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Sustainable Management of Agro Industrial Waste as Potential Adsorbent for Wastewater Treatment: Kinetic, Thermodynamic and Equilibrium Study

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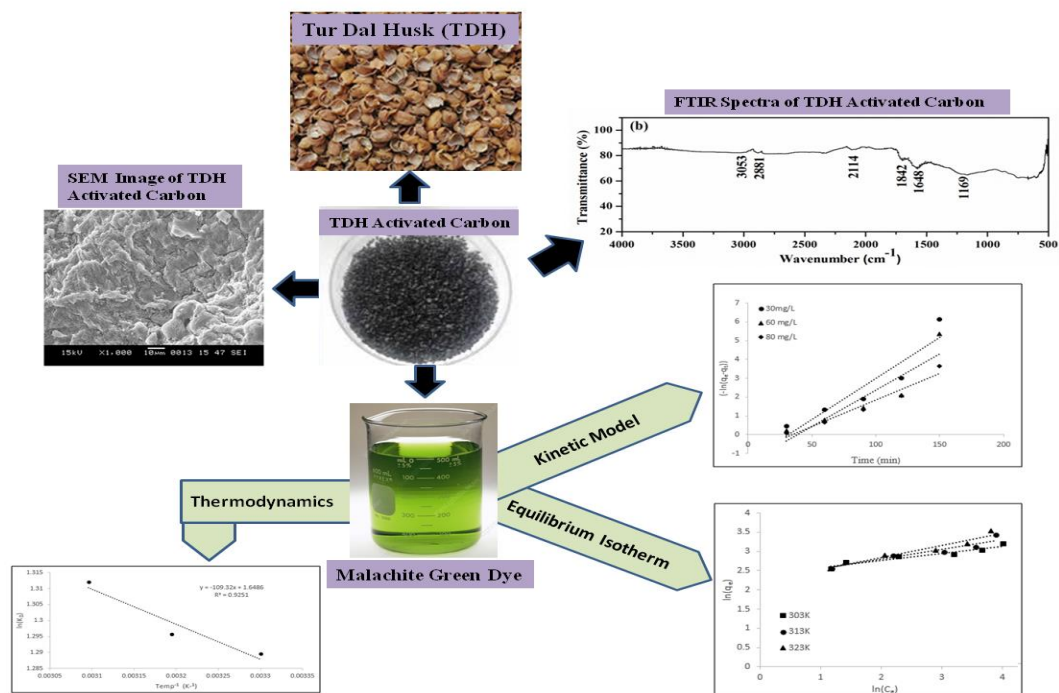
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ABSTRACT

In the current work, the malachite green (MG) dye was removed from synthetic wastewater by employing a sustainable adsorbent *Cajanus cajan* (Tur Dal Husk) as an adsorbent. The activated carbon based on Tur Dal Husk (TDH) was prepared and analyzed by analytical techniques methods like the analyzes surface area involving Brunauer-Emmett-Teller (BET) analysis, scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR). The impacts of multiple causes, specifically pH, adsorbent quantity, contact duration, and the concentration of dye was investigated about the elimination of MG dye. The equilibrium isotherms underwent analysis through the Freundlich and Langmuir models. The highest ability to absorb was obtained as 24.81 mg/g, 30.95 mg/g, and 36.49 mg/g at 303K, 313K, and 323K respectively. The separation factor value confirmed that the adsorption was beneficial at the adsorption conditions. The kinetics exhibited behavior consistent with pseudo-second-order kinetics. The thermal variables, involving entropy (ΔS), Gibbs free energy (ΔG), and enthalpy (ΔH), revealed that adsorption is a process that occurs naturally and absorbs heat during the process.

Keywords: Tur Dal Husk (TDH); Malachite Green; *Cajanus cajan*; Sustainable; Kinetics; Energy

GRAPHICAL ABSTRACT



HIGHLIGHTS

- ❖ A sustainable adsorbent *Cajanus cajan* [Tur Dal Husk] (TDH) activated carbon with bases was utilized for the purpose of eliminating the Malachite Green (MG) synthetic wastewater dyed.

