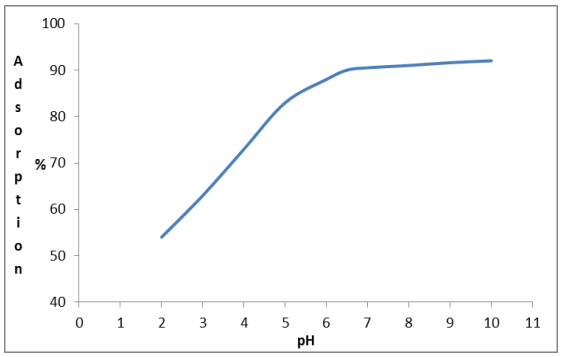


Fig. 1: Effect of pH on the adsorption of MG on to the adsorbent

Effect of adsorbent dose

Effect of adsorbent dose on the removal of Malachite green dye from aqueous solution was investigated by varying adsorbent dose from 25mg to 200 mg for 20mg/l of dye concentration, keeping the other parameters constant, and the results are presented in the fig-2. As the adsorbent dose increases, the MG dye removal also increases and reaches the maximum at 100mg of adsorbent dosage thereafter there was no appreciable increase in the percentage of dye removal. Therefore the adsorbent dosage was maintained at 100mg for further studies. The increase in the dye removal with an increase in the adsorbent dosage can be attributed to increased carbon surface area and the availability of more adsorption sites. This is an agreement with already reported[22].

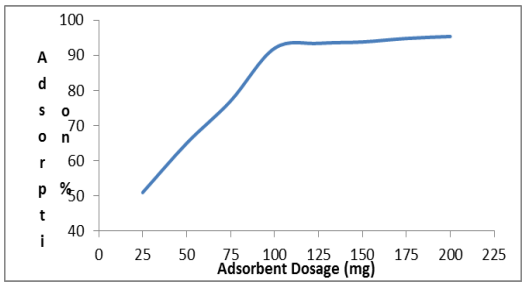


Fig. 2: Effect of adsorbent dose on the adsorption of MG on to the adsorbent

Effect of dye concentration

The rate of adsorption is a function of the initial concentration of the adsorbate. The effect of different initial dye concentration on the adsorption of MG onto the adsorbent is depicted in Fig. 3. The percentage removal of dye decreased with increase in initial dye concentration. This can be explained that all adsorbents have a limited number of active sites, which become saturated at a certain concentration.

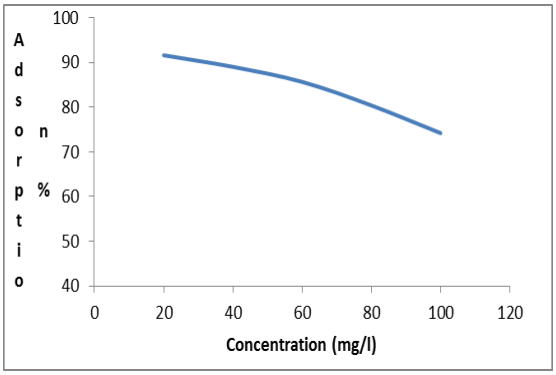


Fig. 3: Effect of dye concentration on the adsorption of MG on to the adsorbent

Effect of contact time

The equilibration time for maximum adsorption was determined by studying the adsorption of the dye of known concentration at different contact time. Fig. 4 is the plot of percentage removal with time for adsorption of malachite green on to the adsorbent. It is observed that initially the percentage removal of dye increases rapidly and reaches the maximum at 90min. The increase in adsorption did not vary much beyond contact time of 90 minutes. Therefore, 90min shaking time was found to be appropriate for the maximum adsorption and was maintained in all subsequent experiments.

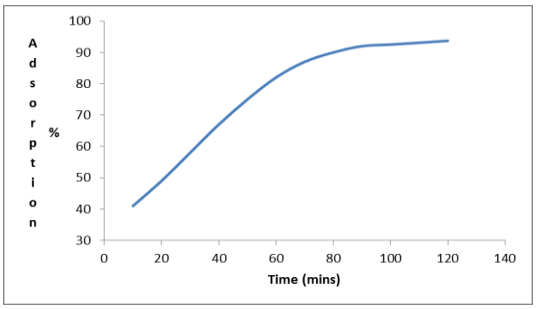


Fig. 4: Effect of contact time on the adsorption of MG on to the adsorbent

IV. ADSORPTION ISOTHERMS

Langmuir Adsorption Isotherm

An adsorption isotherm represents the equilibrium relationship between the adsorbate concentration in the liquid phase and that on the adsorbent's surface at a given condition. The Langmuir model assumes monolayer surface coverage, equal availability of adsorption sites and no interaction among the adsorbed dye molecules. The linear form

of Langmuir equation[23] is expressed as follows

$$\frac{Ce}{Qe} = \frac{Ce}{Q_0} + \frac{1}{Q_0 b}$$

The values of Q_0 and b were calculated from the slope and intercept of the linear plots of C_e/Q_e verses C_e. Langmuir adsorption isotherm is presented in fig-5. Higher value of correlation co-efficient (R^2-0.999) indicates that the experimental data fits well with the Langmuir equation. The values of Q_0 and b are given in Table-1.

