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Utilization of Ground Rice as Eco-Friendly Adsorbent to Remove Malachite Green from Wastewater

This study aims to utilize eco-friendly materials for the removal of toxic dyes from wastewater, specifically using ground rice (GR) to adsorption of malachite green (MG) dye. The results of calculating the ideal weight for adsorption of (MG) showed that the best weight for dye removal was (0.4) g by removal ratio (93.34%) and the maximum adsorption capacity at (25) min. When studying the kinetics and adsorption isotherms for three temperatures (293,313,333) K it was found that the pseudo-second-order (PSO) and Freundlich and Temkin isotherm models were applicable. The results of calculating the thermodynamic functions showed that the reaction is exothermic, physical nature, regular in addition to occurring spontaneously. These results provide an accurate description of the quality of the GR for the removal of MG dye, which highlights the possibility of using GR and improving it for wastewater treatment.

***Keywords*:** Adsorption; Malachite green; Ground rice; Isotherm; Reaction kinetics
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1. Introduction

Treating wastewater by using low-cost, environmentally friendly materials through adsorption technology by applying kinetic and thermodynamic models is very important to get rid of many water pollutants [1]. One of these pollutants is malachite green dye (MG), which we highlighted in this study due to its extreme danger to humans, despite its use as an antibiotic for aquatic organisms to treat gill worms in addition to controlling skin worms that infect these organisms and its use in dyeing silk, wool, leather, cotton, paper and acrylic [2]. MG dye, a triarylmethane dye ($C_{23}H_{26}N_2O$, CI 42,000), is a dark green crystalline substance created by condensing one mole of benzaldehyde with two moles of dimethyl aniline in the presence of concentrated sulphuric acid or zinc chloride. Despite the ban on the use of this dye in many countries, it is still in use due to its low price and abundance in the markets [3]. This dye has been nominated by the US Food and Drug Administration (FDA) to test its ability to cause cancer [2], which confirms the danger of dye to human health [4].

The amount of proteins and starches affects the physical and chemical properties of rice, for example (swelling, stickiness and hardness), in addition to its effect on the efficiency of the adsorption process [5]. The adsorption of dyes on different surfaces containing starches and proteins was studied. This study showed a clear relationship between the dyes and the adsorbing surface, as acidic and basic dyes are strongly associated with proteins of opposite charge (especially proteins with high molecular weight). Recently, this phenomenon has been used to quantitatively determine the protein and identify the active groups on it [6]. To demonstrate the efficiency of dye adsorption on proteins and starches, the isotherms and kinetics of rice adsorption of malachite green dye from wastewater were studied.

2. Materials and Methods

White rice grains were ground using an electric grinder, and a relatively small grain size was obtained, varying in size, as shown in the field-emission scanning electron microscope (FE-SEM) and x-ray diffraction (XRD) analysis. The ground rice was used in the experiments immediately after milling.

The stock solution of the MG dye was prepared by dissolving 1 g of the dye in 1000 mL of deionized water. By dilution, we obtained a series of concentrations of 5-60 mg/L for the study. The maximum absorbance wavelength (λ_{max}) of a dye was calculated by preparing a standard solution of 30 mg/L. The recording was conducted using a UV-visible spectrophotometer within the specified range 500-650nm. For the measurement, a glass cell that was 1 cm thick was employed. The dye's maximum absorption occurred at 618 nm. Figure (1) displays the MG dye's absorption spectrum.

The morphological analysis of the samples produced in this study was carried out using FE-SEM. Scans are carried out at magnifications of 70x, 130x, 4000x, and 60,000x, in addition to EDS, XRD, and AFM analyses. These analyses were conducted to determine the porous structure of the adsorbent surface (MG), the size of the formed particles, the percentage of the present elements, and to know the chemical properties of the sample.

