

## Removal of Malachite Green Dyes By Adsorption onto Activated Carbon – MnO<sub>2</sub> – Nanocomposite – Kinetic Study and Equilibrium Isotherm Analyses

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**Abstract:** This paper presents the feasibility of removal of basic dye malachite green from aqueous solutions by using a low cost AC-MnO<sub>2</sub>-NC. Batch adsorption experiments were carried out as a function of pH, contact time, initial concentration of the adsorbate, adsorbent dosage and temperature. Langmuir, Freundlich and Temkin isotherms were also studied. Pseudo first order, Pseudo second order, intra-particle diffusion model and Elovich kinetic models were studied. Thermodynamic parameters such as  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  were also calculated. Adsorbent used in this study are characterized by FT-IR, XRD and SEM analysis.

**Keywords:** Malachite Green, AC-MnO<sub>2</sub>-NC, adsorption isotherm, Kinetics.

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### I. Introduction

Dyes and pigments are extensively used in paper, textile, food, dye houses and printing to color the final products and they generated waste water. Dyes are synthetic aromatic water-soluble dispersible organic colorants, having potential application in industries. Recently, it was estimated about 10,000 of different commercial dyes and pigments exist and over  $7 \times 10^5$  metric tons are produced annually worldwide [1]. Presence of colour in the waste water is one of the main problems in textile industries. From the environmental points of view; the removal of synthetic dyes is of great concern, because some dyes and their degradation products are carcinogenic and toxic [2].

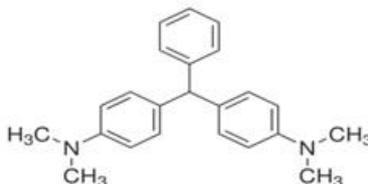
Malachite green [MG] is water soluble basic triphenyl methane dye. It dissociate into anion and coloured cations. The electrostatic attraction builds up between the coloured cations and acidic groups of acrylic fibers lead to form salt and develop the colour fade upon the fabrics. The structural studies will give the idea about the absorption mechanism involved with these dyes.

It is used as an antifungal, anti-bacterial, and anti-parasitical therapeutic agent in aquacultures and animal husbandry. It is also used as a direct dye for silk, wool, jute and leather. Malachite green causes detrimental effects on liver, gill, kidney, intestine and gonads of aquatic organisms. Contact of malachite green with skin causes irritation with redness and pain. Intermediate products after degradation of malachite green are also reported to be carcinogenic [3]. Therefore, the use of malachite green in aquaculture was banned in many countries. When it was inhaled [or] ingested by human, it may cause irritation to the gastrointestinal tract and even cancer [4]. However, MG in fishes, animal milk and other foodstuff is still detected due to illegal use of MG [5] which is create the health hazards against human being.

The most commonly used to remove the dyes are coagulation, electro coagulation, flotation, chemical oxidation, filtration, ion-exchange, ozonation, membrane separation, aerobic and anaerobic microbial degradation. However, all such methods suffer from one [or] other limitations and none of them were successfully removing the colour from wastewater.

Adsorption on activated carbons has been proven to be very effective in removing dyes from aqueous solutions. However, activated carbon is still considered to be expensive and current research is focused on the development of low-cost adsorbents for this purpose. Low-cost adsorbents include natural, agricultural and industrial by product wastes. Previously the Grass-waste [6], Jackfruit peel [7], Chitosan / Oil palm ash [8], Durian peel [9], Papaya seeds [10], Rattan saw dust [11], Palm ash [12], Pomelo [citrus grandis] peel [13], Sunflower seed hull [14], Oil palm trunk fibre [15], Rice straw-derived charcoal [16], Firmiana simplex wood fiber [17], Seaweed Enteromorpha [18], Sulphuric acid treated marble power [SATMP] [19], Cashew nut Bark [20], Acid activated Nirgudi leaf powder [21], Sugarcane bagasse [22], Pandanus Carbon [23], Hydrilla Verticillata [24], Annona Squamosa seed activated carbon [25], Surface of wool fiber [26], Bannana Pseudo-stem fibers [27], Chemically modified silicagel [28], Terminalia catappa linn carbon [TCC] [29], borassus Bark carbon [30], Jambonut [31] and Borassus flabellifer L [32]. The efficiency of the adsorption process mainly depends on the cost and removal capacity of adsorbents used. Now a days, agricultural waste materials are receiving much more attention as adsorbents for the removal of dyes from wastewater due to its low cost and

