Decolorizing of Malachite Green Dye by Adsorption Using Corn Leaves as Adsorbent Material

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ABSTRACT

This paper presents the ability to use cheap adsorbent (corn leaf) for the removal of Malachite Green (MG) dye from its aqueous solution. A batch mode was used to study several factors, dye concentration (50-150) ppm, adsorbent dosage (0.5-2.5) g/L, contact time (1-4) day, pH (2-10), and temperature (30-60)°C. The results indicated that the removal efficiency increases with the increase of adsorbent dosage and contact time, while inversely proportional to the increase in pH and temperature. An SEM device characterized the adsorbent corn leaves. The adsorption's resulting data were in agreement with Freundlich isotherm according to the regression analysis, and the kinetics data followed pseudo-first-order kinetic with a correlation coefficient of 0.9309. The thermodynamic data show that the process is exothermic and reversible. The highest removal of MG was 91%, which gave proof that the corn leaves as adsorbent material have the capability of adsorbing the MG dye for aqueous solutions.

Keywords: Adsorption, malachite green dye, corn leaves, isotherms, kinetics, thermodynamic
The historic discovery of synthetic dye, Mauveine in 1856 led to an increase in the production of over 70x10^4 tones/year of synthetic dyes, which led to the replacement of natural dyes. This increase is mostly associated with water pollution, which causes several health hazards and severe problems to human health such as cancer, eye burns, vomiting, breathing problem, and diarrhea as described by (Geçgel et al., 2016).

Commonly, organic dyes are soluble aromatic toxic compounds used to add color to other substances such as textile industries. The major problem in the polluted and colored wastewater from the textile industries' final processing is that it includes traces of the dyes and reduces the quality of water resources. Since it contains complex aromatic molecular compounds, it must be treated before discharge to its assigned places (Chekwube and Dominic, 2017).

The most common bio-sorbents materials are the ones that are derived from agricultural bio-waste due to their cheapness, availability, and eco-friendly to the environment, which is used for solving environmental pollution problems and the treatment of contaminated wastewater. The adsorption of dyes by bio-waste adsorbents had been studied by many researchers such as the adsorption of methyl orange by corn leaves (Fadhil and Eisa, 2019), rhodamine B by Aleurites Moluccana seeds (Postai et al., 2016), Congo red by Wheat husk (Abeer and Israa, 2019) Malachite green by algae (Al-taee, 2005), methylene blue by coconut leaves (Jawad et al., 2016), Malachite green by corn cob (Ismail et al., 2018), Malachite green by applewood shell (Tewari, Singhal and Arya, 2018), and Malachite green by wood apple shell (Sartape et al., 2017).

Malachite green MG (C_{23}H_{25}ClN_2) is a cationic dye that appears as a green crystalline powder and belongs to the triphenylmethane category. Its applications and toxicity are listed in Table.1. MG usage in industries caused several health problems, and hence, appropriate treatment of wastewater effluent containing MG dye is very necessary. Fig. 1 shows the chemical structure of MG dye.

![Figure 1. Chemical structure of MO dye.](image)

This study aims to characterize MG dye's adsorption by using corn leaves as a low-cost bio-waste adsorbent. Also, to study the effect of several parameters (contact time, the concentration of dye, adsorbent dosage, pH, and temperature) on the adsorption process and investigate the kinetics and isothermal studies.
Table.1 Application and toxicity of Malachite green dye.

| Applications                                      | Toxicity                                                                 |
|--------------------------------------------------|--------------------------------------------------------------------------|
| - Dyeing of paper, cotton, silk, leather products, and acrylic industries | - Environmentally persistent                                              |
| - Antiseptic and fungicidal for humans            | - Damage to the nervous system, brain, and liver                         |
| - Food coloring, Additive, and medical disinfectant.| - Decreases food intake, growth, and fertility rates                     |
|                                                  | - Causes damage to spleen, kidney, and heart                             |
|                                                  | - Acts as a respiratory enzyme poison etc.                               |

2. MATERIALS AND METHODS

2.1. MG dye preparation

MG dye's stock solution (1000 ppm) was prepared by dissolving 1 gm of powder MG in 1L distilled water; then, by diluting the stock solution, different concentrations (50-150) mg/L of the dye were prepared.

2.2. Preparation of Adsorbent

At first, the corns were collected from the farms of the College of Agriculture, University of Baghdad. Then the leaves were washed several times to get rid of dust and other impurities. The leaves were dried in the oven for 24 hrs at 70°C then ground and sieved to get a particle size of <125 μm and dried again in the oven (Gemmy, Taiwan) at 70°C overnight. The sample was stored in clean dried containers for further use.