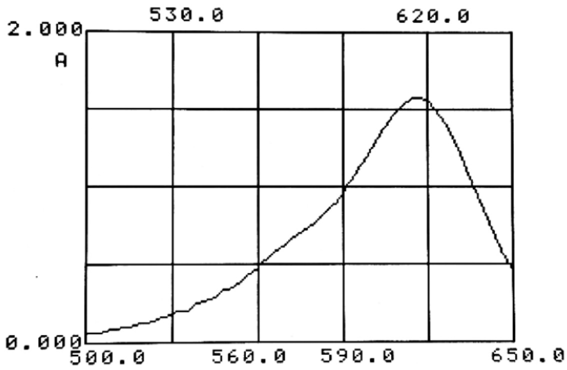
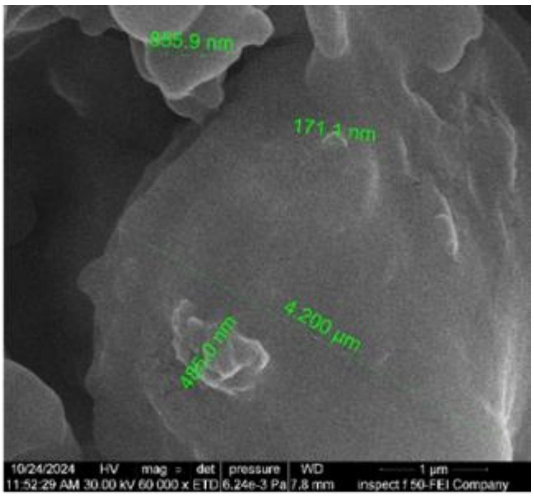


Fig. (1) UV-visible absorption spectrum of MG dye

3. Results and Discussion

The results of the analysis of a sample of the adsorbent surface conducted using FE-SEM showed the size of the granules formed as a result of grinding. The results of the analysis of a sample of the adsorbent surface using FE-SEM showed the size of the granules formed as a result of grinding, where the GR appears as large and very small grains in Fig. (2) at 70x and 130x magnification, Fig. (3) at 4000x and 60000x magnification. The results of FE-SEM show that the surface morphology is not homogeneous and there are still coarse grains, which indicates that the size of the grains is not equal and there are still large particles. Figure (2) shows that the largest particle size of the adsorbent surface ranges 112.7-967.0 µm. The smallest particle size attached to the larger grains in Fig. (3) ranges 171.1-4.2 µm. The reason for the uneven sizes is due to the GR not being grinded well enough to obtain smaller and more homogeneous particles.



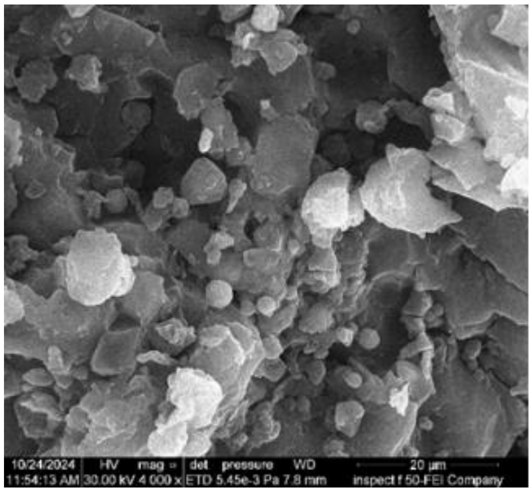
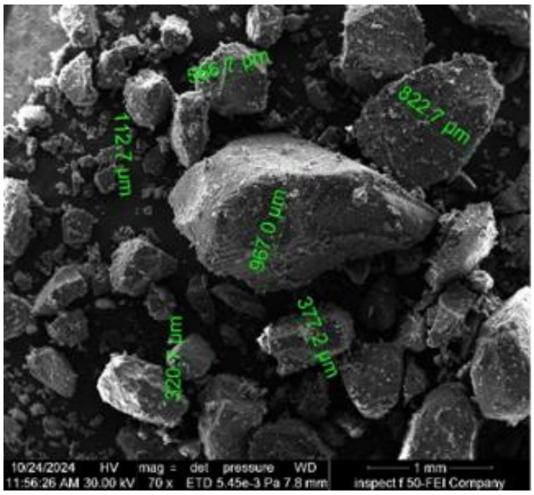