good availability. Many studies have been undertaken for the removals of pollutants by using variety of materials are used as adsorbents [33-38]. The objectives of our investigation were to investigate the potential of using Activated carbon-MnO<sub>2</sub>-Nanocomposite as a low – cost adsorbent to remove malachite green from aqueous solutions, to model the equilibrium and kinetics of the adsorption process. For further study it was indicated as AC-MnO<sub>2</sub>-NC. The Chemical structure of malachite green is given below.



## II. Materials and Methods

### 2.1 Adsorbate

Basic dye used in this study is Malachite Green purchased from S.d. fine chemicals. MG has molecular formula C<sub>50</sub>H<sub>52</sub>N<sub>4</sub>O<sub>8</sub>. The dye concentration in supernatant solution was determined at characteristic wavelength [ $\lambda_{\text{max}} = 617\text{nm}$ ] by double beam UV-visible spectrophotometer [Systronics 2202].

### 2.2. Preparation of Activated Carbon

The Typha Angustata L plant materials were collected from local area situated at Thindal, Erode District, Tamilnadu. They were cut into small pieces and dried for 20 days. Finally it was taken in a steel vessel and heated in muffle furnace. The temperature was raised gradually upto 500<sup>0</sup>C and kept it for half an hour. The carbonised material was ground well and sieved to different particle size. It was stored in a plastic container for further studies. In this study particle size of 0.15 to 0.25mm was used.

### 2.3. Preparation of AC-MnO<sub>2</sub>-NC

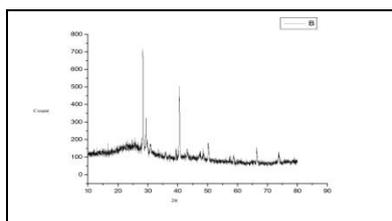
Activated Carbon [3gm] was allowed to swell in 15mL of water-free Alcohol and stirred for 2 hours at 25<sup>0</sup>C to get uniform suspension. At the same time, the Manganese dioxide [3gm] was dispersed into water-free Alcohol [15mL]. Then the diluted Manganese dioxide was slowly added into the suspension of activated Carbon and stirred for a further 5 hours at 25<sup>0</sup>C. To this, 5mL alcohol and 0.2mL of deionised water was slowly added. The stirring was continued for another 5 hours at 25<sup>0</sup>C and the resulting suspension was kept overnight in a vacuum oven for 6 hours at 80<sup>0</sup>C. Characteristics of the AC-MnO<sub>2</sub>-NC were determined and the results are summarized in Table.1.

**Table.1. Physical and Chemical Properties of Adsorbents**

Physical and Chemical Properties	AC-MnO <sub>2</sub> -NC
[1]. Moisture content [%]	9.19
[2]. Volatile matter [%]	62.73
[3]. Ash [%]	17.15

### 2.4 Characterisation of Adsorbent

Physico-Chemical characteristics of the adsorbents were studied as per the standard testing methods [39]. Fig.1,2 shows the XRD pattern of pure AC and AC-MnO<sub>2</sub>-NC respectively. The peaks at 28° [Fig.1] and at 30° [Fig.2] confirm the presence of AC-MnO<sub>2</sub> phase in the nanocomposite. The surface morphology of the adsorbent was visualised via scanning electron microscopy [SEM] are shown in Fig.3 and 4. The diameter of the composite range was 10µm. FTIR spectra indicate the presence of MnO<sub>2</sub> peak at 430cm<sup>-1</sup>.



