Thermodynamic and kinetic analysis on the removal of malachite green dye using activated Pistia Stratiotes leaves

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Abstract: The research of the present work was to investigate the removal of Malachite Green from aqueous solution by using Pistia Stratiotes. Generally, dyes are used in chemical, textile, paper, printing, leather, plastics and various food industries. The need for the treatment of dye contaminated waste water passed out from the industry. In this study, Pistia Stratiotes Leaves was studied for its potential use as an adsorbent for removal of Malachite Green. The various factors affecting adsorption, such as initial dye concentration, contact time, adsorbent dose and effect of temperature, were evaluated. The experimental data were fitted into the pseudo-second order kinetic model. The equilibrium of adsorption was modeled by using the Langmuir and Freundlich isotherm models. The objective of the present work suggests the APSNC may be utilized as a low cost adsorbent for Malachite Green dye removal from aqueous solution.

Keywords: Activated Pistia Stratiotes nano carbon (APSNC); Malachite green dye; Adsorption isotherm; Kinetics; Equilibrium models.

INTRODUCTION

Disposal of dyeing industry wastewater pose one of the major problems, because such effluents contain a number of contaminants including acid or base, dissolved solids, toxic compounds, and color. Out of these, color is the first contaminant to be recognized because it is visible to the human eye. Removal of many dyes by conventional waste treatment methods is difficult since these are stable to light and oxidizing agents and are resistant to aerobic digestion. Possible methods of color removal from textile effluents include chemical oxidation, froth flotation, adsorption, coagulation, etc. Among these, adsorption currently appears to offer the best potential for overall treatment, and it can be expected to be useful for a wide range of compounds, more so than any of the other listed processes. Recognizing the high cost of activated Nano Carbon, many investigators have studied the feasibility of cheap, commercially available materials as its possible replacements. Such materials range from industrial waste products such as waste rubber tyres, blast furnace slag, and lignin to agricultural products such as wool, rice straw, coconut husk, saw dust, and peat mass.
In order to assess the ability of activated Nano Carbon for dye removal, malachite green (MG) has been selected for the present study.

MATERIAL AND METHODS

Preparation of activated nano carbon

Pistia stratiotes (Akayat-tamarai)

Pistia Stratiotes Leaves used in this study was collected from the local Agriculture land of Thiruvarur, Tamilnadu, India. The raw biosorbent was cut into small sizes and then washed thoroughly with hot-distilled water followed by double-distilled water to remove any unwanted particles. It was then dried and activated in a muffle furnace at 1200 °C. The activated material was sieved to get uniform size particles <177µm (80 mesh). The same APSNC was used throughout the experiment.

Adsorbate

The stock solution of malachite green concentration 1000 mg/L was prepared by dissolving 1 g of malachite green in 1000 ml of double distilled water. Different concentration of dyes solution range from (25 to 125 mg/L) was prepared from the stock solution by appropriate dilution.

Material developments

Sorption studies were performed by the batch technique to obtain rate and equilibrium data. For isotherm studies a series of 50 mL Iodine flask were employed. Each test tube was filled with 50 mL of dye solution of varying concentrations and maintained at the desired pH and temperature. A known amount of adsorbent was added into each tube and agitated intermittently for a maximum period of 1 h. A 10-60 Minutes reaction period was found to be quite sufficient for equilibrium attainment for the dye. After this period the supernatent solution was centrifuged and the uptake of the dye was monitored spectrophotometrically at 425 nm. These concentrations were however decided after a good deal of preliminary investigation wherein the adsorbent was found to remove the dye to different extent. Sorption studies were carried out at 30, 40, 50 and 60 °C to find out the effect of temperature. The effect of pH was observed by studying the adsorption of dye over a pH range of 2-10.

Batch adsorption experiments

Batch adsorption was tested by adding 25 mg of APSNC to 50 ml of the dye solution of different initial concentration (25 to 125 mg/L) at a particular pH. The experiment was carried out using a wrist action shaker for the period of 60 min and 120 rpm using 250 ml stopper glass flasks at (30°C to 60°C). The residual concentrations of dyes in each sample after adsorption at different time intervals were determined by UV-Visible spectrophotometer. The equilibrium \( q_e \) (mg/g) was calculated by the following mass balance principle.

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

(1)

Where \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations (mg/L) of dyes, \( V \) is the volume (L), \( M \) is the weight (g) of the adsorbent. The removal efficiency of the adsorbents on dyes was calculated by using the following expression.

\[
R\% = \frac{C_e - C_r}{C_e} \times 100
\]

(2)

Kinetic experiments

The batch kinetic experiments were basically similar to those used testing the adsorption equilibrium method. The dyes samples were taken at specific time
intervals and the concentration of dyes was similarly measured. The all kinetic experiments were carried out at 30, 40, 50 and 60°C with initial dye concentration (25, 50, 75, 100 and 125 mg/ L) the amount of adsorption at time t. The qt (mg/g) was calculated by.

$$q_t = \frac{(C_0 - C_t)V}{M}$$  (3)

Where C₀ (mg/L) is the liquid phase concentration of dye at any time.