- ❖ The characterization results showed that the Activated carbon based on TDH adsorbent exhibited significant adsorption sites to perform the MG dye's adsorption.
- ❖ The maximum adsorption capability achieved was 36.49 mg/g.
- ❖ The adsorption of kinetics adhered to second-order kinetics, and the analysis of thermodynamics showed that the adsorption process spontaneously took place and exhibited an endothermic nature.

1. INTRODUCTION

More than 1,00,000 commercial dyes are available in the market. These colorants have found application in diverse sectors including paper and pulp, leather processing, cosmetic formulation, dyeing processes, plastics, and the food industry [1]. The consumption of the dyes in these industries is rising every year. Even in minute concentrations, the textile dyes exhibit substantial toxicity, being both carcinogenic and mutagenic [2]. According to literature reports, over 7×10^5 tonnes of wastewater from textile industries is produced annually [3]. The disposal of such wastewater constitutes a significant problem because it contains organic pollutants which can affect the terms "chemical oxygen demand" (COD) and "biochemical oxygen demand". These substances can elevate the cloudiness of water ecosystems and potentially give rise to various challenges for aquatic organisms [4]. The dye being examined is malachite green (MG), this cationic dye is water-soluble, and a part of the triphenyl methane group. It is employed as an antifungal and antiprotozoal agent in aquaculture [5]. Furthermore, it finds application in coloring materials like wool, cotton, and leather. For mammalian cells, it is cytotoxic and serves as a tumor-promoting substance [6]. MG was reported to have a mutagenic and carcinogenic effect on humans once it goes into the food chain. Also, carcinogenic products are produced after the degradation of MG dye [7]. Due to these reasons, its use has been banned in countries like Japan, USA, etc [8].

Numerous methods exist for eliminating dyes from wastewater. These encompass coagulation, filtration, biological processing, flocculation, precipitation, electro-floatation, ion exchange, photodegradation, photocatalytic degradation, advanced oxidation processes (AOPs), and adsorption [9]. However, many of these techniques are hindered by drawbacks such as elevated expenses, substantial oxygen demands huge sludge formation, etc. Among these processes, adsorption is the most efficient, simple, promising, and economical process [10]. Also, the costly toxic substances can be recovered from wastewater by using adsorption.

At present, activated carbon is used to adsorb toxic dyes on a commercial level. However, the production cost of activated carbon to treat the wastewater for such a purpose will be huge. Recent years have seen an increase in study on directed towards the utilization of more affordable options and inexpensive materials as an adsorbent [11]. These may include natural and agricultural by-product waste. These are available abundantly at negligible or inexpensive. Previously, several materials namely biomass fly ash [12], rice straw-derived char [13], neem leaf powder [14], banana pith [15], banana and orange peels [16], soyabean hull [17], chitosan/oil and palm ash [18], sunflower seed hull [19], were applied to eliminate dyes from wastewater. A list of adsorbents used for the elimination of various dyes has been compiled by Crini recently [20].

The Tur dal husk (TDH) is an agro-waste obtained from a dal mill and it is being used as a cattle feed. During processing, it is often treated with alkali, lime water, and other chemicals which makes it unfit to be used as cattle feed. In this current study, a sustainable adsorbent TDH is utilized to eliminate MG dye from synthetic wastewater, and the influences of factors like dye concentration in wastewater, adsorbent quantity, wastewater pH, and contact duration between wastewater and adsorbent were examined.

2. MATERIALS AND METHODS

2.1. Adsorbate Preparation

The malachite green (MG) dye, with the chemical formula $C_{52}H_{54}N_4O_{12}$, a molecular weight of 927 g/mol, also known as basic green 4, designated as C.I. No. 42000, and having a maximum absorption wavelength (λ_{max}) of 616.9 nm, was provided by LOBA Chemie Pvt. Ltd. A 100 mg/L The dye's stock solution was created using deionized water, and solutions of desired concentrations were formulated using this stock solution.