Fig. (2) FE-SEM images of GR with a magnification of 75X and 130X



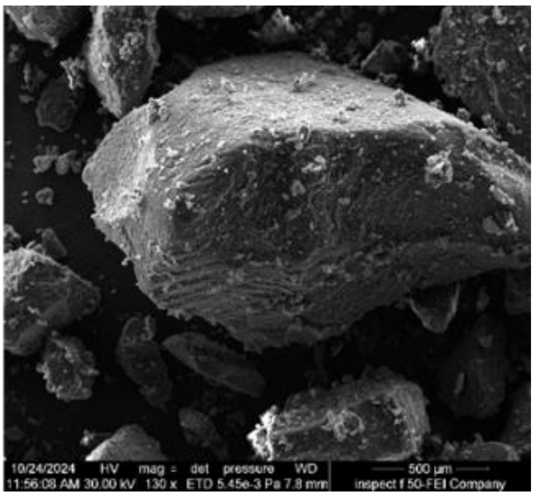


Fig. (3) FE-SEM images of GR with a magnification of 4000X and 60000X

Results of the analysis of the sample under the AFM showed morphological images of GR in Fig. (4) for a section of 4 µm^2, that the highest peak reached by the amount of surface was 101.8 nm and the lowest depression was 49 nm. The results also showed a different distribution of grains and that the average surface roughness was 5.4 nm, as shown in the Abbott-Firestone curve in Fig. (5).

The 3D AFM image shows the variation in granular distribution and roughness due to the different size of the adsorbent surface GR granular as shown in FE-SEM. That variation in surface roughness provides effective sites for contaminant adsorption and adhesion to the ground rice (GR).

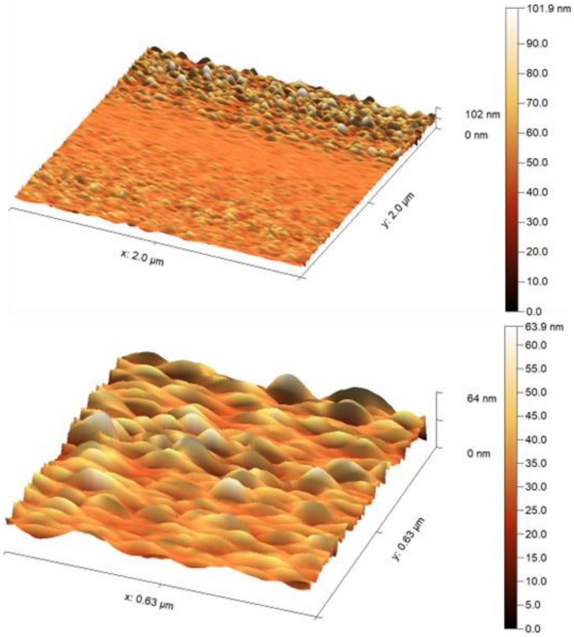


Fig. (4) 3D AFM image of (GR) surface

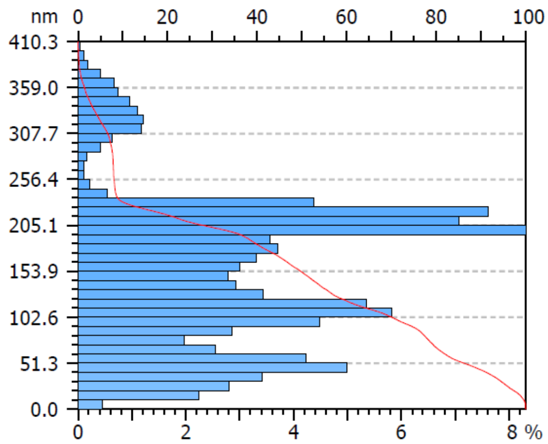


Fig. (5) Abbott-Firestone curve

The results of the analysis of a sample of the adsorbent surface using XRD showed the size of the granules formed as a result of grinding the surface, as the examination after applying the Scherrer's equation to calculate the size as in Eq. (1) shows a difference in size as shown in table (1) and Fig. (6).

$$D = \frac{k\lambda}{\beta\ cos\theta} \quad (1)$$

where D is the crystallite size, k is shape factor (0.89), λ is the x-ray wavelength, β is the line broadening at half the maximum intensity (FWHM), θ is the Bragg's angle. This system supplied with Cu-ka radiation at a wavelength of 1.5406Å produced at 40kV. The samples were scanned at 2θ ranging from 10° to 70° at room temperature [7]

