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Research Article

REMOVAL OF MALACHITE GREEN FROM AQUEOUS SOLUTIONS BY ADSORPTION USING LOW COST ADSORBENT OBTAINED FROM *CENTELLA ASIATICA* LEAVES

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ABSTRACT

Activated carbon prepared from *Centella asiatica* leaves was employed as an adsorbent for the removal of cationic dye, Malachite green from an aqueous solution. Effect of pH, adsorbent dose, dye concentration, contact time and temperature on the removal of the dye was investigated. Equilibrium data were analyzed using Langmuir and Frendlich isotherm models. The result shows that *Centella asiatica* leaf could be employed as an effective low cost adsorbent for the removal of MG.

Keywords: Malachite green, low cost adsorbent, Centella asiatica leaf, Isotherm models.

I. INTRODUCTION:

Industries such as textile, paper, leather, pharmaceutical, cosmetic, etc use many dyes to colour their products[1-3].This resulted in the generation of huge amount of coloured waste water. When these are discharged into the nearby water bodies, the environment is severely disturbed. This not only affects the aesthetic nature of water, but also the photosynthetic process is hindered due to the reduction in the light penetration[4]. Under aerobic conditions many dyes present in the effluents may undergo decomposition resulting in the formation of carcinogenic aromatic amines which can cause serious health problems to human and animals[5,6]. Dyes can also cause skin irritation, allergy, dermatitis and even cancer in humans[7]. Most of the dyes employed for coloration are known to be carcinogenic, mutagenic, teratogenic and genotoxic[8].

Malachite green is one of the most widely used dyes for colouring purpose[9]. It is used as a biocide in the aquaculture industry[10]. It is also used as a food coloring agent, disinfectant and anthelminthic as well as a dye in leather, cotton, paper, silk and jute indistries[11,12]. However there are several reports mentioning its hazardous and carcinogenic effects[13]. Therefore the treatment of effluents containing Malachite green is vital due to its harmful nature before it is discharged.

Various methods are available for dye and colour removal, such as coagulation, chemical oxidation, membrane separation, filtration, reverse osmosis, aerobic and anerobic microbial degradation[14-16]. However all these methods have limitations and none of them were successful in removing the dye and colour from wastewater completely. Adsorption is the simplest process for dye removal. Activated carbon has been widely employed for adsorption of dyes[17-21]. However the high cost involved in production and regeneration restrict its use. Hence extensive research is undertaken to develop economic adsorbents. In the literature numerous reports are found about the non conventional adsorbents for their ability to remove malachite green from wastewater, such as de oiled soya[22],baggase fly ash[23], modified rice straw[24], chitin[25],orange waste[26],lemon peel[27] and raw barley straw[28].

In the present study, acid activated carbon obtained from *centell asiatica* leaf is employed to remove malachite green from an aqueous solution.

II. EXPERIMENTAL

Preparation of adsorbent

Centella asiatica leaves was collected locally and washed with tape water several times to remove soil dust and finally washed with DD water. It was then dried in sun shade. The dried leaves were powdered and soaked in con.H_2SO_4 (1:1,w/w), for a day, then filtered and dried. The charred mass was kept in a muffle furnace at 400^0C for 1 hour, it was taken out, ground well to fine powder and stored in vacuum desiccators. The Characteristics of the adsorbent is presented in the table-1

Table 1: Characteristics of the adsorbent

pH	6.5
Moisture Content, %	13.5
Ash Content, %	10.2
Volatile Matter, %	21.3
Water Soluble matter, %	0.45
Acid Soluble Matter, %	0.89
Porosity, %	48.1
Micropore volume cm^3/g	0.194194
Average pore width ^0A	28.2065
BET Surface Area, m^2/g	604.27

Preparation of adsorbate

The adsorbate used in this study is Malachite Green was obtained from Merk, India, with molecular formula–$C_{23}H_{25}ClN_2$, Molecular weight 364.92- λmax-618nm.

A stock solution of 1000mg/l of MG was prepared with distilled water. Desired concentration of dye solution was obtained from the stock solution by dilution.

Batch equilibrium method

Different initial concentrations ranging from 10mg/l to 50mg/l was taken in a series of 250ml conical flasks. A known weight of the adsorbent was added to 50ml of the dye solutions. A fixed amount of adsorbent was placed in 250ml flasks containing 50ml of dye solution at different pH. Then the flasks were kept in an orbitary shaker with a speed of 120rpm at room temperature for one and half hours. After filteration, the dye solutions were analysed by UV-Visible spectrophotometer. 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 Ci = initial concentration (mg/l),Ce = equilibrium concentration

The adsorption capacity Qe, is obtained from the following equation

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

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

III. RESULTS AND DISCUSSION

Effect of pH

The pH of the solution has significant impact on the adsorption of the dye, since it determines the surface charge of the adsorbent, the degree of ionisation and speciation of the adsorbate. In order to study the effect of pH on the adsorption of the dye molecules the batch equilibrium studies were conducted in the pH range of 1 to 10.The pH of the solution was adjusted to 1 to 10 by adding 1NHCl or 1NNaOH solution and the results are presented in the fig1. From the figure it can be seen that the adsorption increases with an increase in pH and reaches a maximum at pH=5 and thereafter no appreciable change was observed. At low pH the H^+ ions are high so the surface becomes positively charged. The H^+ ions compete with MG cations for vacant adsorption sites causing a decrease in dye uptake. At high pH the adsorbent surface is negatively charged which favours the uptake of cationic dye by increased electrostatic force of attraction. Hence the pH of the medium was maintained at pH 5 for further studies.

