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Adsorption of Some Industrial Pollutants from their Aqueous Solutions

Dafer Rafeed Qasim Mohsen, Liqaa Hussein Alwan
Samarra University, College of Education, Department of Chemistry

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Annotation: This study investigates the adsorption of Malachite Green (MG) dye from aqueous solutions using activated charcoal. UV–Visible spectroscopy at 424 nm was used to determine removal efficiency. Batch experiments examined the influence of contact time, adsorbent mass, and temperature. Optimal conditions were found at a dye concentration of 25 ppm, 0.05 g of adsorbent, and 20 minutes of contact time. Removal efficiency increased with time until equilibrium, indicating gradual occupation of adsorption sites. Adsorption isotherms were analyzed using Langmuir, Freundlich, and Temkin models. The data fit well with Freundlich and Temkin models, suggesting heterogeneous surface adsorption, while the Langmuir model showed poor correlation. Thermodynamic parameters (ΔG, ΔH, ΔS) were determined at 293–313 K. Negative ΔG values at all temperatures indicated spontaneous adsorption, while the negative ΔH (< 40 kJ/mol) suggested an exothermic and physical adsorption process.Kinetic analysis revealed that the pseudo-second-order model best described the adsorption behavior, indicating chemisorption predominance. Overall, activated charcoal demonstrated high efficiency in removing MG dye, supported by favorable kinetic, thermodynamic, and isotherm data, suggesting its suitability for industrial wastewater treatment applications.

Keywords: Pollution, adsorption,

Malachite Green Dye.

1. Introduction:

Pollution is the introduction of contaminants into the natural environment that cause adverse change. It can have detrimental impacts on legitimate environmental needs like farming, drinking water and industry [1]. This encompasses pollutants in the air, water, and soil, and leads to changes in the physical, chemical or biological nature of the environment. This definition is adopted by the United Nations Environment Programme (UNEP) [2]. Pollution is one of the most acute problems affecting the environment globally. Some researches have reported that some pollutants can be harmful to human growth, particularly during prenatal period, and can also damage the health of other organisms [3]. Water, as an essential life resource, is very important for drinking, cooking, and other daily activities [4]. With the increasing environmental problems, access to clean and safe water has emerged as one of the great challenges in the modern scientific community [5].

There are various kinds of pollution to water sources, one of the most serious being pollution from industrial sources resulting from effluent discharge from dye factories, raw domestic sewage, agricultural effluent, rich in pesticides and fertilizers, heavy metals, organic matters, chemicals from human activities, in addition to oil spill, that itself deteriorating the water quality, and that is the danger impact of human health, the living organisms and their habitat [6]. Industrial dyes are compounds that are used in the coloration of different goods such as textile, leather, plastic and paper; there are globally about 10,000 different dyes that are produced in amounts most of which surpass 0.7 × 10 6 ton per annum, which are prevalent ingredients in most industries, everywhere [7]. These dyes are characterized by their complex structure, allowing them to resist biodegradation and persist in the environment [8].

Malachite Green Malachite Green (MG) is a common cationic dye first developed in the 19th century, by the German scientist Hermann Fischer. It is an artificial dye characterized by a bright green color [9]. Molecular Weight of Malachite Green is 364.90 g/mol The chemical structure of malachite green, as Formula(CC6H4N(CH3)2)(C6H42)ClUnlike many other dyes, malachite green is readily soluble in water. It is primarily employed in the textile industry (for dyeing of cotton, silk, wool and paper) [10] and some veterinary applications, for example cestodicidal agent for parasitic diseases of fish. Although Malachite Green shows excellent industrial application, it has been identified as a threat to the environmental pollution because of its high stability and recalcitrance to degradation, which means that it could remain in the environment for a long time. In addition, its release into water systems may be toxic to aquatic animals, such as fish and crustaceans [11,12]. Malachite Green is also harmful to humans and exposure to large amounts can result in health issues. For these reasons this dye is considered as a hazardous industrial chemical that may cause serious environmental and health problems when discharged into waters without adequate treatment. Hence, an effective approach like adsorption and chemical oxidation becomes necessary for removal of this dye from wastewater in order to minimize its deleterious effects and promote sustainable use of environmental resources [13].

The chemical structure of Malachite Green is depicted in Figure (1-2)

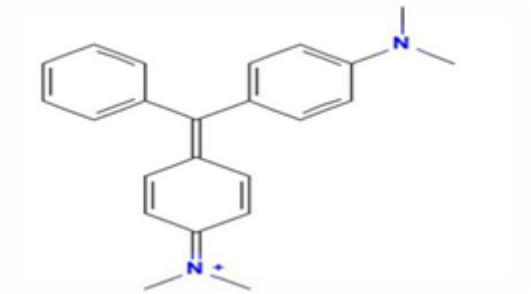


Figure (1-3) Chemical structure of Malachite Green.