RESULTS AND DISCUSSION

Effect of contact time and initial dye concentration

The experimental results of adsorption of various dye concentrations with contact time are shown in Figure 1. This figure shows that the % removal initially increases and reaches the limiting value. So, that the equilibrium was established at 40 minutes. Hence all the remaining experiments were carried out at 40 minutes. The equilibrium data were given in TABLE 1 reveals that, the percentage removal was decreases with increase in initial dyes concentration. This was due to the number of available active sites was remains constant but the initial concentration of dyes increases, so that % removal decreases[10,11].

Effect of adsorbent dosages

The effect of the APSNC doses was studied at 30°C by varying the amount of adsorbent dose 10-250 mg for the initial concentration of 50 mg/L Figure 2 reveals that increase in percentage removal of MG dye with increases in dose of adsorbent due to the increase in adsorbent surface area and the availability of more adsorption sites.

Effect of pH

The solution pH is one of the most important factors that control the adsorption of MG dye. To examine the effect of pH on the % removal of MG dye the pH of initial solution were varied from 2.0 to 10.0 by adding

Figure 1: Effect of contact time on the removal of MG dye [MG]=50 mg/L; temperature 30°C; adsorbent dose=25mg/50ml
TABLE 1: Equilibrium parameters for the adsorption of MG dye onto APSNC

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Figure 2: Effect of adsorbent dose on the removal of MG dye [MG]=50mg/L; contact time 60min; temperature 30°C

NaOH or HCl in to them. The % removal increases as the pH increases up to 6.5. There after the % removal decreases. At pH 6.5 the optimum % removal takes place. So the remaining experiment was carried out at pH 6.5. The experimental result was shown in Figure 3.

Adsorption isotherm studies

To quantify the sorption capacity of the absorbent for the removal of dyes, the most commonly used isotherms, are the Freundlich and Langmuir isotherms and hence these were used in this study.

(A) Freundlich isotherm

Linear form of Freundlich isotherm model\(^{(12)}\) is represented by the equation

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]

Where \(q_e\) is the amount of dyes adsorbed per unit weight of the adsorbent (mg/L) \(K_f\) is (mg/g(L/mg)) the measure of adsorption capacity and 1/n is the adsorption intensity. The value of \(K_f\) and n are calculated from the intercept and slope of the plot of \(\log q_e\) Vs \(\log C_e\) respectively. The constant \(K_f\) and n values are given in TABLE 2. In general the \(K_f\) value increases 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\(^7\) (or) the value of n are in the range of 1 to 10 confirms the favorable condition for adsorption. The adsorption coefficient \(K_f\) of dyes on Pistia Stratiotes Leaves was found from 4.7157 to 4.7866 L/g. The \(K_f\) value indicates that the saturation time for adsorption of dyes is attained quickly due to the high affinity of activated Nano Carbon towards the adsorbate. The values of n were in the range of 1.6382 to 2.2913 (mg/L) for MG dyes adsorption. So Freundlich isotherm is suitable for this adsorption. The \(K_f\) values also indicate the multilayer adsorption were possible. This reveals that the activated Nano Carbon was more efficient for the removal of MG dyes.

**(B) Langmuir isotherm**

The Langmuir isotherm model\(^{13}\) 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

\[
\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b q_{max}}
\]

Where \(C_e\) (mg/L) is the equilibrium concentration of the dye, \(q_e\) (mg/g) is the amount of dye per unit weight of adsorbent, \(Q_m\) and \(b\) are Langmuir constants related to adsorption capacity and rate of adsorption respectively. \(Q_m\) is the amount of dye at complete monolayer coverage (mg/g) which gives the maximum adsorption capacity of the adsorbent and \(b\) (L/mg) is the Langmuir isotherm constant that relates to the energy of adsorption or rate of adsorption. The linear plot of \(C_e/q_e\) against the equilibrium concentration \(C_e\) shows the Langmuir model. The Langmuir constant \(Q_m\) and \(b\) were determined from the slope and intercept of the Langmuir plot.
and these values are given in TABLE 2. The feasibility of the Langmuir isotherm can also be expressed in terms of the dimensionless constant separation factor $R_L^{14,15}$ by the equation

$$R_L = \frac{1}{1 + b C_0}$$  \hspace{1cm} (6)

Where $C_0$ (mg/L) is the initial concentration of absorbent and $b$ (L/mg) is Langmuir isotherm constant. The parameter $R_L$ indicates the nature of the isotherm.