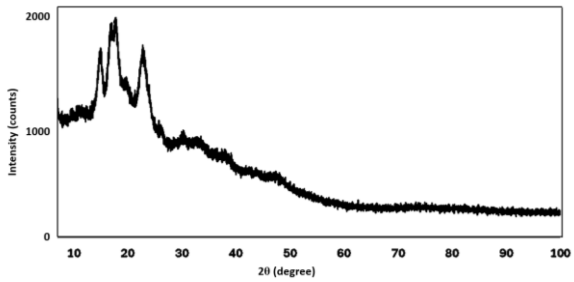


Fig. (6) XRD pattern of ground rice (GR)

Table (1) XRD data of ground rice (GR)

Position 2θ (deg)	FWHM Left (deg)	d-spacing (Å)	Crystallite size (nm)
14.8909	0.889	5.9445	9.41
17.3086	1.9252	5.1192	4.36
19.1355	4.6725	4.63439	1.8
23.0971	1.8952	3.84769	4.47
33.3464	6.9398	2.68479	1.25
99.9934	0.022	1.0056	586.72

The proportions of elements in the sample according to Fig. (7) show that the highest proportion was for the element carbon 53.5%, and oxygen 45.0%, then magnesium, phosphorus, sulfur, calcium, and nickel in very small proportions.

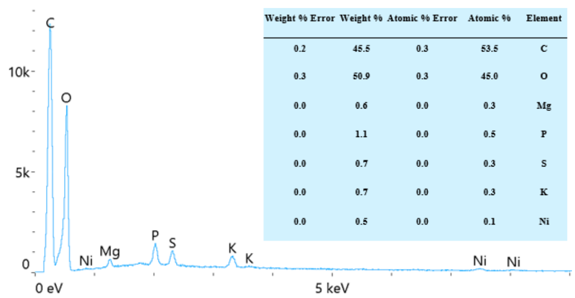


Fig. (7) EDS spectrum and analysis of ground rice (GR)

A series of different concentrations of the MG dye (5-50 mg/L) were prepared and using a UV-visible spectrometer at the maximum absorbance wavelength (618nm), the absorbance of the series of prepared concentrations was measured and by plotting between the absorbance and the concentration, the calibration curve was obtained and the straight line equation and the correlation coefficient were extracted as shown in Fig. (8).

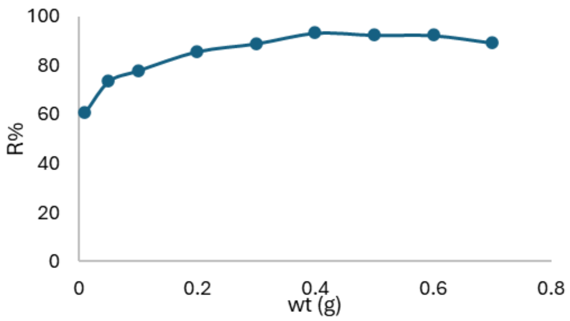


Fig. (8) Calibration curve for malachite green dye

The influence of the weight of GR was investigated using an initial concentration of the dye of 50 mg/L at 30 min in shaking water bath in order to ascertain the optimal weight for the adsorption of malachite green dye on the surface of the ground rice, at 293 K and against a range of adsorbent surface weights 0.01-0.7. Based on the results, figure (9) shows that as the weight of the ground rice is within 0.05-0.3g, the percentage of removal (%R) increased steadily, which was equal to 60.76-89.03%. This is due to the increase in the number of active sites on the absorbent surface, which increases its efficiency in eliminating the dye from its aqueous solution. At the optimal weight of 0.4g of the GR, the %R stabilizes with a removal ratio of 93.34% [8].

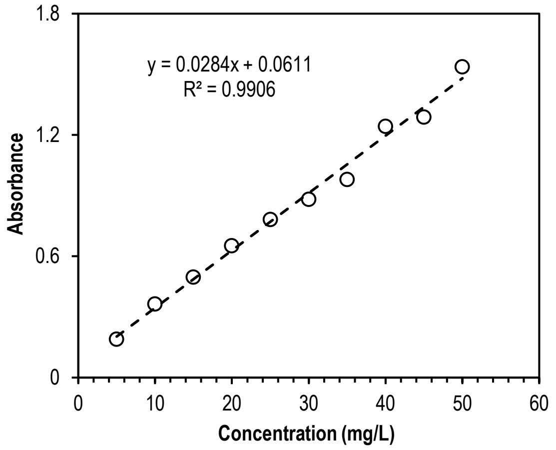


Fig. (9) Effect of weight of adsorbent surface (GR) on adsorption of MG dye

Using an initial dye concentration of 50 mg/L, various temperatures (293, 313, 333 K), and ideal weight of GR 0.4 g under investigation was used. This is to calculate the equilibrium time of the dye adsorbate on the absorbent surface. Figure (10) illustrates how time affects the adsorption process on GR. The findings indicated that 25 min is the equilibrium time necessary for the adsorption process of malachite green on ground rice.

