

# Removal of Malachite Green from Aqueous Solutions by Adsorption Using Low Cost Adsorbent *Andrographis Paniculata* Leaves

S.Nirmala\*, A.Pasupathy\*\*, M.Raja\*\*\*

Department of Chemistry, Urumu Dhanalakshmi College, Tiruchirappalli, Tamil Nadu

**Abstract-** Activated carbon prepared from *Andrographis paniculata* leaves was employed as an adsorbent for the removal of Malachite green dye 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 Freundlich isotherm models. Kinetic studies were also made. The maximum removal was obtained for the adsorbent dose of 100mg at 10mg/l dye concentration at pH 5 and agitation speed of 120rpm. The result shows that *Andrographis paniculata* leaf could be employed as an effective low cost adsorbent for the removal of MG.

**Index Terms-** Malachite green, low cost adsorbent, *Andrographis paniculata* leaf, Isotherm models, kinetics.

## I. INTRODUCTION

Rapid industrialization, urbanization and over exploitation of the natural resources lead to environmental pollution. It arises due to the discharge of untreated or partly treated effluents from industries such as paper, textile, plastic to the water bodies. Due to the complex aromatic molecular structure and synthetic origin it is very difficult to remove the dyes from the environment. Most of the dyes and their breakdown products may be toxic to living organisms<sup>2</sup>. Polluted water is unfit for human consumption and agricultural purposes.

Physical, chemical and biological methods are available for the removal of dyes<sup>3,4</sup>. Among these methods adsorption is widely used for dye removal from waste waters<sup>5</sup>. Activated carbon is the best adsorbent because of its excellent adsorption efficiency for the organic compounds<sup>6</sup>. The activated carbon is expensive, hence the current research is focused mainly on low cost adsorbent from plants origin. Many low cost adsorbents were prepared from materials such as coir pith<sup>7</sup>,Neem leaf<sup>8</sup>, Sugarcane bagasse<sup>9</sup>, Rice bran<sup>10</sup>, Tea waste<sup>11</sup>, Cotton plant wastes<sup>12</sup>, Jute stick powder<sup>13</sup>, Jackfruit peel<sup>14</sup>,parthenium plant<sup>15</sup>, hazelnut shell<sup>16</sup>, redmud<sup>17</sup>, activated sludge<sup>18</sup> and Rice husk<sup>19</sup>.These adsorbents are easily available and highly effective.

Malachite green dye is mainly used in leather and paper industries. In the present study, acid activated carbon obtained from *Andrographis paniculata* leaf is employed to remove malachite green from an aqueous solution.

## II. EXPERIMENTAL

### Preparation of adsorbent materials

*Andrographis paniculata* leaves was collected and washed with tape 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 soaked in con.H<sub>2</sub>SO<sub>4</sub>(1:1,w/w), for a day, then filtered and dried. The charred mass was kept in a muffle furnace at 400<sup>0</sup>C 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

pH	6.9
Moisture Content, %	11.8
Ash Content, %	9.9
Volatile Matter, %	20.8
Water Soluble matter, %	0.40
Acid Soluble Matter, %	0.92
Bulk Density, g/mL	0.43
Specific Gravity	0.91
Porosity, %	49.8
BET Surface Area, m <sup>2</sup> /g	478.529
Fixed Carbon, %	45.2

**Table-1 Characteristics of the adsorbent**

### Preparation of adsorbate

The adsorbate used in this study is Malachite Green was obtained from Merk, India, with molecular formula-C<sub>23</sub>H<sub>25</sub>ClN<sub>2</sub>, Molecular weight 364.92- λ<sub>max</sub>-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 filtration, the dye solutions were analysed by UV-Visible spectrophotometer. The

percentage of MG dye removal was calculated by using the following equation

$$\% \text{ MG dye removal} = \frac{C_i - C_e}{C_i} \times 100$$

Where  $C_i$  = initial concentration(mg/l),  $C_e$  = equilibrium concentration

The adsorption capacity  $Q_e$ , is obtained from the following equation .

$$Q_e = \frac{(C_i - C_e)V}{M}$$

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. As the pH is further increased the dye removal decreases rapidly. 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.