Among the processes adsorption is one of the most efficient and economical methods. This technique is applied for purifying water by degrading organic pollutants like industrial dyes and toxicants. Adsorption is regarded as a popular process for the treatment of water, because of its simplicity, high removal efficiency, and potential for low cost especially where the shabby adsorbent such as active carbons are used [14]. Its porous texture that results in a high surface area make it a promising candidate for the removal of a broad list of dyes as well as industrial pollutants [15]. In this research, nano-activated charcoal was obtained from industrial cardboard waste, and its adsorption of Malachite Green in aqueous solution was examined as a function of several parameters, including equilibration time, thermodynamic and isotherm models, and kinetic models, in order to illuminate the mechanisms of adsorption.

2. Materials and Methods

2.1 Malachite Green Dye Solution.

A standard Malachite Green solution at 1000 ppm was prepared by dissolving 0.273 g of Malachite Green in a 250 ml volumetric flask and brought to volume with distilled water. Heating and ultrasound bath were used to assist the complete dissolution. A set of diluted solutions of varying concentrations were then made from standard solution.

2.2 The maximum absorption wavelength was detected (λ_max).

λ_max of Malachite Green: A solution of maximum absorbance (concentration) was prepared and was kept in 1 cm path length quartz cell and its absorption was measured using a UV-Visible Spectrophotometer. Maximum absorption was at 424 nm [6]

3.2 Construction of Calibration Curve of Malachite Green.

To calibration, the series of dilutions from the standard solution (10-40 ppm) was made. The absorbance of these solutions was recorded against distilled water as blank solution using UV-Visible Spectrophotometer. The absorbances were then plotted against concentration of (a) Depending on the solvents used, flowers of Royal Poinciana (PFB) b Depending on the solvents used, seed of Sesbania (PSB) (where A is absorbance).

4.2 Adsorption

Equilibrium time, adsorbent mass, temperature and initial dye concentration were studied to evaluate the adsorption of Malachite Green on the prepared nano-activated charcoal.

5.2 Equilibrium Time Determination [7]

Adsorption was monitorediliu by determining the equilibrium lium in aqueous solution. A 25 ppm dilution was diluted and prepared in a 100 ml volumetric flask. After that, 0.05 g of adsorbent prepared was introduced to the solution. The mixture was put into a shaker bath at 25°C and shaken at 60 rpm. At different time intervals (5, 10, 15, 20, 25 and 30 min), samples were withdrawn and absorbance was determined using UV-Visible Spectrophotometer after filtering the solution. The same process was followed under identical conditions for Malachite

GreenEffect of **6.2 Adsorbent Mass [8]**

The influence of adsorbent mass (nanocarbon) on the adsorption process was investigated by adding different weights (0.01 g, 0.03 g, 0.05 g) to 100 ml solution (25 ppm) of Malachite Green. The mixtures were then placed in a shaker bath at 25°C with a shaking speed of 60 rpm until equilibration (25 minutes). After filtering all samples at the same time, their absorbances were measured using a UV-Visible Spectrophotometer.

7.2 Calculation of Adsorption Percentage

The amount of adsorbate removed was determined by calculating the percentage of adsorption, which expresses the removal efficiency of the prepared adsorbent for Malachite Green from its aqueous solution, by applying equation (1).

$$\% \text{ Adsorption} = \frac{Co - Ce}{Co} \times 100 \quad \text{----------(1)}$$

Where %Adsorption denotes the adsorption efficiency, the adsorption capacity of the prepared activated charcoal — which expresses the amount of adsorbate that can be retained — can be represented by equation (2) [16,17]

$$q_e = \frac{Co - Ce}{M} \times V \quad \text{----------(2)}$$

Where:

M = mass of the activated charcoal.

V = volume of the solution in litres (L).

Co = initial dye concentration in liquid phase (ppm).

Ce = dye concentration at equilibrium.

qe = adsorption capacity of the dye.

8.2 Effect of temperature

The effect of temperature was investigated by preparing a dilute solution of Malachite Green with a concentration of (25 ppm) from the standard solution in a (100 ml) volumetric flask, then adding (0.05 g) of the prepared cardboard-derived activated charcoal. The solution was placed in a water bath equipped with a shaker (60 rpm) until equilibrium was reached (25 minutes) at different temperatures (20°C, 25°C, 30°C, 40°C). A thermometer was used to monitor the temperature. At each temperature, the solution was filtered, and its absorbance was measured using a UV-Visible Spectrophotometer, and the percentage of adsorption was subsequently calculated.