**Fig.1. XRD analysis of Activated Carbon**

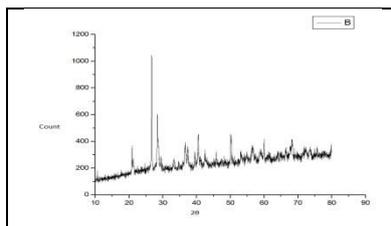


Fig.2. XRD analysis of AC-MnO<sub>2</sub>-NC

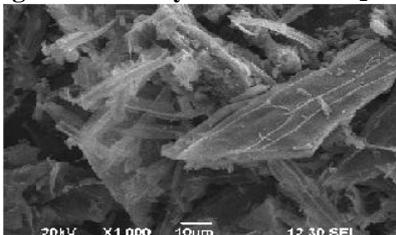


Fig.3. SEM of Activated Carbon

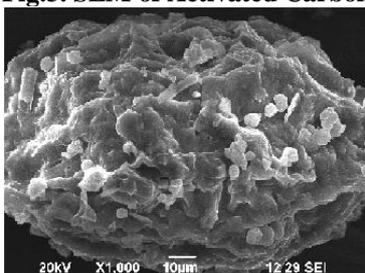


Fig. 4. SEM of AC-MnO<sub>2</sub>-NC

### 2.5 Batch adsorption method

A stock solution [1000mg/L] of MG was prepared by dissolving an appropriate amount of each dye in double distilled water, which was diluted to desired concentrations of 10, 20, 30 and 40mg/L. Batch adsorption [40] experiments were carried out to investigate the effect of P<sup>H</sup>, temperature, adsorbent dose, initial dye concentration, contact time on the adsorption of MG on AC-MnO<sub>2</sub>-NC by varying the parameters under study and keeping other parameters constant. In each experiment pre weighed amount of adsorbent was added to 50mL of dye solution taken in a 150mL of conical flask and the pH was adjusted by using 0.1M NaOH or 0.1M HCL. The resulting solution was agitated at 200rpm on a stirrer at constant temperature and centrifuged [Remi Research Centrifuge].

The percentage removal of dye and amount of dye adsorbed on AC-MnO<sub>2</sub>-NC was calculated by equation (1) and equation (2) respectively.

$$\% \text{ removal} = \frac{100[C_0 - C_e]}{C_e} \text{ -----> (1)}$$

$$q_e = \frac{[C_0 - C_e] V}{W} \text{ -----> (2)}$$

Where q<sub>e</sub> is the quantity of dye adsorbed on the adsorbent at the time of equilibrium [mg/g], C<sub>0</sub> and C<sub>e</sub> are the initial and equilibrium concentrations [mgL<sup>-1</sup>] of the dye in solution respectively, V is the volume [L] of solution and W is the weight of adsorbent [g]. All adsorption experiments were performed in triplicate and the mean values were used in data analysis.

### 2.6. Batch Kinetic Studies

The batch kinetic [40] experiments were basically identical to these of adsorption equilibrium method. The amount of adsorption q<sub>t</sub> [mg/g] at time t, was calculated by,

$$q_t = \frac{[C_0 - C_t] V}{W} \text{ -----> (3)}$$

W

Where C<sub>t</sub> [mg/L] is the liquid phase concentration of dye at any time.

**III. Theory of Adsorption isotherm**

To quantify the adsorption capacity of the adsorbent for the removal of dyes, the most commonly used isotherm, namely Freundlich, Langmuir and Tempkin have been adopted.

**3.1. Freundlich Isotherm**

The linear form of Freundlich isotherm [41] is represented by the equation.

$$\log q_e = \log k_f + 1/n \log C_e \text{ -----} > (4)$$

Where q<sub>e</sub> is the amount of dyes absorbed per unit weight of the adsorbent, [mg/L], k<sub>f</sub> is [mg/g [L/mg]] measures of adsorption capacity and 1/n is the adsorption intensity. In general k<sub>f</sub> Value increases the adsorption capacity for a given adsorbate increases. The magnitude of the exponent 1/n gives an indication of the favorability of adsorption. The value of n > 1 represents favorable adsorption condition [42, 43] or the value of 1/n are lying in the range of 1 to 10 confirms the favourable condition for adsorption. The linear plot of log q<sub>e</sub> Vs log C<sub>e</sub> shows that the adsorption obeys the freundlich model.