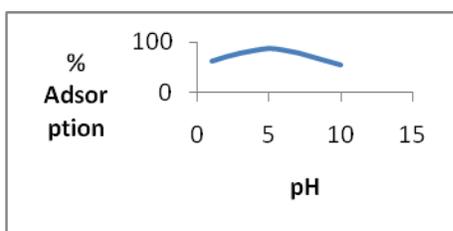


Fig:1 Effect of pH on the adsorption of MG on to the adsorbent

#### 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. This can be attributed to the availability of large number of vacant sites for adsorption.

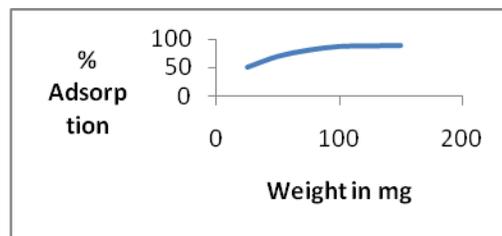


Fig:2 Effect of adsorbent dose on the adsorption of MG on to the adsorbent

#### 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 from 87% to 63%

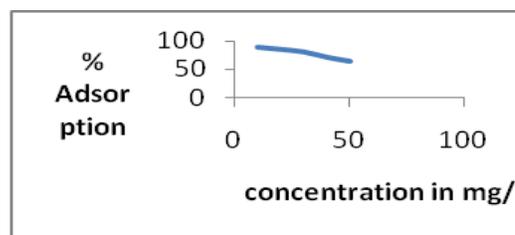


Fig:3 Effect of dye concentration on the adsorption of MG on to the adsorbent

#### 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 increased from 55 to 93 at 90min. There was no appreciable change in the adsorption percentage above 90min. Hence all the experiments were conducted for a period of 90min.

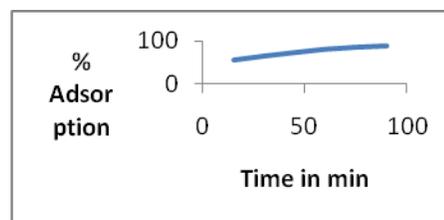


Fig:4 Effect of contact time on the adsorption of MG on to the adsorbent

### 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.

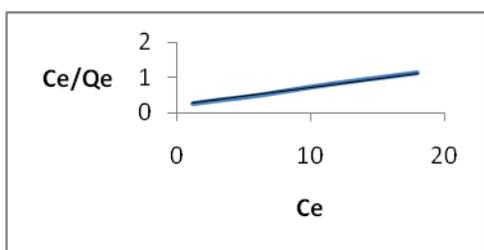
The Langmuir isotherm<sup>20</sup> was based on the assumption that maximum adsorption corresponds to a saturation monolayer of adsorbate molecules on the surface of the adsorbent, the energy of adsorption was constant and there was no interaction among the adsorbate molecules on the surface of the adsorbate.

The linear form of Langmuir equation is given as

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b}$$

Where,  $Q_e$ , 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),  $C_e$ , is the equilibrium concentration of the adsorbate in solution (mg/L),

A plot of  $C_e/Q_e$  against  $C_e$  for the adsorption of MG was shown in fig.5. 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:5 Langmuir isotherm for the adsorption of MG on to the adsorbent**

$Q_0$ (mg/g)	$b$	$R^2$
19.6078	0.2440	0.999

**Table-2.Langmuir isotherm constants**

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

$$R_L = 1 / (1 + bC_0)$$

Where,  $R_L$  \_ dimensionless separation factor.,  $C_i$  – initial concentration ,  $b$  – Langmuir constant (Lmg<sup>-1</sup>),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
$R_L = 0$	Irreversible

The  $R_L$  value obtained using the above equation for 10mg/l MG concentration is 0.2906. This  $R_L$  value lies between 0 and 1 indicating the favourability of the adsorption.