2.3. Adsorption Study

A batch adsorption study was carried out in which different amounts of the sample corn leaves powder (0.5-0.25) gm were added to aqueous solutions of various concentrations of MG dye (50-150) ppm at an initial pH of 5.8 using 100 ml containers. Using an orbital shaker (JSR. Korea), the dye samples were shaken at 150 rpm at room temperature with a contact time of 4 days. The effect of both the pH and the temperature were investigated at the optimum conditions of the first set of experiments (50 ppm dye concentration and 0.2 gm adsorbent powder) in the ranges of 2-10 pH and 30-60°C respectively. The dye equilibrium concentrations were calculated by measuring the absorbance using a UV-spectrophotometer device (Shimadzu,1800) at a wavelength of 619 nm. The plot of absorbance versus the concentrations is shown in Fig. 2.

\[
y = 105.89x - 1.6963 \\
R^2 = 0.9856
\]

**Figure 2.** Absorbance versus concentration of MG dye at 619 nm wavelength.
The amounts of adsorbate at equilibrium dye and the removal efficiency were calculated using the following equations:

\[
\% \text{ removal} = \frac{C_0 - C_e}{C_0} \times 100
\]  

(1)

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

(2)

where \(C_0\) and \(C_e\) are the initial and equilibrium concentrations of the dye (mg/L), respectively; \(q_e\) is the equilibrium dye concentration on adsorbent (mg/g); \(V\) is the volume of dye solution (L); \(M\) is the mass of adsorbent (gm).

2.4. Isotherm Study

The results obtained from the experimental work are examined by using Langmuir and Freundlich isotherms to describe the equilibrium relationship between the adsorbent uptake with time and the adsorbate dosage.

2.4.1. Langmuir isotherm

Langmuir assumes that monolayer adsorption is formed at the surface, which occurs on localized sites (Ibrahim, M.B and Umar, 2016).

The following equation can represent the Langmuir isotherm linear form:

\[
\frac{C_e}{q_e} = \frac{1}{K_lq_m} + \frac{C_e}{q_m}
\]  

(3)

where \(C_e\) is the equilibrium dye concentration (mg/L), \(q_e\) (mg/gm) is the amount of dye adsorbed at equilibrium, \(q_m\) (mg/gm) is the amount of dye adsorbed at saturation, and \(K_l\) (g/l) is Langmuir constant.

2.4.2. Freundlich isotherm

Freundlich equation assumes that the adsorption occurred on heterogeneous surfaces (Freundlich, 1906). The Freundlich linear form can be expressed as:

\[
\ln q_e = \ln k_f + \frac{1}{n} \ln C_e
\]  

(4)

\(k_f\) (g/l)1/n and \(n\) are Freundlich constants, which measure both intensity and capacity of adsorption, respectively.

2.5. Adsorption kinetic study

The experimental work data were fitted into different kinetic models such as Pseudo first order, Pseudo second-order equation, which can be used to study the adsorption rate, make a model for the process, and predict the information about adsorbent/adsorbate interaction (Khaniabadi et al., 2016).
2.5.1. Pseudo first order
The equation of pseudo-first-order can be expressed as:

$$\ln(q_e - q_t) = \ln q_e - (k_1) t$$  \hspace{0.5cm} (5)

where: \(q_e\) and \(q_t\) are the amounts of dye adsorbed (mg/g) at equilibrium and time \(t\) (min) respectively;
\(k_1\) is the rate constant of adsorption (min\(^{-1}\)).

2.5.2. Pseudo-second-order
The Pseudo-second-order model is expressed by:

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \left(\frac{1}{q_e}\right) t$$  \hspace{0.5cm} (6)

Where \(k_2\) (g/mg.min) is pseudo second order constant.

3. RESULTS AND DISCUSSION
3.1. Characterization of Corn Leaves
The Scanning Electron Microscopy (SEM) VEGA3 shows the morphological picture of the corn leaves particles which are shiny on the surface in Fig. 3.

![SEM image of corn leaves adsorbent.](image)

**Figure 3.** SEM image of corn leaves adsorbent.

3.2. Effect of MG concentration
The effect of MG concentration on percentage removal is shown in Fig. 4. Increasing the concentration of the dye leads to an increase in removal efficiency very fast at the beginning due to the availability of free active sites. Then it starts to decrease until reaching the equilibrium point. The decrease in the adsorption capacity can be explained by the exhaustion of the adsorption capability of the adsorbent, which led to decreased removal efficiency and adsorption capacity. The same conclusion was obtained by (Prepared and Carbon, 2016).