9.2 Determination of Thermodynamics of Adsorption

The value of the adsorption equilibrium constant (Keq) was determined at different temperatures by calculating the ratio between the amount of adsorbate and the amount remaining in solution upon reaching equilibrium, using equation (1) under previously described temperatures. A plot of Ln(Keq) against 1/T produces a straight line with a slope equal to -ΔH/R, from which the enthalpy of adsorption (ΔH) is derived according to the Van't Hoff equation (equ. 3). The values of Free Energy (ΔGº) and Entropy (ΔSº) were subsequently calculated using equations (4) and (5), respectively [15]

$$\ln K_{eq} = -\Delta H / RT + C \quad \text{----------(3)}$$

$$\Delta G^{\circ} = -R \times T \times \ln Keq \quad \text{----------(4)}$$

$$\Delta S^{\circ} = \frac{\Delta H - \Delta G^{\circ}}{T} \quad \text{----------(5)}$$

10.2 Adsorption Isotherms

The adsorption isotherms for Malachite Green were studied by preparing five solutions with different concentrations (25, 30, 35, 40, and 45 ppm) in (100 ml) volumetric flasks from the standard dye solution. Subsequently, (0.05 g) of the prepared charcoal (adsorbent) was added to each solution. The flasks were placed in a water bath equipped with an electric shaker at a temperature of (25°C) until equilibration was reached (20 minutes). The solutions were then filtered, and their absorbance was measured using a UV-Visible Spectrophotometer at the dye's absorption maximum (λ_max). The concentrations at equilibrium (Ce) were determined from the calibration curve, and from these, the amount of adsorbate per mass of adsorbent (qe) was calculated in (mg/g) using equation (2) previously presented. Freundlich and Langmuir isotherm models were then applied.

11.2 Freundlich Isotherm

Freundlich isotherm constants (Kf and n) were determined by plotting Ln(qe) against Ln(Ce). The plot shows a straight line whose slope is 1/n (an indicator of adsorption intensity), while the intercept (Ln Kf) denotes the adsorption capacity [12]. This model is mathematically represented by equation (6).

$$\text{Log } q_e = \log k_f + \left(\frac{1}{n} \times \log C_e\right) \text{---------- (6)}$$

12-2. Langmuir Isotherm:

The Langmuir constants a and b are calculated by plotting Ce/qe against Ce, resulting in a straight line with a slope of b/a and an intercept of 1/a, according to the linear form of the Langmuir equation as per equation (7).

$$\frac{C_e}{q_e} = \frac{1}{a} + (b/a)\ Ce \text{ ---------- (7)}$$

13.2 Equation that allows

The constants BT and kT are calculated by plotting the relationship between qe and lnCe, from which we obtain a slope to extract the value of kT, and from its intersection, we obtain the value of BT 14 according to the application of equations (8) and (9).

$$q_e = B_T \ln K_T + B_T \ln C_e \text{ ---------- (8)}$$

$$B_T = \frac{RT}{b} \text{---------- (9)}$$

14.2Adsorption kinetics [16]

The kinetics were studied by calculating the amount of adsorbed substance at time qt using both the pseudo-first-order Lagergren equation (10) and the pseudo-second-order equation (11). These experiments aimed to evaluate the applicability of these kinetic models to the adsorption behavior at different times. The equilibrium time, which represents the point at which the process shows the maximum possible adsorption capacity, was determined and can be calculated using equation (1) mentioned earlier.

$$\ln(q_e - q_t) = \ln q_e - (k_1) \times t \text{ ---------- (10)}$$

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^{\,2}} + \frac{1}{q_e}\, t \text{----------(11)}$$

Since:

qt = Represents the amount of adsorbed substance at different times (mg/g).

qe = represents the amount of adsorbed substance at equilibrium time (mg/g).

t = time (min)

3. Results and Discussion

1.3 Setting the value of (maxλ) and constructing the calibration curve for the green malachite dye.

The UV spectrum of the dye solution dissolved in an aqueous solution at a specific concentration was recorded, and the absorption spectrum was measured using a (UV-Vis) device within the range of nm (200-1100) using a quartz cell with a thickness of 1 cm. It was found that the (λ max) of the dye is nm 424. As shown in Figure (3), the calibration curve for the dye was constructed with diluted solutions of each compound from the standard solution within the range of (ppm 10-45) to estimate the amount of adsorbed and remaining dye in the solution using the spectrophotometric method. The results showed a linear relationship indicating the impression followed by the system according to the Beer-Lambert law, as illustrated in Figure (4).

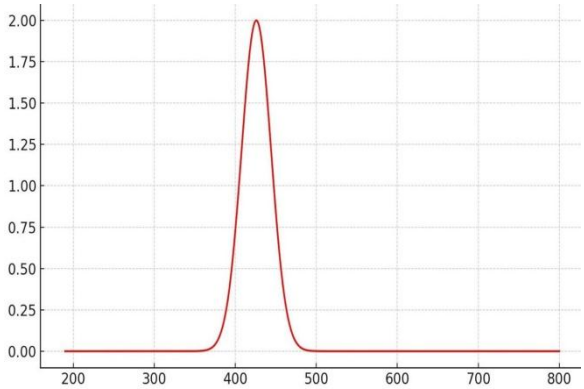


Figure (3): The maximum wavelength of the green malachite pigment.