By following the removal ratio (R%) for the temperatures used in this study, we notice that the removal ratio decreases with increasing temperature. This confirms that the reaction is exothermic, and this is due to the increase in the kinetic energy of the adsorbed dye molecules with increasing temperature, which leads to the separation of the MG dye molecules from the adsorbent surface (GR) and their return to the solution.

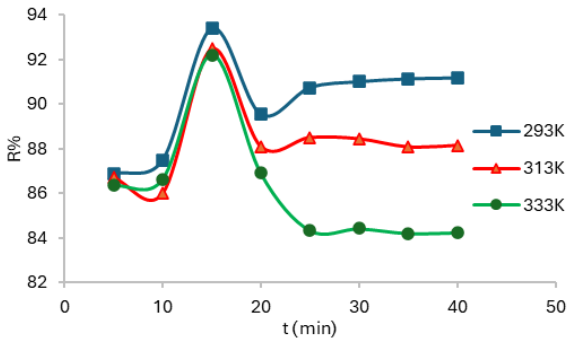


Fig. (10) Effect of equilibrium time on the amount of MG dye adsorbate on the surface of GR

Three kinetic models were utilized in this study; pseudo-first-order (PFO), pseudo-second-order (PSO) and the Elovich kinetic model, according to the following mathematical equations [9]:

$$ln(qe - qt) = -K1 + lnqe \quad (2)$$

$$\frac{t}{qt} = \frac{1}{K2qe} + \frac{t}{qt} \quad (3)$$

$$qt = \frac{1}{\beta} ln(\beta\alpha) + \frac{1}{\beta} lnt \quad (4)$$

where qt (mg/L) and qe (mg/L) are amounts of malachite green dye adsorbate on the surface of the ground rice at equilibrium time, K_1 (L/min) and K_2 (g/mg.min) are the pseudo first-order and pseudo second-order apparent rate constant, respectively, α denotes the initial adsorption rate constant measured in (mg/g.min), while β signifies the desorption process constant expressed in (g/mg) in the Elovich kinetic model

When drawing the mathematical relationship graphically, we obtained Fig. (11). The equilibrium constants for the PFO and PSO and the Elovich constants were calculated, in addition to calculating the correlation coefficient (R^2) for the three temperatures as shown in table (1). The results show the application of PSO for the adsorption of malachite green dye on the surface of GR based on the correlation coefficient values R^2 close to unity for the three temperatures. When following the values, we notice a decrease in the qt values with the increase in temperature and a decrease in the values of the order constant K_2. This indicates that the reaction is exothermic [10]. In addition to the non-applicability of the PFO and Elovich kinetic model based on the values of R^2 calculated for different temperatures in table (2) [11].

The adsorption isotherms were studied using a range of MG dye concentrations of 20-60 mg/L, temperatures of 293, 313, and 333 K, the optimal absorbent surface weight GR of 0.4 g, and equilibrium duration of 25 min. The relationship between the qt (mg/g) and Ce (mg/L) isotherms of the adsorption of malachite green dye on GR at various temperatures is depicted in Fig. (11).

Table (2) values of the kinetic constants of the adsorbent GR surface at different temperatures

Kinetic model	Parameter	Temperature (K)		
		293	313	333
Pseudo 1st order	K_1	0.0063	0.0212	0.0069
	qe	0.0799	0.0565	0.2660
	R^2	0.0005	0.0037	0.0007
Pseudo 2nd order	K_2	0.1839	0.1454	0.0358
	qe	1.1496	1.1284	1.1082
	R^2	0.9969	0.9961	0.9955
Elovich	β	33.7837	32.6797	33.78378
	α (10^{-3})	33.5294	37.10946	33.52941
	R^2	0.1818	0.2566	0.1818