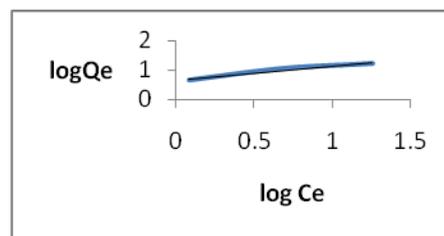
### Freundlich Adsorption Isotherm

The linear form of the Freundlich equation<sup>21</sup> is as follows

$$\log Q_e = \log K_f + 1/n \log C_e$$

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

By plotting  $\log Q_e$  Vs  $\log C_e$ , the values of  $n$  and  $K$  were calculated from slope and intercept respectively (fig-6). The values are given in table-3. The value of linear regression co-efficient ( $R^2$ ) was found to be 0.925 indicating that it follows Langmuir adsorption isotherm more than the Freundlich adsorption isotherm.



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

$n$	$K_f$ (mg/g)	$R^2$
2.1097	4.4771	0.925

**Table-3. Freundlich isotherm constants**

### V. KINETIC STUDY

#### Pseudo first order kinetics

The linear form of first order kinetic equation is

$$\log (q_e - qt) = \log q_e - (k_1/2.303)t$$

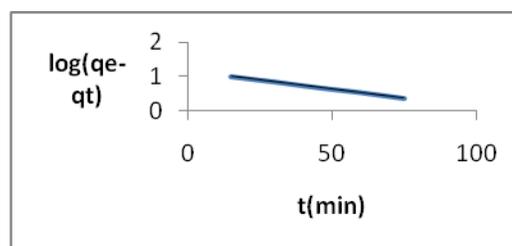
Where  $q_e$  is the amount of dye adsorbed at equilibrium.  $k_1$  is the first order rate constant.

A plot of  $\log (q_e - qt)$  verses  $t$ (min) gives a straight line fig.7. From the slope  $k_1$  and from the intercept  $q_e$  were determined.. These values are presented in the table-4.

$q_e$	$k_1$	$R^2$
14.5211	0.02302	0.999

**Table-4 Pseudo First order kinetic parameters**

The value of  $R^2$  indicates that the first order kinetics was followed by MG adsorption.



**Fig:7.First order kinetics for the adsorption of MG on to the adsorbent**

#### Pseudo second order kinetics

The linear form of pseudo second order kinetic equation is

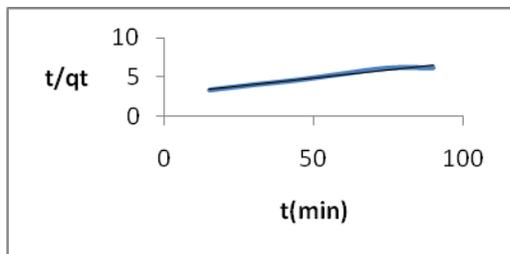
$$t/qt = 1/k_2qe^2 + t/qe$$

Where  $k_2$  is the rate constant of second order adsorption. The values of  $q_e$  and  $k_2$  were obtained from the slope and intercept of a linear plot of  $t/qt$  versus  $t$ . (Fig.8). These values are presented in the table-5.

$q_e$	$k_2$	$R^2$
25.000	0.0005	0.815

**Table-5 Pseudo Second order kinetic parameters**

The result shows that second order kinetics was not favoured by MG adsorption.



**Fig:8. Second order kinetics for the adsorption of MG on to the adsorbent**

## VI. 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  $\Delta G^\circ$ . If the  $\Delta G^\circ$  value is negative, the reaction occurs spontaneously. The Thermodynamic parameters standard free energy ( $\Delta G^\circ$ ), change in Standard enthalpy( $\Delta H^\circ$ ) and change in Standard entropy( $\Delta S^\circ$ ) for the adsorption of MG onto the adsorbent were calculated using the following equations.

$$K_0 = (C_i - C_e)/C_e$$

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

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

Where  $C_i$  is the concentration of the dye at equilibrium and  $C_e$  is the amount of dye adsorbed on the adsorbent

The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  can be obtained from the slope and intercept of a linear plot between  $\log K_0$  and  $1/T$  as are presented in table-6.