**3.2. Langmuir Isotherm**

Langmuir isotherm model [44] is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The linear form of the Langmuir isotherm equation can be described by

$$C_e / q_e = \frac{1}{Q_o K_L} + \frac{C_e}{Q_o} \text{ -----} > (5)$$

Where C<sub>e</sub> [mg/L] is the equilibrium concentration of the adsorbate, q<sub>e</sub> [mg/g] is the amount of adsorbate adsorbed per unit mass of adsorbent, Q<sub>o</sub> and K<sub>L</sub> are Langmuir constants related to adsorption capacity and rate of adsorption respectively. Q<sub>o</sub> is the amount of adsorbate at complete monolayer coverage [mg/g] which gives the maximum adsorption capacity of the adsorbent and K<sub>L</sub> [L/mg] is the Langmuir isotherm constant that relates to the energy of adsorption [or rate of adsorption]. The linear plot of specific adsorption capacity C<sub>e</sub>/q<sub>e</sub> against the equilibrium concentration C<sub>e</sub> shows that the adsorption obeys the Langmuir model. The Langmuir constant Q<sub>o</sub> and K<sub>L</sub> were determined from the slope and intercept of the plot and are presented in Table 2. In order to find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R<sub>L</sub> [45, 46] by the equation,

$$R_L = \frac{1}{1 + K_L C_o} \text{ -----} > (6)$$

Where C<sub>o</sub> [mg/L] is the initial concentration of adsorbate and K<sub>L</sub> [L/mg] is Langmuir isotherm constant. The parameter R<sub>L</sub> indicate the nature of the adsorption isotherm.

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<b>R<sub>L</sub> &gt; 1</b>	<b>Unfavorable adsorption</b>
<b>0 &lt; R<sub>L</sub> &lt; 1</b>	<b>Favorable adsorption</b>
<b>R<sub>L</sub> = 0</b>	<b>Irreversible adsorption</b>
<b>R<sub>L</sub> = 1</b>	<b>Linear adsorption</b>

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The R<sub>L</sub> values lies between 0 to 1 indicate the process is favorable adsorption.

**3.3. Tempkin isotherm**

Tempkin isotherm contains a factor that explicitly takes into account adsorbing species-adsorbate interactions. This isotherm assumes that : [1]. The heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate interactions, and [2]. Adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [47].

Tempkin isotherm is represented by the following equation:

$$q_e = RT/b \ln[AC_e] \text{ -----} > (7)$$

equation (7) can be expressed in its linear form as:

$$q_e = RT/b \ln A + RT/b \ln C_e$$

$$q_e = B \ln A + B \ln C_e \text{-----} > (8)$$

Where  $B = RT/b$

The adsorption data can be analyzed according to equation (8). A plot of  $q_e$  Versus  $\ln C_e$  enables the determination of the isotherm constants A and B. A is the equilibrium binding constant [1/mol] corresponding to the maximum binding energy and constant B is related to the heat of adsorption. For MG adsorption by AC-MnO<sub>2</sub>-NC and values of the parameters are given in Table [2].

#### IV. Adsorption Kinetics

The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the Solid-Solution interface. The kinetics of MG adsorption by the AC-MnO<sub>2</sub>-NC were analyzed using Pseudo first-order, Pseudo second – order, Elovich and intra particle diffusion model. The conformity between experimental data and the kinetic models was expressed by the correlation coefficient [ $R^2$ ] value, the  $R^2$  values close or equal to 1. A relatively high  $R^2$  value indicates that the model successfully describes the kinetics of MG dye adsorption.