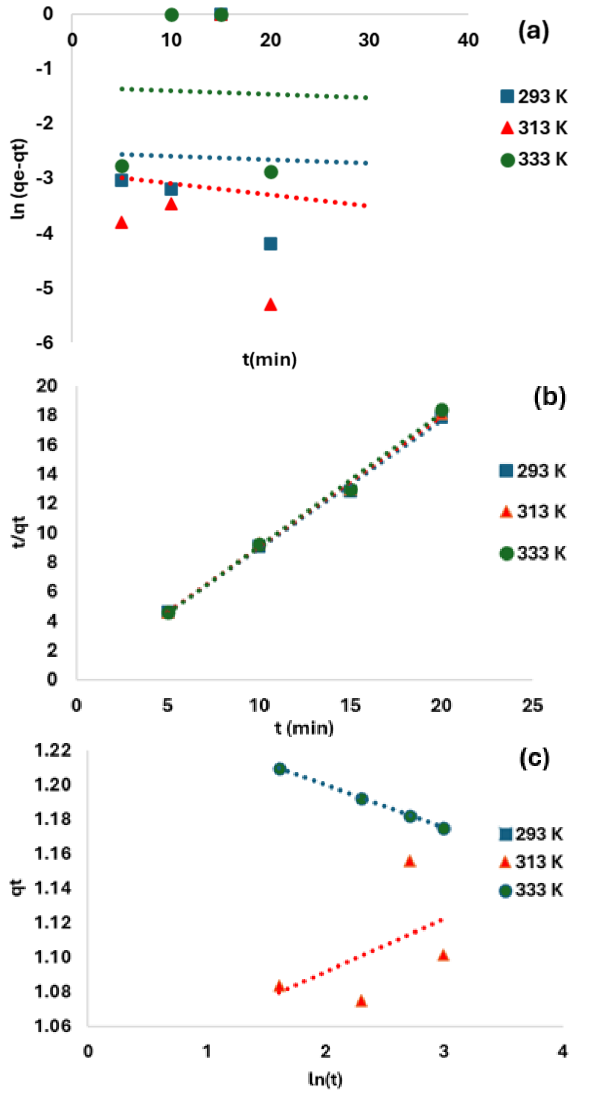


Fig. (11) PFO (a), PSO (b), Elovich (c) kinetic models for the adsorption of the MG dye on the surface of the GR at different temperatures

Figure (12) shows the isotherm of MG adsorption on the surface GR of type "L_3", that is, the orientation of the adsorbed dye molecules is horizontal on the surface of the GR. This type is attributed to Langmuir and takes a concave shape and the adsorption is single-layer, which means that the axis of the molecules is parallel to the adsorbent surface [12].

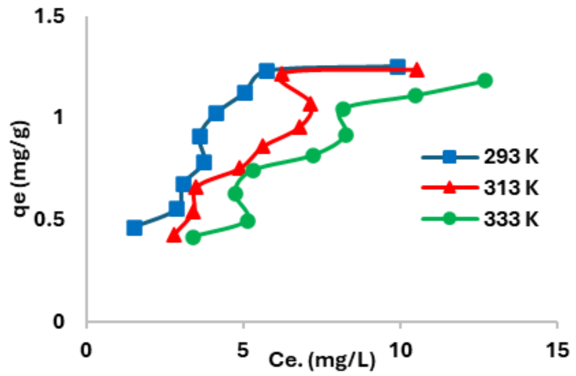


Fig. (12) Isotherm of the adsorption process of MG dye on GR

The initial rate of the dye adsorption process on the adsorbent surface was calculated according to Eq. (5) and was equal to 0.2430, 0.1851, and 0.0439 mg/g.min at 293, 313, and 333 K temperatures, respectively. By following these values, we notice a decrease in the adsorption rate with increasing temperature. This is consistent with the decrease in the amount of MG dye adsorbate on GR surface, which confirms the exothermic nature of this surface [13].

$$Ri = K_2 qe^2 \quad (5)$$

Three models of the adsorption process isotherm were applied in this study (Freundlich, Langmuir, and Temkin) according to the following mathematical equations [14]:

$$log(qe) = log(Kf) + \left(\frac{1}{n}\right) log(Ce) \quad (6)$$

$$\frac{Ce}{qe} = \frac{Ce}{qe\ max} + \frac{1}{qe\ max\ KL} \quad (7)$$

$$qe = BT\ ln\ KT + BT\ ln\ Ce \quad (8)$$

To calculate the heat of adsorption values, we applied the following equation [15]:

$$b = \frac{RT}{BT} \quad (9)$$

Where Freundlich constants K_f (mg/g), K_L(L/mg) Langmuir constants, K_T (L/mg) Temkin constants and b(KJ/mol) heat of adsorption values, qt (mg/L) and qe (mg/L) amount of malachite green dye adsorbate on the surface of the ground rice at equilibrium time.