2.2. Adsorbent Preparation

Tur dal husk (TDH) was obtained from a pulse processing facility situated in Nagpur. Initially, it underwent a set of preparation steps. It was first cleaned with double distilled water, then tap water to eliminate any dust particles. Afterward, it was sun-dried and further dehydrated in a heating oven set at approximately $110^{\circ}C$ for a duration of 8 hrs to reduce its moisture content. The material was subsequently crushed and sifted to obtain particles within the size range of 50 to 100 μm . Following this, carbonization was carried out using a muffled furnace at around $450^{\circ}C$ for a span of 4 hrs. The subsequent treatment involved using concentrated hydrochloric acid (HCl) to eliminate ash content from the carbon, followed by repeated rinsing until double-distilling water achieving a pH of 7. The material was then subjected to another drying phase in a heating oven at $110^{\circ}C$ for 8 hrs to extract any remaining moisture content. Ultimately, activation was achieved by subjecting the material to a temperature of $450^{\circ}C$ for a duration of 4 hours in a muffle furnace. The complete sequence of steps is depicted in Fig.1.

2.3. Physical and Chemical Characterization

Scanning electron microscopy (SEM) apparatus were employed to capture the morphological composition of TDH before and subsequent to the adsorption of MG dye. FTIR spectrum was conducted to determine the groupings of functions that are present, encompassing the range of the scanning between 400-4000 cm⁻¹. The area of the surface adsorbent was assessed through the utilization of BET Smart sorb 92/93 equipment.

2.4 Adsorption Study

Batch-mode adsorption experiments were executed utilizing 250 ml conical flasks, each having dye solution in a 100 ml volume. The experiments were conducted at varied temperatures (303K, 313K, and 323K), various concentrations of the dye (30, 60, and 80 mg/L), diverse pH levels ranging from 3 to 9, and varying adsorbent doses spanning 1 to 6 g/L of the solution of dye. After agitation for the designated duration, the mixture was filtered, and the MG supernatant's dye concentration was quantified employing a UV-spectrophotometer (Jasco V530) by measuring the 618 nm absorbance, which showed the highest level of dye absorption. A calibration curve was established through the utilization of known MG dye concentrations. The dye separation percentage (% R) and the quantity of dye adsorbed onto the surface of TDH (q_e in mg/g) were established by employing formulas (1) and (2), similarly.

$$\%R = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

$$q_e = \frac{(C_o - C_e) \times V}{M} \quad (2)$$

In this context, C_o signifies the initial amount of the mixture's dye (mg/L), while C_e stands for the solution's dye concentration equilibrium (mg/L). V is the amount of the solution in liters, and M represents the quantity of the material used for adsorption in grams, respectively.

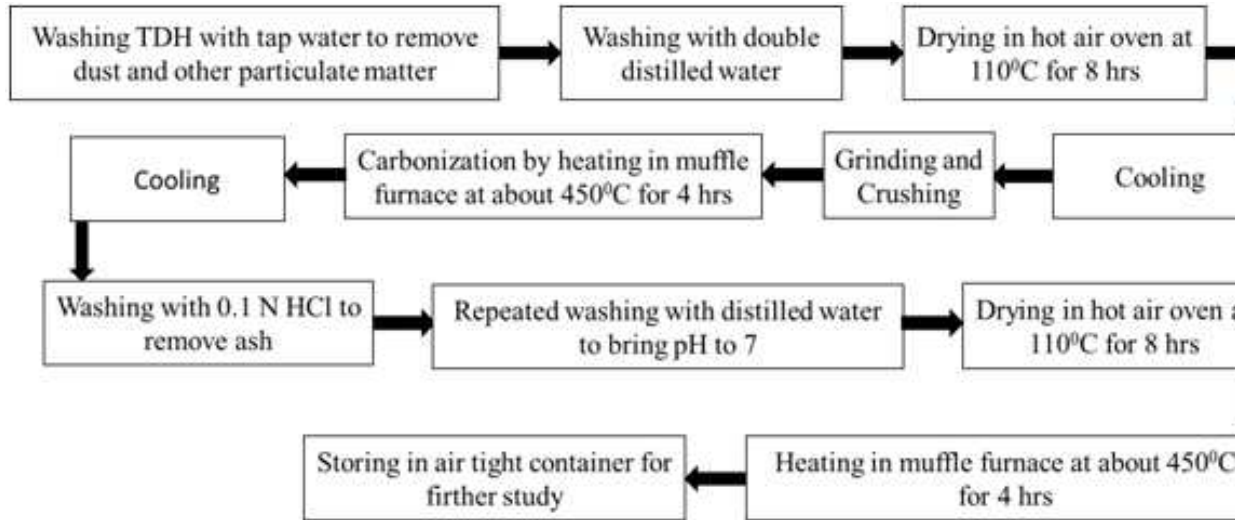


Fig. 1: Schematic representation of procedure for the preparation of activated carbon from TDH