##### 4.1. Pseudo first order kinetic model

The linear form of Langergren's first order rate equation is as follows [48],

$$\ln [q_e - q_t] = \ln q_e - K_1 t \text{-----} > (9)$$

Where  $q_e$  is the amount of dye adsorbed onto the adsorbent at equilibrium [mg/g],  $q_t$  is the amount of dye adsorbed on to the adsorbent at any time t [mg/g] and  $K_1$  [ $\text{min}^{-1}$ ] is rate constant of the pseudo first order adsorption which can be calculated from the slope of the linear plot of  $\ln [q_e - q_t]$  Vs t [slope =  $K_1$ ,  $q_e$  = intercept]. The adsorption of pseudo first order rate constant and correlation coefficient [ $R^2$ ] values are summarized in Table [3].

##### 4.2 Pseudo second order kinetic model

The linearised form of the pseudo second order model as given by Ho [49] is

$$t/q_t = 1/K_2 q_e^2 + t/q_e \text{-----} > (10)$$

Where  $K_2$  [ $\text{gmg}^{-1}\text{min}^{-1}$ ] is the rate constant of the pseudo second order adsorption,  $q_e$  is the amount of dye adsorbed on the adsorbent at equilibrium [mg/g], and  $q_t$  is the amount of dye adsorbed on the adsorbent at any time, t [mg/g]. The plot of  $t/q_t$  Vs t should give a linear relationship from which  $q_e$  and  $K_2$  can be determined from the slope and intercept of the plot respectively. The pseudo second order rate constant  $K_2$ , the correlation coefficient [ $R^2$ ] values are summarized in Table [3].

##### 4.3. Elovich model

The elovich model equation is generally expressed as [50]

$$q_t = 1/\beta \ln[\alpha\beta] + 1/\beta \ln t \text{-----} > (11)$$

Where  $\alpha$ - is the initial adsorption rate [ $\text{mg g}^{-1}\text{min}^{-1}$ ],  $\beta$  is the desorption constant [ $\text{gmg}^{-1}$ ] during any one experiments. A plot of  $q_t$  Vs  $\ln t$  should yield a linear relationship with a slope of [ $1/\beta$ ] and an intercept of [ $1/\beta \ln[\alpha\beta]$ ]. The elovich model parameters  $\alpha$ ,  $\beta$  and correlation coefficient [ $R^2$ ] are summarized in Table [3].

##### 4.4. Intraparticle diffusion model

The intraparticle diffusion model used here refers to the theory proposed by Weber and Morris [51] based on the following equation for the rate constant

$$q_t = K_{id} t^{1/2} + C \text{-----} > (12)$$

Where  $K_{id}$  is the intraparticle diffusion rate constant [ $\text{mg g}^{-1} \text{min}^{-1/2}$ ] and C is constant. If the rate limiting step is intraparticle diffusion, the graphical representation of adsorbed dye  $q_t$  [ $\text{mgg}^{-1}$ ] depending on the square root of the contact time [ $t^{1/2}$ ] should yield a straight line passing through the origin [40]. The plot of  $q_t$  Vs  $t^{1/2}$  will give the value of the intraparticle diffusion rate constant [ $K_{id}$ ] and correlation coefficient [ $R^2$ ] can be determined from the slope respectively. The intraparticle diffusion rate constant  $K_{id}$ , the correlation co-efficient [ $R^2$ ] values are summarized in Table [3].

#### V. Thermodynamic treatment of the adsorption process

The effect of temperature on the adsorption of MG by AC-MnO<sub>2</sub>-NC adsorbents was investigated at 303, 313, 323 and 333K. Thermodynamic parameters, such as change in enthalpy [ $\Delta H^\circ$ ], entropy [ $\Delta S^\circ$ ] and Gibb's free energy [ $\Delta G^\circ$ ] were determined for the MG by AC-MnO<sub>2</sub>-NC using equation (13) & (14). [52].

$$\ln [q_e m / C_e] = \Delta S^\circ / R - \Delta H^\circ / RT \text{ -----> (13)}$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \text{ -----> (14)}$$

Where m is the adsorbent dose [mg/L], C<sub>e</sub> is the equilibrium concentration [mg/L] of the dye in solution and q<sub>e</sub>m is the solid-phase concentration [mg/L] at equilibrium. R is the gas constant [8.314J/mole/K] and T is the temperature [K]. ΔH°, ΔS° and ΔG° are changes in enthalpy [KJ/mol], entropy [J/mol/K] and Gibb's free energy [KJ/mol] respectively.