- $R_L > 1$ unfavorable
- $R_L = 1$ Linear
- $0<R_L< 1$ Favorable
- $R_L = 0$ Irreversible

The $R_L$ values lies between 0 and 1 indicate favorable adsorption for all initial concentration study. The calculated $R_L$ values were given in TABLE 3. The calculated $R_L$ values were within the range of 0.0554 to 0.2993. So the adsorption of MG follows the Langmuir isotherm.

**Thermodynamic study**

Thermodynamic parameter such as change in free energy ($\Delta G^0$) (KJ/mol), Enthalpy ($\Delta H^0$) (KJ/mol) and entropy ($\Delta S^0$) (JK/mol) were calculated by using the following equation (7,8) and (9)

$$K_o = \frac{C_{Solid}}{C_{Liquid}}$$  \hspace{1cm} (7)

$$\Delta G^0 = -RT \ln K_o$$  \hspace{1cm} (8)

$$\log K_o = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT}$$  \hspace{1cm} (9)

Where $K_o$ is the equilibrium constant, $C_{Solid}$ is the solid phase concentration at equilibrium (mg/L). $C_{Liquid}$ is the liquid phase concentration at equilibrium (mg/L). T is temperature in Kelvin and R is the gas constant (8.314 J mol$^{-1}$K$^{-1}$). A graph was drawn between log $K_o$ vs 1/T. The $\Delta H^0$ and $\Delta S^0$ values obtained from the slope and intercept of van’t Hoff plots. These values were given in TABLE 4. The negative $\Delta G^0$ are indicate the adsorption is spontaneous in nature and also the magnitude of $\Delta G^0$ indicate the adsorption is physical adsorption (ie, less than 70 KJ/mol). The value of $\Delta H^0$ is positive, this indicates the adsorption is endothermic process. The positive $\Delta S^0$ indicates increased randomness during the adsorption. This also support the adsorption was physical adsorption$^{16,17}$

**Adsorption kinetics**

The kinetics studies were done by using pseudo second order$^{18}$ Elovich$^{19,20}$ and intra-particle diffusion$^{22}$ models.

(A) The pseudo-second-order kinetic model

The linear form of pseudo second order equation is expressed as

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2$$  \hspace{1cm} (10)

Where $k_2$ (g/mg min) is the pseudo second order rate constant. For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ integrated form of Eq. (10) becomes:

$$(q_e - q_t) = \frac{1}{k_2 q_e} + K_2 t$$  \hspace{1cm} (11)

This is the integrated rate law for a pseudo second order reaction. Equation (11) can be rearranged to obtain Eqs (12) which has a linear form:

| TABLE 3 : Dimensionless seperation factor ($R_L$) for the adsorption of MG dye onto APSNC |
|----------------------------------|------------------|-----------------|-----------------|------------------|
| (C_i)                           | 30°C             | 40°C            | 50°C            | 60°C            |
| 25                              | 0.2269           | 0.2543          | 0.2993          | 0.2487          |
| 50                              | 0.1279           | 0.1457          | 0.1760          | 0.1420          |
| 75                              | 0.0891           | 0.1020          | 0.1246          | 0.0993          |
| 100                             | 0.0683           | 0.0785          | 0.0965          | 0.0764          |
| 125                             | 0.0554           | 0.0638          | 0.0787          | 0.0621          |

| TABLE 4 : Thermodynamic parameter for the adsorption of MG dye onto APSNC |
|----------------------------------|------------------|-----------------|-----------------|------------------|
| (C_i)                           | 30°C             | 40°C            | 50°C            | 60°C            | $\Delta H^0$ | $\Delta S^0$ |
| 25                              | -5684.75         | -5618.43        | -6493.9         | -6252.78        | 2.249        | 25.980       |
| 50                              | -4909.13         | -5028.07        | -6383.4         | -6750.91        | 16.00        | 68.455       |
| 75                              | -4091.94         | -4764.78        | -4691.6         | -4951.46        | 3.513        | 25.592       |
| 100                             | -2538.76         | -2880.94        | -5578.6         | -3775.23        | 17.500       | 66.648       |
| 125                             | -1630.21         | -2082.58        | -4018.3         | -2971.9         | 16.85        | 61.414       |
If the initial adsorption rate \( h \) (g/mg min) is

\[
h = K_2 q_e^2
\]  
(13)

Then Eqs. (12) and (13) becomes:

\[
\frac{1}{q_t} = \frac{1}{h} + \frac{1}{K_2 q_e}
\]  
(14)

Where \( K_2 \) (g/mg min) is the pseudo second order rate constant, \( q_e \) is the amount of dye adsorbed on the per unit mass of adsorbent (mg/g) at equilibrium, \( q_t \) is the amount of dye adsorbed at time \( t \). A Graph is drawn between \( t/q_t \) versus \( t \), the \( q_e \) and \( K_2 \) can be calculated from the slope and intercepts of the graph. The correlation coefficient value (\( \gamma \)) were also calculated. These values are given in TABLE 5. The correlation coefficient value (\( \gamma \)) for the pseudo second order was greater than 0.9900 (ie, \( \gamma > 0.9900 \)) and also \( q_e \) value calculated from the model was almost equal to the experimental value. So the adsorption of MG follows pseudo second order model.