2.5 Isotherms of Adsorption

The adsorption isotherm provides information about how molecules are distributed between the adsorbed states in both solid and liquid states. The equations describing the Langmuir [21] and Freundlich [22] Equations (3) and (4) are shown as isotherms, respectively.

$$\frac{C_e}{q_e} = \frac{1}{Q_{\max} \times k_L} + \frac{C_e}{q_e} \quad (3)$$

$$\ln q_e = \ln k_f + \frac{1}{n} + \ln C_e \quad (4)$$

In this context, C_e refers to the appropriate amount of dye within the mixture (in mg/L), q_e signifies the adsorbent dye concentration (mg/g), $Q_{\max}$ denotes the highest adsorption capability achievable by the adsorbent (mg/g), k_L stands for the Langmuir value (L/mg), while k_f and n are the Freundlich constants. The Langmuir constant, denoted as k_L is utilized to forecast the desirability of the adsorption procedure by employing the factor of separation R_L which is determined by the subsequent equation [13].

$$R_L = \frac{1}{1 + k_L \times C_o} \quad (5)$$

The adsorption isotherm is deemed unfavorable when the separation factor R_L is higher than 1, linear when R_L equals 1, positive when R_L falls within 0 and 1, and irreversible whenever R_L is equals to 0.

2.6. Adsorption Kinetics

The study examined the adsorption kinetics of MG dye using Ho's pseudo-second-order and Lagergren's pseudo-first-order kinetic models, applying the respective equation (6) and (7).

$$\ln(q_e - q_t) = \ln q_e - k_1 \times t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{t}{q_e} \quad (7)$$

In this context, q_t (mg/g) represents the quantity of absorbed dye over time t (min), k_1 (min^{-1}) signifies the rate determinant for the pseudo-first-order reaction, and k_2 (g/mg.min) signifies the pseudo-second-order reaction's rate coefficient. The interparticle diffusion was determined by using equation (8).

$$q_t = k_i \times t^{0.5} + C \quad (8)$$

In this context, k_i ($\text{mg/g.min}^{0.5}$) stands for the rate determinant of interparticle diffusion, and C (mg/g) denotes the deviation.

2.7. Thermodynamic Adsorption

The thermodynamic characteristics, consisting of alteration in Gibbs free energy, denoted as ΔG in units of J/mol, entropy alteration represented as ΔS in J/mol·K, and the modification in enthalpy denoted as ΔH in J/mol, were assessed utilizing equations (9) and (10) [23].

$$\Delta G = \Delta H - T \times \Delta S \quad (9)$$

$$\ln k_D = \frac{\Delta S}{R} - \frac{\Delta H}{R \times T} \quad (10)$$

In this equation, k_D is defined as the ratio of q_e to C_e , where C_e represents the equilibrium condition (mg/L) of A solution containing MG dye, q_e (mg/g) represents the quantity of dye on the adsorbent, and the standard gas constants are denoted by R , which is 8.314 J/mol·K.

3. RESULT AND DISCUSSION

3.1. Analysis of the adsorbent's chemical and physical attributes

3.1.1 SEM analysis

SEM was applied to study the surface structure of the adsorbent. Images depicting the adsorbent's condition both before and following the adsorption of MG dye are displayed in Fig. 2(a and b), respectively. In Fig. 2(a), pores and cavities were observed, while Fig. 2(b) displayed the MG dye adhering to the adsorbent's pores.