Figure (13) shows the mathematical relationship for adsorption isotherms. By calculating the Freundlich constant and the values of the adsorption intensity in addition to the value of the Langmuir constant, the value of q_{max}, the Temkin constants and the values of the adsorption heat (b).

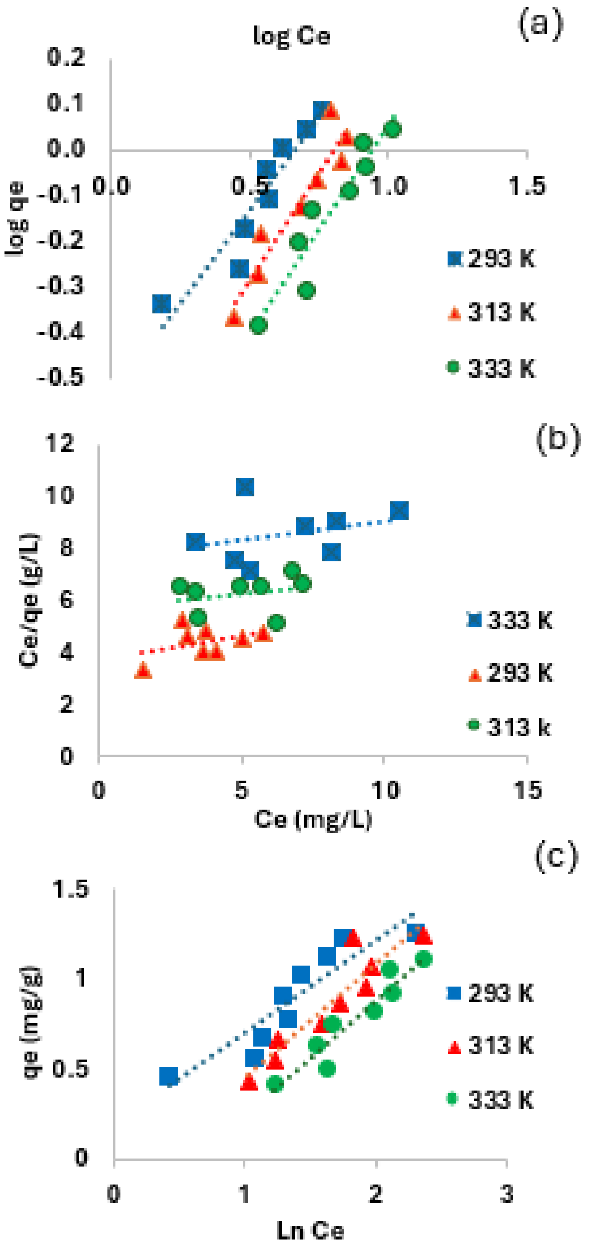


Fig. (13) Freundlich (a), Langmuir (b), Temkin (c) isotherm for the adsorption of MG dye on the surface of the GR at different temperatures

According to the values of the standard deviation (R^2) in table (3) at the temperatures considered in this study, it was shown that the Freundlich and Temkin isotherms apply because R^2 approaches one, and the values of n within 1-10 indicate that the adsorption is controlled by physical forces, in addition to the decrease in the values of the Freundlich constant, indicating that the nature of the adsorption process is exothermic and that the adsorption process occurred on heterogeneous surfaces and has different locations of adsorption energies [16]. This is what applies to the difference in the particle size of the adsorbent surface during its examination in FE-SEM, AFM and XRD.