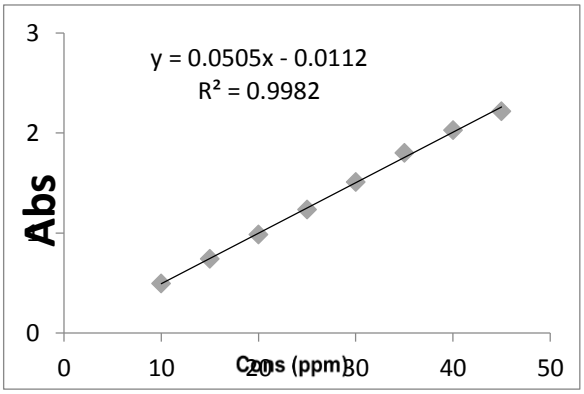


Figure (4): Calibration curve for the malachite green dye. The passage of time

2.3 Monitoring the Change in Dye Concentration over Time Using the Prepared Adsorbent Surface

The change in the concentration of the studied dye was monitored over time using both the dye solution and the adsorbent surface spectrophotometrically, until equilibrium time was reached. The experiment was conducted under controlled conditions: temperature fixed at 298 K, dye concentration at 25 ppm, adsorbent mass at 0.05 g, and at a wavelength of 424 nm corresponding to malachite green dye .The surface absorbance of the dye was calculated, and the equilibrium time was determined to be 20 minutes with the prepared surface. Upon comparing the absorbance values after the addition of the prepared activated carbon—presented in Table (1)—with the values prior to its addition, a significant decrease in absorbance was observed. This reduction is attributed to the occupation of active sites by the adsorbate at the initial stage of the adsorption process. Subsequently, a gradual increase in adsorption occurs until equilibrium is reached. After this point, no significant change in the amount of adsorption is observed, and the

absorbance remains nearly constant. At equilibrium, the rate of adsorption equals the rate of desorption .Following this phase, a slight increase in absorbance and a decline in adsorption efficiency were noted, which may be due to the repulsion between dye molecules and their return to the solution, resulting from the saturation of the pores on the surface of the prepared activated carbon.The adsorption efficiency for the dye reached approximately 93%, as shown in Figure (5).

Table (1): Determination of Equilibrium Time and the Effect of Contact Time on the Adsorption Efficiency of Malachite Green Dye Using the Prepared Activated Carbon Surface

Tim (min)	Absorption	C_e (mg/L)	C_{abs} (mg/L)	q_e (mg/g)	Absorption%
0	1.236				
5	0.111	2.4	22.58	45.1	90.3
10	0.104	2.2	22.7	45.4	90.8
15	0.093	2.0	22.9	45.8	91.7
20	0.076	1.7	23.2	46.5	93.1
25	0.076	1.7	23.2	46.5	93.1
30	0.098	2.1	22.8	45.6	91.4

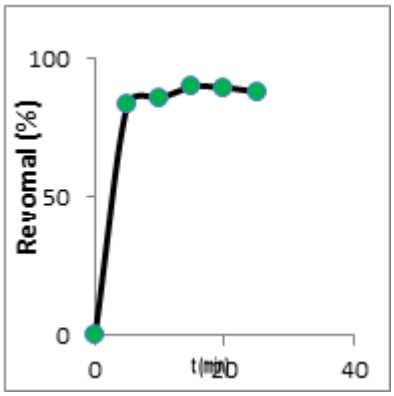


Figure (5): Effect of Contact Time on the Removal of Malachite Green Dye Using the Prepared Activated Carbon Surface

3.3 Effect of Adsorbent Dosage on Adsorption Efficiency

Different masses of the prepared nano-activated carbon surface (0.01 g, 0.03 g, and 0.05 g) were employed to investigate the effect of adsorbent dosage on the adsorption of malachite green dye. The experimental conditions were kept constant: temperature at 298 K and dye concentration at 25 ppm. The adsorption process was monitored spectrophotometrically until the equilibrium time of 20 minutes was reached.

The results, presented in Table (2), demonstrate that the optimal adsorbent mass is 0.05 g. This dosage resulted in the highest adsorption efficiency (percentage of dye removal) and contributed to the saturation of most available adsorption sites.

Table (2): Effect of the Prepared Adsorbent (CN) Dosage on the Adsorption Efficiency of the Two Dyes

Weight of CN (g)	Abs.	$C_\circ$ (mg/L)	C_e (mg/L)	Adsorption %
0.01	0.261	25	5.4	**78.4**
0.03	0.165	25	3.3	**86.8**
0.05	0.076	25	1.7	**93.1**

4.3 Effect of Temperature on the Adsorption Process

The effect of temperature on the adsorption of the studied dye onto the adsorbent surface was investigated at different temperatures (293 K, 298 K, 303 K, and 313 K), using the optimal dye concentration (25 ppm) and an adsorbent dosage of 0.05 g. The adsorption process was monitored spectrophotometrically at the equilibrium time of 20 minutes. The obtained results are presented in Table (3).