3.3. Effect of adsorbent dosage
Fig. 5 shows the effect of corn leaves adsorbent dosage on the adsorption of MG dye. As the dosage increases, the dye’s percentage removal increases due to the increase of the surface area of the free active sites until it reaches the equilibrium point. A similar observation was previously reported (Prasad and Santhi, 2012).
3.4. Effect of contact time

Fig. 6 shows the effect of contact time on the adsorption of MG dye by corn leaves adsorbent. The change of contact time (4 days) was investigated. As time increases, the capacity of adsorption and the removal efficiency increase at the initial time then starts to be slower until it reaches the equilibrium state (day 4). This can be explained by the fact that the active sites reach the saturation state in which it does not allow for further adsorption to occur. Similar behavior is also reported by (Lafi, Montasser, and Hafiane, 2019).

3.5. Effect of pH

Fig. 7 shows the effect of pH on the adsorption of MG dye. The effect of pH on the adsorption was studied in the range of (2-10 step 2) by adjusting the samples using HCl and NaOH solutions. It is found that as the pH increases from 2 to 10, the adsorption capacity decreases, and the removal efficiency decreases from (91.15% to 19.13%) then increase to 38.10 at pH 10. This may be explained that MG is a cationic dye, and at higher pH, OH⁻ ions are plenty, and due to the electric attraction between charges, it accounts for higher adsorption (Parvin et al., 2018).

3.6. Effect of temperature

The effect of temperature was studied at the range of (30-60°C). The results in Fig. 8 show that as the temperature increases from 30 to 60°C, the removal efficiency decreases (90%-13%), and the adsorption capacity decreases. This can be attributed to the exothermic of the adsorption process and the weak bonds at high temperatures between the MG dye molecules, and the active sites of the corn leave adsorbent. These results are in agreement with (Nwodika and Onukwuli, 2017).

Figure 4. Effect of initial dye concentration on the percentage removal pH 5.8, temp. 25°C, time 4 days and agitation speed 150 rpm.

Figure 5. Effect of corn leaves dosage on the percentage removal at pH 5.8, temp. 25°C, time 4 days, dye concentration 50 ppm agitation speed 150 rpm.
Figure 6. Effect of contact time on the percentage removal at pH 5.8, dye concentration 50 ppm, adsorbent dosage 0.2 gm, agitation speed 150 rpm, and temp. 25°C.

Figure 7. Effect of pH on the percentage at temp. 25°C, time 4 days, dye concentration 50 ppm, agitation speed 150 rpm, and adsorbent dosage 0.2 gm.

Figure 8. Effect of temperature on the percentage removal of MG dye by using corn leaves at pH 5.8, dye concentration 50 ppm, adsorbent dosage 0.2 gm, and agitation speed 150 rpm.
4. ADSORPTION ISOTHERM
To select the suitable isotherm, the equilibrium relations of the batch adsorption of malachite green dye using corn leaves as adsorbent material were studied. According to the relations in Eq. (3) and (4), regression analysis was applied to calculate the constants of the model and the correlation coefficients. Based on Freundlich isotherm, the plot of ln $q_e$ versus ln $C_e$ gives the constant values $k_f$ and $n$ with the coefficient of determination $R^2$ as shown in Fig. 9. The observed data agrees with Freundlich isotherm with $R^2 = 92.44\%$.

In the assumption of Langmuir isotherm, regression analyses using Gauss-Newton's method were used to find the constants' values, which are given in Table 2, the results fixed in Table 2 column 2 and assure that the adsorption did not fit with Langmuir adsorption isotherm.

![Image](image.png)

**Figure 9.** Fitting the adsorption data to Freundlich isotherm.

| Parameter | Value |
|-----------|-------|
| $q_m$     | 6.4599|
| $K_L$     | -0.39866|
| $R^2$     | 0.7688|

**Table 2.** The adsorption isotherm parameters for MO removal using corn leaves at 30°C.

5. ADSORPTION KINETICS
Two models, pseudo-first-order and pseudo-second-order, were used to study MG dye's adsorption kinetics on the corn leaves adsorbent. The correlation coefficient ($R^2$) was used to show the stratification between the kinetic and experimental data. Kinetic plots were represented in Fig. 10 and 11. The plot of ln $(q_e-q_t)$ versus time gives a straight line for the (PFO), while $(t/q_t)$ versus time plot gives the (PSO) representation and its linear parameters. It is obvious that the adsorption process follows the PFO kinetics according to the $R^2$ values of the two figures,
Figure 10. Pseudo-first-order plot of MG adsorption corn leaf.

Figure 11. Pseudo-second-order plot of MG adsorption by corn leaf.