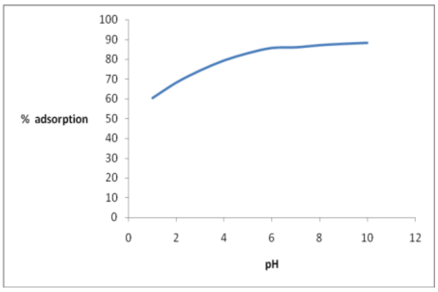

Fig. 1: Effect of pH on the adsorption of MG on to the adsorbent

Effect of adsorbent dose

The effect of adsorbent dose was studied at room temperature by varying the dose from 25mg to 150mg 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 100 mg of adsorbent dosage , thereafter there was no appreciable increase in the percentage of dye removal. Therefore the adsorbent dosage was maintained at 100 mg for further studies. This can be attributed to the availability of large number of vacant sites for adsorption.

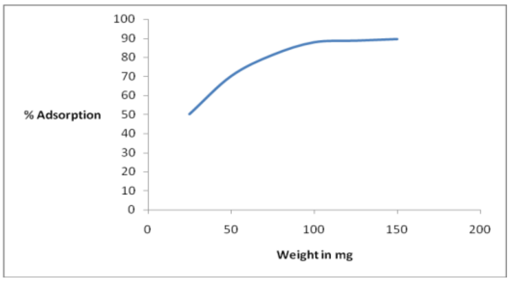

Fig. 2: Effect of adsorbent dose on the adsorption of MG on to the adsorbent

Effect of dye concentration

The effect of initial dye concentration was studied with 10mg/l to 50mg/l solution with an adsorbent dosage of 100mg for a contact time of 90 min. From the fig.3, it can be observed that the percentage removal of MG gets decreased gradually. As the initial concentration is increased the ratio of the number of vacant sites on the adsorbent to the dye molecules decreases.

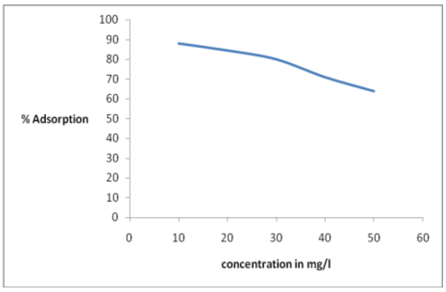

Fig. 3: Effect of dye concentration on the adsorption of MG on to the adsorbent

Effect of contact time

Effect of contact time on the adsorption of MG is shown in fig.4. As the contact time was increased from 15 min to 90 min, the adsorption percentage also increased and reaches a maximum at 90min. There was no appreciable change in the adsorption percentage above 90min. Hence all the experiments were conducted for a period of 90min.

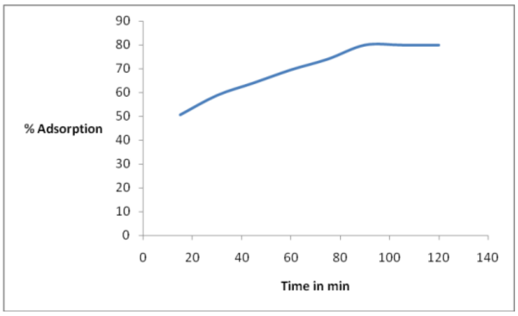

Fig. 4: Effect of contact time on the adsorption of MG on to the adsorbent

Effect of Temperature

Effect of temperature on the adsorption of MG is shown in fig.5. As the temperature was increased from $30C^0$ to $60C^0$ the adsorption percentage also increased. As the temperature is increased there may be an increase in the porosity and in the total pore volume of the adsorbent. This may also be a result of an increase in the mobility of the dye molecule with the rise of temperature.

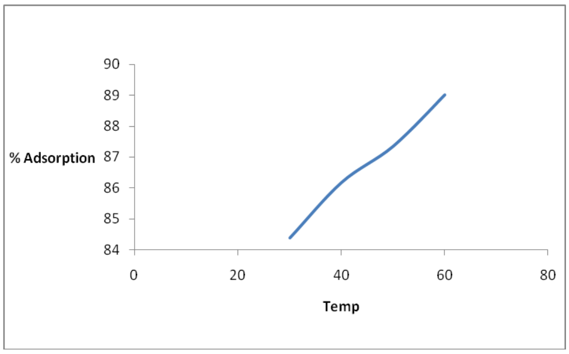

Fig. 5: Effect of temperature on the adsorption of MG on to the adsorbent

IV. ADSORPTION ISOTHERMS

Langmuir Adsorption Isotherm

The adsorption isotherm indicate the relationship between the amount of the dye adsorbed by adsorbent and the amount of dye remaining in the solution. In this study, two most commonly used isotherms, namely Freundlich and Langmuir were tested.