The data indicate that adsorption efficiency decreases with increasing temperature, suggesting that the adsorption process is exothermic in nature. This behavior aligns with the thermodynamic requirements of adsorption processes: as the temperature increases, the kinetic energy of malachite green dye molecules—both in solution and those adsorbed onto the activated carbon surface—increases. Consequently, the van der Waals forces responsible for anchoring the dye molecules to the adsorbent surface become weaker, leading to desorption and a decline in adsorption efficiency .This trend is illustrated in Figure (6).

Table (3): Effect of Temperature on the Adsorption Efficiency of Methyl Orange and Malachite Green Dyes

T(K)	Absorption	q_e(mg/g)	Adsorption%
293	0.068	46.8	93.7
298	0.076	46.5	93.1
303	0.091	45.9	91.9
313	0.119	44.8	89.6

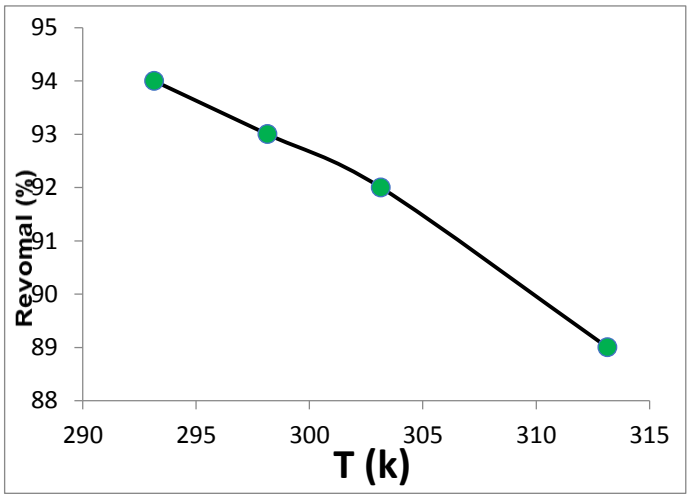


Figure (6): Decrease in Adsorption Efficiency of Malachite Green Dye with Increasing Temperature on the Adsorbent Surface

5.3 Calculation of Thermodynamic Parameters

Thermodynamic parameters were calculated to better understand the nature of the adsorption process. These parameters—namely, the change in standard Gibbs free energy (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°)—are important analytical tools used to evaluate the spontaneity of the adsorption process and to determine whether the adsorption is physical or chemical in nature. These insights were derived by studying the effect of temperature on the adsorption behavior, as temperature has a direct impact on the distribution of adsorbed dye molecules. For the calculation of these thermodynamic functions, equilibrium constants (K_eq) were determined by calculating the ratio between the concentration of dye adsorbed on the surface and the concentration remaining in solution at equilibrium.

A plot was constructed between the natural logarithm of the equilibrium constant (ln K_eq) and the reciprocal of the absolute temperature (1/T), as shown in Figure (7). The enthalpy change

(ΔH°) was calculated from the slope of the linear plot using the Van't Hoff equation (Equation 3.(

The study was conducted under constant conditions: using the optimal dye concentration (25 ppm), the best adsorbent mass (0.05 g), and an equilibrium time of 20 minutes. The calculated thermodynamic parameters are presented in Table (4).

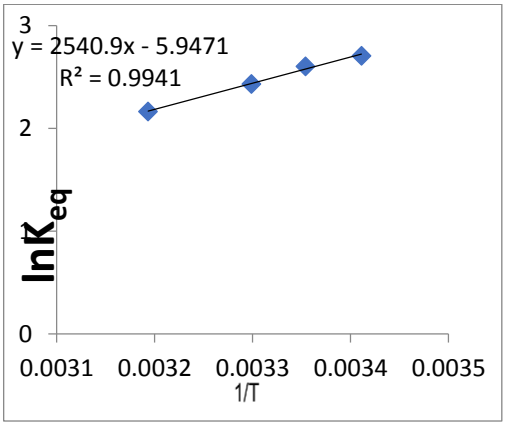


Figure (7): Van't Hoff curve for the adsorption of malachite green dye on the surface of the maz

Table (4): Thermodynamic function values for the adsorption of malachite green dye on the adsorbent surface

T(K)	1/T (K^{-1})	K_{eq}	lnK_{eq}	$G^{o}\Delta$ J/mol	$H\Delta$ kJ/mol	$S^{o}\Delta$ J/mol.K
293	0.00341	14.9	2.7	- 6590.53	- 21.125	- 49.5805
298	0.00335	13.4	2.6	- 6447.59		- 49.2284
303	0.00329	11.3	2.4	- 6123.29		- 49.4862
313	0.00319	8.7	2.1	- 5631.26		- 49.4772

Based on the thermodynamic parameter values, the negative enthalpy change (ΔH°) indicates that the adsorption process of the studied dye onto the adsorbent surface is exothermic in nature. The physical nature of the adsorption suggests that the dominant forces involved are weak van der Waals interactions, confirming the physisorption mechanism. In addition, the negative values of the standard Gibbs free energy (ΔG°), calculated using Equation (4), indicate that the adsorption process between the studied dye and the prepared adsorbent surface is spontaneous. From the ΔG° values, the entropy change (ΔS°) was calculated using the Gibbs equation (Equation 5). The negative values of ΔS° reflect a decrease in system randomness after adsorption, due to the attachment of dye molecules to the adsorbent surface, which limits their random motion in the solution. This behavior is consistent with previous studies.