Table 3. kinetic parameters with $R^2$ for MG adsorption using corn leaves adsorbent.

| Parameter                | Value         |
|--------------------------|---------------|
| $q_e$                    | 126.507       |
| $k_1$                    | -2.7587       |
| $R^2$                    | 0.9309        |

| Parameter                | Value         |
|--------------------------|---------------|
| $q_e$                    | 13.2275       |
| $k_2$                    | 0.03008       |
| $R^2$                    | 0.8285        |

6. ADSORPTION THERMODYNAMICS

The parameters of thermodynamic adsorption of MG onto Corn leaves were calculated from the experimental data at 303, 313, 323, and 333 K. The standard change in Gibbs free energy ($\Delta G^o$), enthalpy ($\Delta H^o$), and entropy ($\Delta S^o$) were calculated using the following equations([Karaçetin, Sivrikaya, and Imamoğlu, 2014]):

$$K_d = \frac{q_e}{c_e}$$

$$\Delta G^o = -RT \ln K_d$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$
The values of $K_d$ and $\Delta G^\circ$ were calculated from equations (7) and (8), respectively, whereas $\Delta H^\circ$ and $\Delta S^\circ$ were calculated from the slope and intercept of the plot of ln $k_d$ vs. $1/T$ from equation (9). The thermodynamic parameters are listed in Table 4. The results show that the values of $\Delta G^\circ$ are positive in a sign, indicating that the adsorption process of MG on the surface of corn leaves is reversible (Adamson, 1977). The negative change for the enthalpy of MG adsorption indicates the exothermic tendency but follows a physisorption mechanism. The negative change of the entropy (94.4304) J/mol shows an increase in the randomness at the solid/liquid interface and a loss in the binding between the molecules of MG and the corn leaf surface (Jawad et al., 2016). The value of $E_a$ (290.7323 kJ/mol) indicates that the mechanism is chemisorptions.

Table 4. Thermodynamic Parameters of MG dye Adsorption.

| Parameters     | Temperature(K) | $K_d$  | $\Delta G^\circ$ (KJ/mol) | $\Delta H^\circ$ (KJ/mol) | $\Delta S^\circ$ (J/mol) | $k$       | $E_a$ (KJ/mol) |
|----------------|----------------|--------|---------------------------|---------------------------|-------------------------|----------|----------------|
|                | 303            | 0.97   | 0.07577                   | -28.3724                  | -94.4304                | -0.032   | 290.7323       |
|                | 313            | 0.523  | 1.6871                    |                           |                         | 0.0011   |               |
|                | 323            | 0.546  | 1.6228                    |                           |                         | 8E-05    |               |
|                | 333            | 0.31   | 3.2434                    |                           |                         | 3E-05    |               |

7. CONCLUSIONS
- Corn leaves can be used as cheap, available, Eco-friendly, and efficient bio-waste adsorbent to decolorize MG dye from aqueous solutions.
- The percentage removal of the dye increases rapidly at initial concentration then starts to decrease as the dye's concentration increases until it reaches the equilibrium point.
- As the adsorption time and dosage increase, the sorption capacity and removal efficiency increase, then it becomes slower until it reaches the equilibrium point.
- It is found that as the pH increase, the adsorption capacity and the removal efficiency decrease.
- As the temperature increases, the results show that the removal efficiency decreases, and the adsorption capacity decrease.
- The equilibrium data is fit with Freundlich isotherm.
- The rate of adsorption was found to follow the pseudo-first-order kinetic model (PFO)
- The thermodynamic results show that the process is reversible, exothermic, and chemisorptions.

NOMENCLATURE
- $C_e$ = Equilibrium concentration of adsorbate, mg/L
- $C_o$ = Influent concentration, mg/L
- FTIR = Fourier Transform Infrared spectroscopy
- $k_1$ = Rate constant of adsorption of Pseudo First Order, min$^{-1}$
k_2 = Rate constant of adsorption of pseudo second order, g/mg·min
k_f, n = Freundlich constants, dimensionless
k_l = Langmuir constant, L/mg
k_s = Sips constant related to energy of adsorption, (L/mg)^{1/m}
m = Sips parameter, dimensionless
M = mass of adsorbent, (gm)
MO = Methyl Orange
PFO = Pseudo First order
PSO = pseudo second order
q_e = The uptake of adsorbate at equilibrium, mg/g
q_m = Amount of adsorbate required to form a monolayer, mg/g
q_s = Sips maximum uptake of the adsorbate per unit mass of adsorbent, mg/g
q_t = Amounts of the adsorbent at time t, mg/g
SEM = Scanning Electron Microscopy
V = Volume of solution, (L)
E_a = Energy of Activation (KJ/mol)
α = Initial adsorption rate, dimensionless
β = Desorption constant, dimensionless

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