The Langmuir isotherm[29] was based on the assumption that maximum adsorption corresponds to a saturation monolayer of adsorbate molecules on the surface of the adsorbent, the energy of adsorption was constant and there was no interaction among the adsorbate molecules on the surface of the adsorbate.

The linear form of Langmuir equation is given as

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

Where,Qe, is the amount of adsorbate adsorbed per unit mass of carbon, (mg/g), $Q_{0,}$ is constant relating to monolayer adsorption capacity (mg/g), b, is a constant relates to the energy of the adsorption process (L/mg), Ce, is the equilibrium concentration of the adsorbate in solution (mg/L),

A plot of Ce/Qe against Ce for the adsorption of MG was shown in fig.6. From the slope and intercept the values Q_0 and b were calculated. The value of linear regression co-efficient (R^2) was found to be 0.999 (table-2) indicating that it follows Langmuir adsorption isotherm.

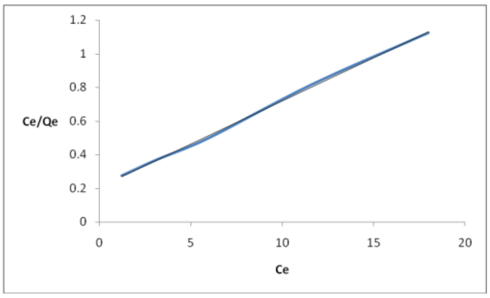

Fig. 6: Langmuir isotherm for the adsorption of MG on to the adsorbent

Table 2: Langmuir isotherm constants

Qo(mg/g)	b	R^2
18.5185	0.1881	0.999

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 unfavorable.

R_L is defined by the following equation

$R_L = 1/ (1+bCo)$

Where, R_L _ dimensionless separation factor, Ci – intial concentration, b – Langmuir constant (Lmg-^{1}),The parameter $R_L$indicates the type of the isotherm accordingly

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 10mg/l MG concentration is 0.3471. This R_L value lies between 0 and 1 indicating the favourability of the adsorption.

Freundlich Adsorption Isotherm

The linear form of the Freundlich equation[30] is as follows

$$\log \mathrm{Qe} = \log \mathrm{K}_F + \frac{1}{n} \log Ce$$

Where Qe = amount of dye adsorbed (mg/g),K = adsorption intensity,n = adsorption capacity

By ploting logQe Vs logCe, the values of n and K were calculated from slope and intercept respectively (fig-7). The values are given in table-3. The value of linear regression co-efficient (R^2) was found to be 0.963 indicating that it does not follow Freundlich adsorption isotherm.

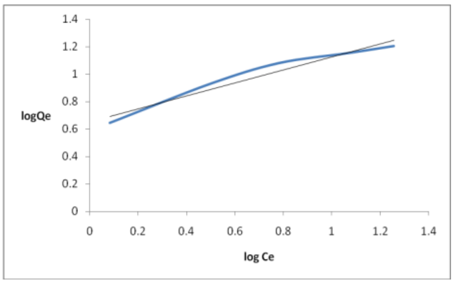

Fig. 7: Freundlich isotherm for the adsorption of MG on to the adsorbent

Table 3: Freundlich isotherm constants

n	K_f(mg/g)	R^2
2.0746	3.6982	0.969

V. THERMODYNAMICPARAMETERS

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 $\Delta G^{o,}$ the ΔG^o value is negative, the reaction occurs 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.

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

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

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

Where Ci is the concentration of the dye at equilibrium and Ce is the amount of dye adsorbed on the adsorbent

The values of ΔH^o(KJmol^{-1}) and ΔS^o (Jmol^{-1}K^{-1}) can be obtained from the slope and intercept of a linear plot between log K_o and 1/T as are presented in table-4.

Table 4: Thermodynamic parameters for the adsorption of MG on to the adsorbent

Conc.of MG dye (mg/l)	-ΔG				ΔH	ΔS
	30^0C	40^0C	50^0C	60^0C		
10	4.253	4.765	5.191	5.792	10.887	49.91
20	3.397	4.034	4.365	4.848	10.699	46.68
30	2.501	2.988	3.458	3.838	11.007	44.61
40	1.752	2.063	2.383	2.999	10.356	39.74
50	0.812	1.274	1.545	2.026	10.913	38.71

The negative values of ΔG^o indicated that the adsorption process is feasible and spontaneous in nature. Positive values of ΔH^o suggested that the adsorption process was endothermic in nature. The positive value of ΔS^o indicates that some structural changes occur on the adsorbent and the randomness at the solid/liquid interface increased during the adsorption process.

IV. CONCLUSION

The adsorption was found to highly dependent on various parameters like contact time, pH, intial concentration, and temperature. It was concluded that maximum adsorption of MG from aqueous solutions occurred at pH5. 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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