6.3 Adsorption Isotherms

Adsorption isotherms are used to describe the relationship between the adsorbent (prepared activated carbon) and the adsorbate (the studied dye). They are also useful for evaluating the efficiency of the adsorption process. At equilibrium, adsorption isotherms provide better insight into the distribution of molecules between the solid phase (adsorbent surface) and the liquid phase (solution). Several models of adsorption isotherms are used to interpret this behavior, and in this study, three major isotherm models were applied to analyze the results:

7.3 Freundlich Isotherm

The Freundlich isotherm model (Equation 6) was applied to the experimental data for the adsorption of malachite green dye at various concentrations (15, 20, 25, 30, and 35 ppm) at a constant temperature of 293 K, with all other parameters held constant. The Freundlich constants

were derived from the linear form of the equation and are presented in Table (5). These include Kf, which represents the adsorption capacity, and n, which indicates the adsorption intensity. The plot is illustrated in Figure (8).

Table (5): Values of ln qe and ln Ce, Correlation Coefficients, and Freundlich Isotherm Constants for the Adsorption of Methyl Orange and Malachite Green Dyes onto the Adsorbent Surface at 25 °C

C Ppm	C_e mg/L	LnC_e	q_e mg/g	Lnq_e	K_f mg/g	n L/mg	R^2
15	1.1	0.17	27.7	3.32	26.09	1.05	0.984
20	1.4	0.35	37.1	3.61			
25	1.7	0.54	46.5	3.84			
30	2.1	0.64	55.6	4.01			
35	2.6	0.77	64.6	4.16			

The results presented in Table (5) show that the correlation coefficient (R^2) value for the dye is satisfactory, indicating that the Freundlich isotherm model provides a good fit for the adsorption data of the dye onto the adsorbent surface.

Regarding the adsorption constants, the Kf value, which represents the theoretical adsorption capacity, was found to be 26 mg/g, suggesting a reasonably good capacity in theory. However, when compared to the experimental adsorption capacity at equilibrium, which was 46.5 mg/g, it is evident that the theoretical value is lower than the actual measured value.

This discrepancy can be attributed to several factors affecting the actual adsorption capacity. These include properties of the adsorbent material itself—such as surface area, pore volume, and structural characteristics—as well as the nature of the adsorbate. The chemical composition of the dye, including the presence of functional groups, its molecular geometry (steric structure), and its ability to interact or diffuse into the adsorbent surface, all influence the adsorption process .Additionally, the adsorption of the solvent (water) by the prepared activated carbon may reduce the effective adsorption capacity, thereby lowering the actual efficiency compared to the theoretical estimate.

The n value for the dye falls within the range of 1 to 10, which indicates that the adsorption is favorable and further supports that the process is physical in nature, as values greater than 1 are typically associated with physisorption.

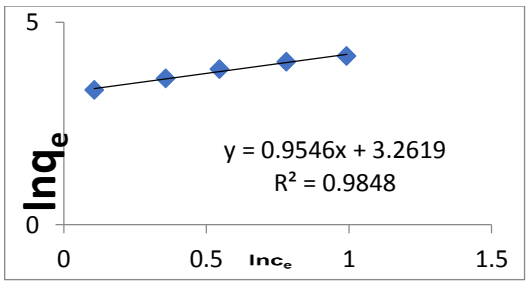


Figure (8): Freundlich Isotherm for Dye Adsorption onto the Adsorbent Surface at 25 °C

8.3 Langmuir Isotherm

The Langmuir isotherm model (Equation 7) was applied to the experimental data for the adsorption of the studied dyes onto the prepared adsorbent surface. The experiments were conducted at various initial dye concentrations (15, 20, 25, 30, and 35 ppm) and at a constant temperature of 293 K, while keeping all other experimental conditions fixed.

The Langmuir constants (a and b) were determined from the slope and intercept of the linearized Langmuir equation, as illustrated in Figure (9). The obtained values are summarized in Table (6).

Table (6): Values of (Ce/qe and qe), Correlation Coefficients, and Langmuir Isotherm Constants for the Adsorption of Malachite Green Dye onto the Adsorbent Surface at 25 °C

C ppm	C_e mg/L	q_e mg/g	C_e / q_e	a (mg/g)	b (L/mg)	R^2
15	1.1	27.7	0.040	27.1	0.03	0.232
20	1.4	37.1	0.038			
25	1.7	46.5	0.037			
30	2.1	55.6	0.039			
35	2.6	64.6	0.041			

Based on the values presented in Table (7) and the trend observed in Figure (9), it is evident that the low value of the Langmuir constant (b)—which represents the binding strength between malachite green dye molecules and the surface of the prepared nano-activated carbon—indicates weak interactions. This confirms that the adsorption process is physical in nature. [18, 19]

Moreover, the correlation coefficient (R^2) obtained from applying the Langmuir isotherm model to the experimental adsorption capacity was relatively poor, with a value of 0.232, indicating a poor fit of the Langmuir model to the adsorption data for this dye.