Table (3) Values of the isotherm constants of the adsorbent surface GR at different temperatures

Kinetic model	Parameter	Temperature (K)		
		293	313	333
Freundlich	K_f	0.3549	0.2133	0.1772
	n	1.5805	1.2373	1.2682
	R^2	0.8306	0.878	0.894
Langmuir	K_L	0.1721	0.0577	0.0348
	qe_{max}	2.1372	3.5323	4.0933
	R^2	0.7456	0.4663	0.3478
Temkin	K_T	1.4284	0.7393	0.5538
	b	4.7209	4.0974	4.4575
	R^2	0.8355	0.8727	0.9226

By observing the R^2 values of the Langmuir isotherm model at the three temperatures shows that the model does not apply, while qe_{max} values decrease with increasing temperature this indicates the exothermic nature of the adsorption process in this study [17]. In addition to the adsorption heat values calculated from the Temkin model, which were less than 40 kJ/mol. This confirms the physical nature of adsorption [18]. Calculating thermodynamic functions standard enthalpy (ΔH°), Gibbs free energy (ΔG°), and standard entropy (ΔS°) and understanding the behaviour of the adsorption process depend on the effect of temperature on adsorption.

When graphing Fig. (14) between lnKeq and 1/T, the linear Eq. (10) can be used to calculate ΔH° and ΔS° was derived. At each temperature within the study, ΔH° of adsorption and ΔS° were calculated using the linear relationship shown in Fig. (14), where the slope of this curve is -ΔH°/R and the intercept is ΔS°/R, according to Eq. (10) [19].

$$\ln Keq = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad (10)$$

To compute the variation in the ΔG°, equation (11) is applied [20]

$$\Delta G^\circ = -RTlnKeq \qquad (11)$$

ΔG°, measured in kJ/mol, denotes the change in Gibbs free energy, while R, expressed in J/mol·K, signifies the universal gas constant. The thermodynamic function values for the adsorption of MG dye on GR are presented in table (4).

The enthalpy associated with the adsorption process on the adsorbent surface (GR) indicates that the process is exothermic. The enthalpy values recorded were below 40 kJ/mol, suggesting that the adsorption mechanism is physical in nature, and the negative sign for the enthalpy value indicates that the reaction is exothermic [21]. Irregularity and diminished randomness in adsorption process, indicated by the negative entropy values. The Gibbs free energy estimates for MG dye adsorption on GR are negative, indicating that the adsorption process was spontaneously [22].

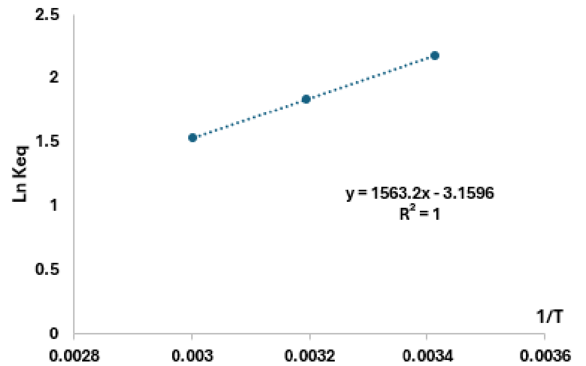


Fig. (14) Vant Hof's equation for adsorption of malachite green dye on the adsorbent surfaces of ground rice

Table (4) Values of the thermodynamic equilibrium constants for adsorption of MG dye on the adsorbent surface of GR and at different temperatures

Adsorbent	T (K)	ΔG° kJ/mole	ΔH° kJ/mole	ΔS° J/mole.K
Ground rice	293	-5.2975	-12.9964	-26.2689
	313	-4.7799		
	333	-4.2460		

4. Conclusion

In this study, the morphology of the GR showed variation in grain size and roughness. The adsorbent surface had adsorption good efficiency with removal ratio of 93.34% of the MG dye at 298 K. The results of applying kinetic models indicated the application of the pseudo-second order. While the results of applying the isothermal models indicated the application of Freundlich and Temkin models. The isothermal data (ΔH°= -12.9964 kJ/mole, ΔS°= -26.26.2689 J/mole.K, ΔG°= -5.2975, -4.799, -4.2460 kJ/mole) showed that the reaction is exothermic, influenced by physical forces, regular, and occurs spontaneously. However, the surface needs further applications to demonstrate its effectiveness on heavy metals and different dyes and thus determine the mechanisms of the interaction of the adsorbent surface with various pollutants for water purification.

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