Conc. of MG dye (mg/l)	- $\Delta G$ (KJ/mol)				$\Delta H$ (KJmol <sup>-1</sup> )	$\Delta S$ (J/k/mol)
	30°C	40°C	50°C	60°C		
10	4.995	5.411	5.928	6.996	14.417	63.62
20	4.250	4.596	4.896	5.914	11.457	51.42
30	3.486	3.881	4.182	4.860	9.722	43.44
40	2.252	2.823	3.199	3.618	11.222	44.59

50	1.446	1.837	2.148	2.472	8.744	33.67
----	-------	-------	-------	-------	-------	-------

**Table-6 Thermodynamic parameters for the adsorption of MG on to the adsorbent.**

The negative values of  $\Delta G^\circ$  indicated that the adsorption process is feasible and spontaneous in nature. Positive values of  $\Delta H^\circ$  suggested that the adsorption process was endothermic in nature. The positive value of  $\Delta S^\circ$  indicates that some structural changes occur on the adsorbent and the randomness at the solid/liquid interface increased during the adsorption process.

## VII. CONCLUSION

The adsorption was found to highly dependent on various parameters like contact time, pH, initial concentration, and temperature. It was concluded that maximum adsorption of MG from aqueous solutions occurred at pH5. Kinetic and isotherm studies revealed that *Andrographis paniculata* leaves can be effectively employed for the adsorption of MG. The experimental data were correlated well by the Langmuir adsorption isotherm. The adsorption process was well described by pseudo first order kinetics. The result of this study indicates that this adsorbent can be successfully utilized for the removal of MG from aqueous solution.

## REFERENCES

- [1] S. Seshadri, P.L. Bishop and A.M. Agha, Waste Manag.(1994),15,127.
- [2] N. Kannan, and M.M. Sundaram, Dyes Pig.,51(2001)25-40.
- [3] Y.M.Slokar A. Majcen Le Marechal, Dyes Pig., 37(1998):335-336.
- [4] O.J. Hao, H. Kim, PC. Chiang, Crit. Rev Environ Sci Technol.30(2009)449-505.
- [5] G.M.Walker, and L.R.,Weatherley Environ. Pollut., 99(1998) 133-136.
- [6] R.S., Juang F.C. Wu and R.L., Tseng Physicochemical and Engineering Aspects,201(2002)191-199.
- [7] C. Namasivayam, R. Radhika, S. Suba, Waste Manag.,(2001)381.
- [8] K.G. Bhattacharyya, A. Sarma Dyes Pig. 57(2003) 211.
- [9] S.Saiful Azhar, A.Ghaniey Liew, D.Suhardy, K.Farizul Hafiz and M.D Irfan Hatim, American Journal of Applied sciences,2(11),(2005),1499-1503.
- [10] S.Hashemian, S.Dadfarnia, M.R. Nateghi and F.Gafoor African Journal of Biotechnology, 7(5),(2008),600-605.
- [11] .M.Tamez Uddin, M.Akhtarul Islam, S.Mahmud and M. Rukanuzzaman., J. Hazard Mater., 164,(2009),53-60.
- [12] Ozlem Tunc, Hacer Tanac and Zumriye Aksu, J. Hazard Mater., 163(1),(2009)187-198.
- [13] G.C. Panda, S.K. Das, and A.K. Guha J. Hazard Mater.,164(1),(2009),374-379.
- [14] B.H.Hameed, J Hazard Mater.,162(1),(2009),344-350.
- [15] S. Rajeshwari and V. Subburam Bioresour Technol, 85,(2002)205-206.
- [16] M. Dogan, H.Abak and M. Alkan, J.Hazard. Mater.,164,(2009),172-181.
- [17] C.Namasivayam, D.Arasi, Chemosphere 34(1997)401.
- [18] R.L.Tseng, F. Wu,R.S. Ch.,Juang Carbon 41(2003)487.
- [19] Vadivelan and K.V. Kumar, J.Colloid Interf. Sci.,286,(2005),90-100.
- [20] I.Langmuir, J.Am.chem.soc.,40(1918)1361-1403
- [21] J.Freundlich,J.phys.chem.,57(1906)385-470.

AUTHORS

**First Author** – S.Nirmala, Department of Chemistry, Urumu Dhanalakshmi College, Tiruchirappalli, Tamil Nadu

**Second Author** – A.Pasupathy, Department of Chemistry, Urumu Dhanalakshmi College, Tiruchirappalli, Tamil Nadu  
**Third Author** – M.Raja,, Department of Chemistry, Urumu Dhanalakshmi College, Tiruchirappalli, Tamil Nadu