The values of ΔH° and ΔS° were determined from the slope [-ΔH°/R] and the intercept [ΔS°/R] of the plots of ln [q<sub>e</sub>m/C<sub>e</sub>] Vs 1/T. The ΔG° values were calculated by using equation (14). The values of the thermodynamics parameters are presented in Table [4].

## VI. Results and discussions

### 6.1. Effect of Agitation time Vs initial dye concentration

Effect of Agitation time Vs initial dye concentration [10, 20, 30 and 40 mg/L] on the percent removal of MG by AC-MnO<sub>2</sub>-NC are increased with increase in agitation time and reached equilibrium at 210min. The percent dye removal at equilibrium decreased from 82.16 to 53.73 as the dye concentration was increased from 10 to 40 mg/L. It is clear that the removal of dye depends on the initial concentration of the dye. The removal curves are single, smooth and continuous leading to saturation.

### 6.2. Effect of adsorbent dosage

The removal of MG by AC- MnO<sub>2</sub>-NC at different adsorbent dosage [10mg to 600mg/50mL] was tested for the dye concentrations 10, 20, 30 and 40mg/L. The adsorption increases with increase in adsorbent concentration; this is due to the increase in surface area and availability of more adsorption site. The percentage removal of MG is greatly increases in the range of 10-600mg/50mL after that small change occur. So the optimum adsorbent carbon dosages for the experiments were carried out using 100 mg / 50mL.

### 6.3. Effect of pH

The solution pH is one of the most important factors that control the adsorption of MG on the adsorbent material. Therefore an increase in pH may cause an increase [or] decrease in the adsorption capacity. The adsorption capacity can be attributed to the chemical form of MG in a solution at the specific pH [or] due to different functional group on the adsorbent surface. To examine the effect of pH on the percentage removal of MG gradually increases as the pH increases. The pH value up to 7.35 the percentage removal is up to 27.92 after that suddenly increases. At that solution pH the adsorbent surface negatively charged and favours uptake of cationic dyes due to increased electrostatic force of attraction. Therefore, all the experiments were carried out at the pH 7.35. For 40mg/L dye concentration the percent removal increased from 27.92 to 74.86 when the pH was increased from 2 to 14 and the percent removal remained almost the same above pH 8.

### 6.4. Effect of Temperature

The effect of temperature on adsorption of MG by AC-MnO<sub>2</sub>-NC for concentration 40 mg/L adsorbent was carried out at 30°, 40°, 50° and 60°C. The percent removal of dye increased from 11.90 to 79.87. This indicates that increase in adsorption with increase in temperature may be due to increase in the mobility of the large dye ions. Moreover, increasing temperature may produce a swelling effect within the internal structure of the adsorbent, penetrating the large dye molecule further.

### 6.5. Adsorption isotherms

Three different isotherm models were used to fit the experimental data the Langmuir, Freundlich and Tempkin models are given in Fig.5,6 and 7 and the parameter values are given in the Table 2.