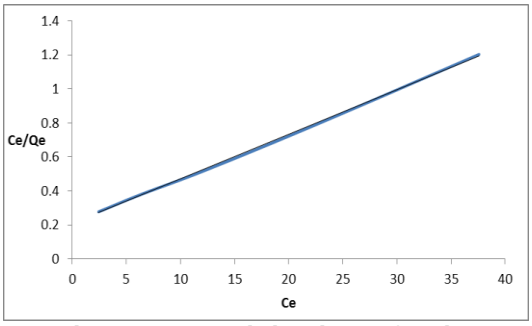


Fig. 5: Langmuir isotherm for the adsorption of MG on to the adsorbent

Table 1: Langmuir constants

Qo(mg/g)	b	R^2
38.4615	0.1256	0.9995

The essential characteristics of the Langmuir adsorption isotherm is expressed by a dimensionless constant called separation factor. This value indicates whether the adsorption is favorable or not.
R_L is defined by the following equation

$$R_L = 1/ (1+bCo)$$

Where,R_L _ dimensionless separation factor[24], C_o – intial concentration , b – Langmuir constant (Lmg^{-1}),The parameter R_L indicates the type of the isotherm.

Values of R_L	Types of isotherms
R_L>1	Unfavourable
R_L = 1	Linear
0<R_L<1	Favourable
R_L = 0	Irrevisible

The R_L value obtained using the above equation for 20mg/l MG concentration is 0.2847. This R_L value lies between 0 and 1 indicating the favourability of the adsorption.

Freundlich Adsorption Isotherm

The Freundlich isotherm considers multilayer adsorption with interactions among the adsorbed molecules. The linear form of the Freundlich equation[25] is as follows

$$\log Qe = \log K_F + \frac{1}{n}\log Ce$$

Where Qe, amount of dye adsorbed (mg/g), K_F, (adsorption capacity) and n, (adsorption intensity). By ploting logQe Vs logCe, the values of n and K_F were calculated from slope and intercept respectively (fig-6). The values of K_F and n are given in table-2. The value of linear regression co-efficient (R^2) was found to be 0.9535.This indicates that the adsorption process follows Langmuir adsorption isotherm more than Freundlich adsorption isotherm.

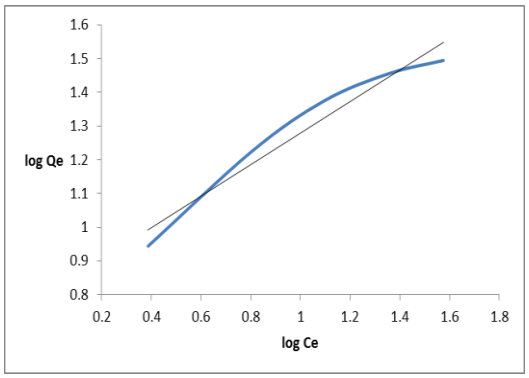


Fig. 6: Freundlich isotherm for the adsorption of MG on to the adsorbent

Table 2: Freundlich constants

n	K_f(mg/g)	R^2
2.1413	6.4565	0.9535

The value of n lies between 1 and 10 indicating the favourable adsorption.

V. THERMODYNAMIC PARAMETERS

Thermodynamic studies related to the adsorption process is essential to conclude whether a process will occur spontaneously or not, The fundamental criteria for spontaneity is the standard Gibbs free energy change $\Delta G^{o,}$ if the ΔG^o value is negative, the reaction will occur spontaneously. The thermodynamic parameters, standard free energy (ΔG^o), change in Standard enthalpy(ΔH^o) and change in Standard entropy(ΔS^o) for the adsorption of MG onto the adsorbent were calculated using the following equations.

$$K_0 = \frac{C_{solid}}{C_{liquid}}$$

$$\Delta G^0 = -RT \ln K_0$$

$$\log K_0 = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT}$$

The values of ΔG^o (KJ/mol), ΔH^o(KJ/mol) and ΔS^o (J/K/mol) can be obtained from the slope and intercept of a linear plot of log K_o verses 1/T and are presented in table-3.

Table 3: Thermodynamic parameters for the adsorption of MG on to the adsorbent

Conc.of MG (mg/l)	$-\Delta G^o$ (KJ/mol)				ΔH^o (KJ/mol)	ΔS^o (J/k/mol)
	35^0 C	45^0 C	55^0 C	65^0 C		
20	5.0596	5.4489	5.8727	6.2818	7.5631	40.9556
40	4.2517	4.6245	5.0321	5.4240	7.8675	39.3090
60	3.4149	3.7744	4.1693	4.5464	8.2830	37.9496
80	2.3507	2.7009	3.0875	3.4522	9.0489	36.9731
100	1.2994	1.6529	2.0429	2.4051	10.1480	37.1454

The negative values of ΔG^o indicates that the adsorption process is spontaneous and highly favorable. The positive values of ΔS^o indicates the increased randomness at the solid solution interface. The values of ΔH^o indicates that the adsorption process is endothermic and physical in nature.

VI. CONCLUSION

The adsorption of malachite green from aqueous solution was studied with various parameters like contact time, pH, intial concentration and adsorbent dose. Thermodynamic and isotherm studies revealed that *Adhatoda zeylanica* leaves can be effectively employed for the adsorption of MG. The experimental data were correlated well by the Langmuir adsorption isotherm. The result of this study indicates that this adsorbent can be successfully utilized for the removal of MG from aqueous solution.

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