As for the Langmuir constant (a), which represents the theoretical maximum adsorption capacity, it was found to be lower than the actual experimental capacity, which reached 27.1 mg/g. This discrepancy can be explained by the same factors previously discussed in the evaluation of the Freundlich model, such as the structural characteristics of the adsorbent and the nature of the adsorbate. [20]

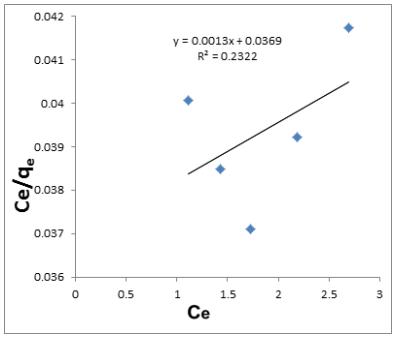


Figure (9): Langmuir Isotherm for the Adsorption of Malachite Green Dye onto the Adsorbent Surface at 25 °C

9.3 Temkin Isotherm

The Temkin isotherm model was applied using Equations (8) and (9) to determine the Temkin constants for the adsorption of the studied dye onto the prepared adsorbent surface. The experiments were conducted at a temperature of 298 K and at various initial dye concentrations (15, 20, 25, 30, and 35 ppm**).**

The obtained results are presented in Table (8) and illustrated graphically in Figure (10)**.**

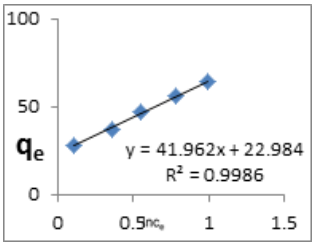


Figure (10): Temkin Isotherm for the Adsorption of Malachite Green Dye onto the Adsorbent Surface at 25 °C

Table (8): Values of (ln Ce and qe), Correlation Coefficients, and Temkin Isotherm Constants for the Adsorption of Malachite Green Dye onto the Adsorbent Surface at 25 °C

C ppm	C_e mg/L	lnC_e	q_e mg/g	lnq_e	K_T L/g	B_T	b J/mol	R^2
15	1.1	0.10	27.7	3.32	1.72	41.9	59.0	0.998
20	1.4	0.35	37.1	3.61				
25	1.7	0.54	46.5	3.84				
30	2.1	0.78	55.6	4.01				
35	2.6	0.99	64.6	4.16				

Based on the values presented in Table (8), it is observed that the correlation coefficient (R^2) is high for the studied dye, which confirms that the Temkin isotherm model fits well with the adsorption data. Furthermore, the Temkin constant (b)—representing the heat of adsorption—was found to be 59 J/mol, indicating a favorable interaction between the dye and the adsorbent surface, consistent with physisorption .Additionally, the value of the Temkin constant (K_T) exceeded 1, suggesting strong adsorption and a good affinity between the adsorbent surface and the adsorbate (i.e., the studied dye). Specifically, the K_T value for the dye was 1.72 L/g, supporting the conclusion of effective adsorption. [30]

10.3 Adsorption Kinetics

The kinetics of malachite green dye adsorption onto the prepared adsorbent surface were also studied. Analyzing the effect of contact time (equilibrium time) on the system's behavior revealed that the process involves two distinct stages before reaching equilibrium:

Stage One: Covers the first 15 minutes of the adsorption process, during which the dye concentration decreases rapidly. This rapid decline is attributed to the abundance of available active adsorption sites on the freshly prepared adsorbent surface. [16]

Stage Two: In this phase, the rate of concentration change becomes slower compared to Stage One, due to the depletion of available adsorption sites on the surface. The kinetics of this stage were evaluated by studying the effect of contact time on the adsorption capacity from the first 5 minutes until equilibrium at 20 minutes. In this phase, contact time no longer significantly influences dye concentration, as the system approaches dynamic equilibrium between the adsorbent and adsorbate.

To model the kinetics, the pseudo-first-order Lagergren equation (Equation 10) was applied to the experimental data. A plot of ln(qe − qt) versus time was constructed, as shown in Figure (11). From the plot, the theoretical adsorption capacity (qe) and rate constants (k_1 and k_{-1}) were calculated.