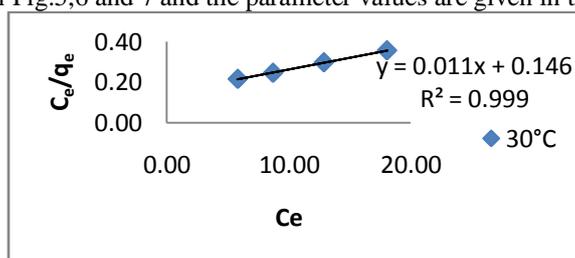


Fig.5. Plot of Langmuir isotherm

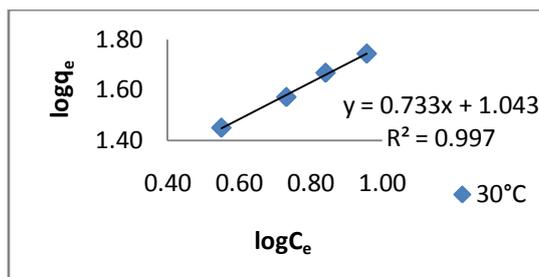


Fig.6. Plot of Freundlich isotherm

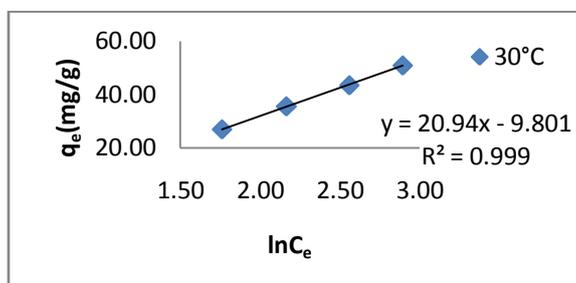


Fig.7. Plot of Tempkin isotherm

Table.2. Langmuir, Freundlich and Tempkin isotherm parameter for adsorption of MG by AC-MnO<sub>2</sub>-NC adsorbent.

Initial dye concentration mg/L	Langmuir				Freundlich			Tempkin			
	Q <sub>0</sub> [mg /g]	K <sub>L</sub> [L/g]	R <sup>2</sup>	R <sub>L</sub>	K <sub>f</sub> [mg/g/ [L/g]]	n	R <sup>2</sup>	A	b	B	R <sup>2</sup>
60	90.909	0.0753	0.999	0.1812	11.0407	1.3642	0.997	0.6262	118.31	20.94	0.999
80				0.1423							
100				0.1172							
120				0.0996							

From the Table.2, it is clear that, the Langmuir isotherm constant value indicate the adsorption capacity Q<sub>0</sub> = 90.9090 mg/g. The Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor [R<sub>L</sub>]. The R<sub>L</sub> Value lies in between 0 to 1 indicate the adsorption is favorable for all the initial dye concentration.

From the Table.2, it is clear that, the Freundlich isotherm constant value indicate 1/n [or] n is the adsorption intensity. The ‘n’ values lies in between 1 to 10 confirm the favorable condition for adsorption.

From the Table.2, it is clear that, the Tempkin isotherm constant value indicate maximum binding energy B= 20.94 and it is related to the heat of adsorption.

All the three models explain correlation co-efficient [R<sup>2</sup>]. From Table.2, MG on AC-MnO<sub>2</sub>-NC to fit Langmuir model. This indicates monolayer adsorption. In addition to that it obey Tempkin model.

### 6.6. Adsorption Kinetics:

The kinetics of MG dye adsorption on MG by AC-MnO<sub>2</sub>-NC was studied with respect to different initial concentration. For evaluating the adsorption kinetics of MG, the Pseudo first order, the pseudo second order, Elovich model and intraparticle diffusion model were used to fit the experimental data by using linear regression analysis method. The parameters of this model are summarized in Table.3. The high correlation coefficient [R<sup>2</sup>] values indicate the fitness of the model.

**Table.3. The kinetic parameter for the adsorption of MG by AC-MnO<sub>2</sub>-NC adsorbent.**

Initial dye concentration	Pseudo first order				Pseudo second order				Intraparticle diffusion			Elovich		
	q <sub>e</sub> exp	q <sub>e</sub> cal	K <sub>1</sub>	R <sup>2</sup>	q <sub>e</sub> exp	q <sub>e</sub> cal	K <sub>2</sub>	R <sup>2</sup>	K <sub>id</sub>	C	R <sup>2</sup>	α	β	R <sup>2</sup>
10	99.25	7.178	9.212 x 10 <sup>-3</sup>	0.626	99.25	52.631	3.539 x 10 <sup>-3</sup>	0.999	0.657	39.83	0.918	1.478 x 10 <sup>15</sup>	0.3396	0.97
20	89.14	16.03	1.515x 10 <sup>-2</sup>	0.934	89.14	47.619	1.500 x 10 <sup>-3</sup>	0.998	1.199	26.09	0.929	91.676	0.19	0.943
30	63.47	14.03	9.212 x 10 <sup>-3</sup>	0.964	63.47	33.333	1.840 x 10 <sup>-3</sup>	0.997	0.9	17.26	0.957	37.573	0.2523	0.979
40	53.73	15.92	9.212 x 10 <sup>-3</sup>	0.939	53.73	29.411	1.172 x 10 <sup>-3</sup>	0.997	1.16	8.779	0.937	3.3065	0.1924	0.984