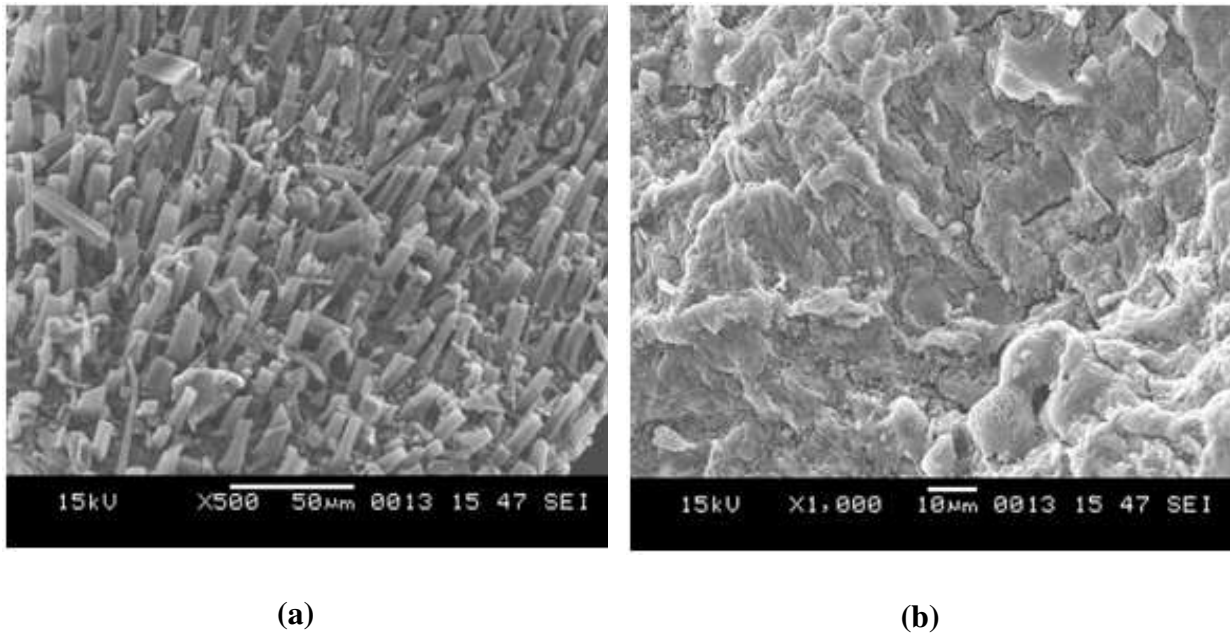


Fig 2: SEM pictures of TDH **(a)** Before dye adsorption **(b)** After dye adsorption

3.1.2 Fourier Transformed Infrared Spectroscopy

FTIR spectra were known to the different functioning groups present at the sites for adsorption onto TDH-based activated carbon. The FTIR spectrum of the adsorbent was recorded the adsorption on before and after the MG dye, and these are presented in Fig. 3. (a and b).