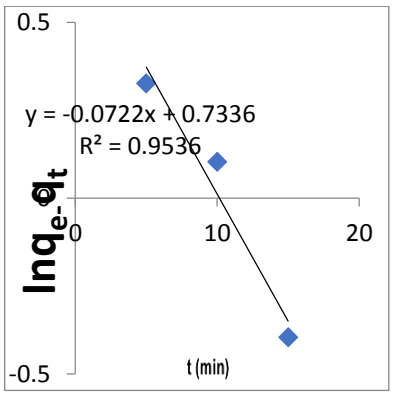
For the adsorption system to follow the pseudo-first-order kinetic model, the following conditions must be met:

11.3 A linear relationship in the plot,

A correlation coefficient (R^2) close to unity,

The calculated qe value from the intercept (ln(qe)) must be close or identical to the experimental qe value at equilibrium.

Any deviation from these conditions would suggest that the adsorption process does not conform to pseudo-first-order kinetics. [38]



The results were summarized in Table (9).

Figure (11): Pseudo-First-Order Kinetic Model for the Adsorption of Malachite Green Dye onto the Adsorbent Surface at 25 °C

Table (9): Correlation Coefficients and Kinetic Parameters of the Pseudo-First-Order Model for the Adsorption of Malachite Green Dye onto the Adsorbent Surface at 25 °C

Experimental (q_e) mg/g	Theoretical (q_e) mg/g	K_1 min^{-1}	K_{-1} min^{-1}	R^2
46.54	**2.08**	**0.067**	**0.0049**	**0.9536**

According to the results presented in Table (9), although the correlation coefficient (R^2) was relatively high, a significant discrepancy was observed between the theoretical and experimental adsorption capacities. This indicates that the studied adsorption system does not follow the pseudo-first-order kinetic model for either of the two dyes.The pseudo-second-order kinetic equation (Equation 10) was applied to the experimental adsorption data by plotting (t/qt) against time (t), as shown in Figure (12). From the resulting linear plot, the theoretical adsorption capacity (qe) and the rate constant (k_2) were determined. The results obtained from this model were summarized in Table (10).

Based on these findings, for the pseudo-second-order model to be valid for the studied adsorption system, similar criteria must be satisfied—namely:

A correlation coefficient (R^2) close to unity,

A close agreement between the calculated (theoretical) qe and the experimentally observed qe at equilibrium. [21]

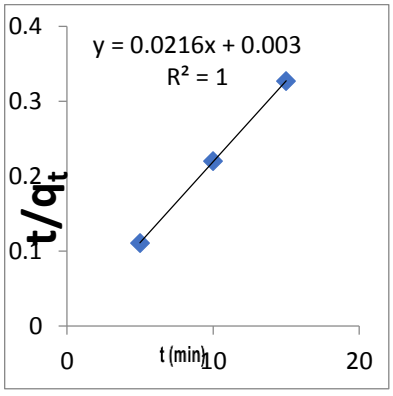


Figure (12): Pseudo-Second-Order Kinetic Model for the Adsorption of Malachite Green Dye onto the Adsorbent Surface at 25 °C

Table (10): Correlation Coefficients and Kinetic Parameters of the Pseudo-Second-Order Model for the Adsorption of Malachite Green Dye onto the Adsorbent Surface at 25 °C

Experimental (q_e) mg/g	Theoretical (q_e) mg/g	K_2 $g.mg^{-1}$ min^{-1}	R^2
46.54	46.2	0.15	1

Figure (12): Pseudo-Second-Order Kinetic Model for the Adsorption of Malachite Green Dye onto the Adsorbent Surface at 25 °C

Table (10): Correlation Coefficients and Kinetic Parameters of the Pseudo-Second-Order Model for the Adsorption of Malachite Green Dye onto the Adsorbent Surface at 25 °C

Based on the results presented in Table (10), there is a strong agreement between the theoretical and experimental adsorption capacities for both dyes. Furthermore, the correlation coefficient (R^2) was found to be equal to 1, indicating a strong linear relationship when applying the pseudo-second-order kinetic model to the studied adsorption system.

These results confirm that the adsorption process for the studied dye follows a pseudo-second-order kinetic model, suggesting that the rate constant is influenced not only by the concentration of the adsorbate but also by the surface characteristics of the adsorbent and associated factors. [22]

4. Conclusions

1. The study demonstrated that nano-carbon derived from industrial cardboard waste exhibits high adsorption capacity for industrial dyes in water. The adsorption efficiency for malachite green dye reached 93.1%.
2. The results indicated that the equilibrium time for dye adsorption was 20 minutes, at an adsorbent dosage of 0.05 g and a temperature of 25 °C.
3. The adsorption isotherm models of Freundlich and Temkin showed acceptable linearity and good correlation with the experimental data. Among them, the Temkin isotherm model provided a better fit for the studied dye system.
4. The amount of adsorbed dye was found to decrease with increasing temperature, indicating that the adsorption process is exothermic in nature. This conclusion is supported by the negative values of the enthalpy change (ΔH) calculated for the adsorbent surface.
5. Additionally, the negative values of Gibbs free energy (ΔG°) confirm the spontaneity of the adsorption process, while the negative entropy change (ΔS°) suggests a decrease in system randomness, implying a more ordered distribution of dye molecules on the surface of the activated carbon.

The same results were maintained under loading conditions, with only slight variations observed.

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