From the kinetic data, the q<sub>e</sub> value calculated from the pseudo first order model is less than that of the experimental value. But the q<sub>e</sub> values calculated from the pseudo second order model are nearly equal to the experimental value. The correlation co-efficient [R<sup>2</sup>] is high for pseudo second order. So that the adsorption of MG by AC- MnO<sub>2</sub>-NC is to follow the pseudo second order kinetic model.

The experimental data were used for intraparticle diffusion model, the intraparticle diffusion constant [K<sub>id</sub>], intercept and the correlation co-efficient [R<sup>2</sup>] are calculated. From these data the intercept value indicates that the lines are not passing through origin, therefore some other process that may affect the adsorption. The correlation co-efficient [R<sup>2</sup>] is value is less than that of pseudo second order model.

The same experimental data were used for Elovich model, the initial adsorption rate [α], desorption constant [β] and the correlation co-efficient [R<sup>2</sup>] are calculated. But, the correlation Co-efficient [R<sup>2</sup>] is less than that of pseudo second order model.

Finally, From Table.3 indicates all these four kinetic models, MG by AC- MnO<sub>2</sub>-NC is to follow pseudo second order kinetic model.

### 6.7. Thermodynamic parameter

The Thermodynamic parameters for the adsorption process of MG by AC-MnO<sub>2</sub>-NC are the changes in standard free energy change [ΔG<sup>0</sup>], standard enthalpy change [ΔH<sup>0</sup>] and standard entropy change [ΔS<sup>0</sup>]. The values of these parameters were calculated and are shown inTable.3

**Table.4. Thermodynamic parameter values of MG by AC-MnO<sub>2</sub>-NC**

ΔG°[kJ/mol]				ΔS° [J/mol/K]	ΔH° [kJ/ mol]
303K	313K	323 K	333 K		
-44.6210	-46.0950	-47.5691	-49.0432	147.4072	43.3658

The adsorption data indicates that ΔG° values were negative at all temperatures. The negative ΔG° confirms the spontaneous nature of adsorption of MG by AC-MnO<sub>2</sub>-NC. The magnitude of ΔG° suggests that adsorption is physical adsorption process. The positive value of ΔH° were further confirms the endothermic nature of adsorption process. The positive ΔS° showed increased randomness at the solid – solution interface during the adsorption of MG by AC-MnO<sub>2</sub>-NC adsorbent.

## VII. Desorption Studies

After activated carbon is saturated with dye molecules, different solvents could be used to regenerate the activated carbon to restore its dye adsorptive capability [53]. Desorption with acetic acid revealed that the regeneration of adsorbent was satisfactory, which confirms the physisorptive nature of adsorption.

## VIII. Conclusions

The present study shows that AC-MnO<sub>2</sub>-NC is an effective adsorbent for the removal of MG from aqueous solution. Adsorption followed the Langmuir isotherms. The adsorption capacity was found to be 90.9090 mgg<sup>-1</sup>. The thermodynamic parameters were found to be thermodynamically favourable physical adsorption process. Evaluation of thermodynamic parameters showed the process as endothermic and spontaneous. The kinetic parameters fit for Pseudo second order model. Desorption studies reveals that satisfactory desorption taking place confirming physisorptive nature of adsorption. Complete removal of the dye can be achieved using an appropriate dosage of the adsorbent and pH for waste waters. The results would be

useful for the fabrication and designing of waste water treatment plants for the removal of dye. Since the raw material is freely available in large quantities the treatment method, seems to be economical.

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