\( B) \) The Elovich equation

The Elovich model equation is generally expressed as

\[
\frac{dq_t}{dt} = \alpha \exp(-\beta q_t)
\]  
(15)

Where \( \alpha \) is the initial adsorption rate (mg g\(^{-1}\) min\(^{-1}\)) and \( \beta \) is the desorption constant (g mg\(^{-1}\)) during any one experiment. To simplify the Elovich equation. Chien and Clayton assumed \( \alpha \beta t >> t \) and by applying boundary conditions \( q_t = 0 \) at \( t= 0 \) and \( q_t = q_e \) at \( t = t \) Eq.(15) becomes:

\[
q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t
\]  
(16)

If dyes adsorption fits the Elovich model, a plot of \( q_t \) vs. ln (t) yields a linear relationship with a slope of \( (1/\beta) \) and an intercept of \( (1/\beta) \ln (\alpha \beta) \). The Elovich parameters \( \alpha \), \( \beta \) and correlation coefficient (\( \gamma \)) were given in TABLE 5. The initial adsorption rate (\( \alpha \)) and desorption constant (\( \beta \)) increases with increase in initial concentration of MG dyes and also the correlation

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coefficient ($\gamma$) were greater than 0.9900 (i.e., $\gamma > 0.9900$). The Elovich model can also be suitable for the MG adsorption onto APSNC.

(C) Intra–particle diffusion model

According to Weber and Morris suggested the intra-particle diffusion model is:

$$q_t = K_d t^{1/2} + C$$  \hspace{1cm} (17)

Where $K_d$ is the intra-particle diffusion constant (mg/g min), and $q_t$ is the amount of the dye adsorbed at time $t$. According to Weber and Morris model, a graph is drawn between $q_t$ and $t^{1/2}$, the line was passing through the origin. But here the intercept value indicates the lines were not passing through origin. This was due to that the intra-particle diffusion takes place along with some other process. This may be boundary layer adsorption or instantaneous adsorption.

Effect of the ionic strength on the adsorption of malachite green

The effect of sodium chloride on the adsorption of malachite green on to APSNC is shown in Figure 4. In a low solution concentration of NaCl had less influence on the adsorption capacity. The partial neutralization of the positive charge on the adsorbent surface and a consequent compression of the electrical double layer by the Cl$^-$ anion cause the increase in the adsorption of the malachite green at higher ionic strength. The chloride ions can also enhance adsorption of malachite green ion onto activated calcite by pairing of their charges and hence reducing the repulsion between the malachite green molecules adsorbed on the surface. The APSNC to adsorb more of positive malachite green dye$^{[16,17,22,23]}$

SEM and FTIR of APSNC

The SEM images of APSNC (Figure 4a and 4b) Shows the SEM micrographs of APSNC sample before and after dye adsorption. It is clear that APSNC has considerable numbers of heterogeneous layer of pores where there is a good possibility for dye to be adsorbed. The surface of dye-loaded adsorbent, however, clearly shows that the surface of APSNC is cov-

![Figure 4: Effect ionic strength on the adsorption of MG dye [MG]=50 mg/L; contact time=60 min; dose=25 mg/50 ml](image-url)
Figure 4a : SEM image of APSNC before adsorption

Figure 4b : SEM image of APSNC after the adsorption of malachite green

Figure 5a : FT-IR spectrum APSNC before adsorption

Figure 5b : FT-IR spectrum of APSNC after adsorption of malachite green
ered with dye molecules.

The FTIR spectrum of APSNC before and after adsorption (Figure 5a and 5b) shows that some peaks were shifted or disappeared and that new peak were also detected. These changes observed in the spectrum indicated the possible involvement of those functional groups on the surface of the APSNC in adsorption process.

CONCLUSIONS

The adsorption characteristics of MG dye onto Activated Nano Carbon are strongly affected by the initial dye concentration, initial pH and the adsorbent dose. The pH 6.5 was favorable for the optimum adsorption of MG dye by APSNC. The $R_l$ values and other adsorption parameters indicate both Langmuir and Freundlich isotherms favorable for APSNC adsorption. The pseudo second order, Elovich and intra-particle kinetic model were found to applicable for the adsorption of MG onto APSNC reaction model. The thermodynamics parameters $\Delta G^0$, $\Delta H^0$ and $\Delta S^0$ values indicate the adsorption is endothermic and physical adsorption.

REFERENCES