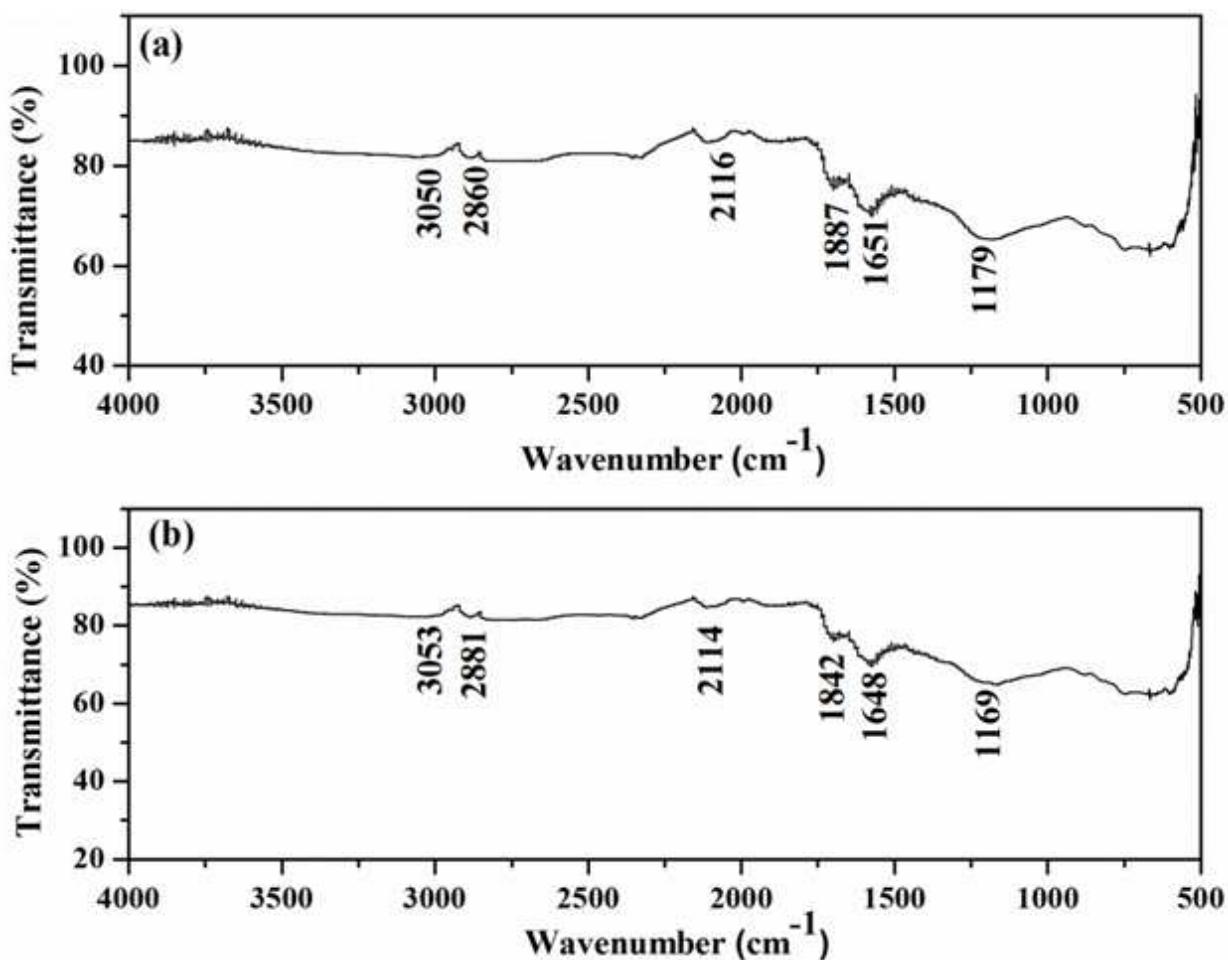


Fig 3: Activated Carbon FTIR spectra (a) Before adsorption (b) After adsorption

The FTIR spectrum of activated carbon, as displayed in Fig. 3 (a), reveals the existence of several functional groups. The stretching of C-H bonds is indicated by the peak at 3050 cm^{-1} , at 2860 cm^{-1} to the elongation of (CO)-H bonds, at 2116 cm^{-1} to the elongation of C=C bonds, and at 1887 cm^{-1} to the stretching of C=O bonds. When activated carbon was treated with MG dye, as seen in Fig. 3 (b), a shift in the bands was observed: 3053 cm^{-1} is indicative of stretching of C-H bonds, 2881 cm^{-1} corresponds to the elongation of (CO)-H bonds, 2114 cm^{-1} corresponds to the stretching of C=C bonds, and 1842 cm^{-1} coincides with the stretched of C=O bonds.

3.1.3 Brunauer-Emmett-Teller (BET)

In the present study, the area of the surface on the adsorbent was calculated to be 385.31 m²/g. This large size of the surface reveals that the TDH-based activated carbon possesses significant adsorbent capacity

3.2. Adsorption of dye as a function of solution pH

The solution's pH influences the aqueous chemistry and the adsorbent's surface-bounding elements. In the present research on the effects of absorption and the impacts of solution pH of The investigation into MG dye at a dye concentration 80mg/L, shaking time 120 min, temperature 303K and the adsorbent dose 5g/L of solution within pH range 3-9. The impacts of pH is represented in Fig. 4.

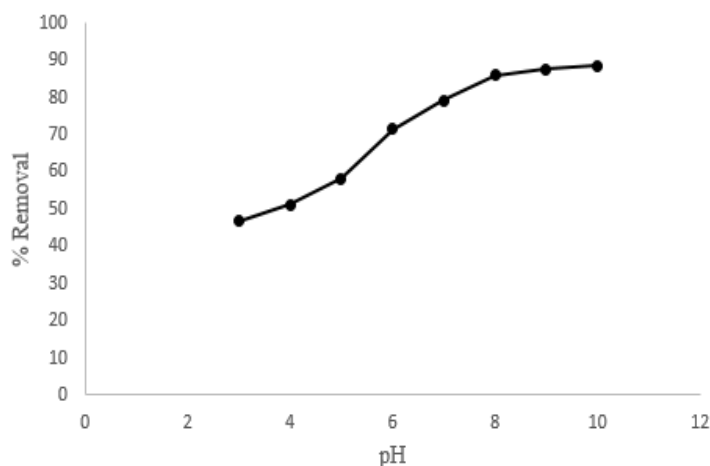


Fig 4: Adsorption of dye as a function of solution pH

The research indicated that the percentage removal of MG dye was a minimum value (46.83%) when the solution's pH value was 3 and it reached a maximum value (86-87%) when the pH was between 8-10. Beyond pH 8, the removal percentage of the dye remains unchanged. Therefore pH 8 was fixed for the adsorption study. At low pH, the percentage removal of MG dye was low. This can be explained by the concentration is increasing of H⁺ ions at acidic pH, which

competes with positively charged dye ions and consequently reduces the quantity of dye removal. At an above pH level of the solution, there is a rise in the quantity of surface groups carrying negative charges on the adsorbent. This augmentation amplifies the adsorption of cations from positively charged dyes via the attractive electrostatic force.

3.3. The impact of the contact duration and dye concentration on dye adsorption

The duration of approach between the amount of dye, the adsorbent, and the adsorbate present in the mixture influences the removal percentage of the solution's MG dye. To investigate this, we conducted a study at a pH of 8, utilizing 0.5 g dose of the adsorbent and temperature of 303K. Fig. 5 illustrates the percentage removal of dye for solution concentrations of 30, 60, and 80 mg/L at various contact times.

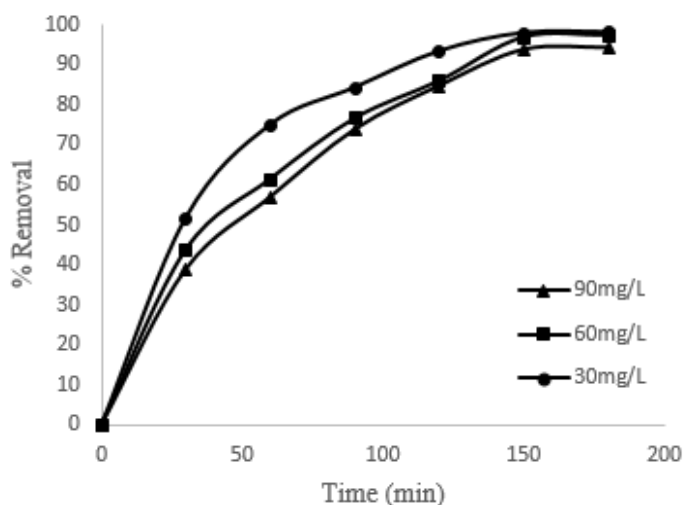


Fig 5: The impact of contact time and dye concentration on dye adsorption

The percentage of dye removal reached the maximum at 150 min and it was 97.83%, 96.84%, and 93.78% for 30, 60, and 80 mg/L subsequently. Hence 150 min was fixed for the adsorption study. The figure illustrates that the removal efficiency is swift at the beginning and

gradually diminishes in the later stages until it reaches a state of saturation. This is because of the fact that at initial stages huge numbers of sites of activity are present for the dye adsorption. However, as time progressed, the quantity of available sites reduced and it became difficult to occupy the remaining sites experienced repulsion due to the interaction among the molecules of the substance present in both the solid and bulk phases. The reduction in dye removal percentage was observed to decline as the dye concentration increased, a phenomenon that can be illustrated by the point at which the surface's adsorption sites become fully occupied.

3.4 Effect of adsorbent dose on dye adsorption

The adsorbent's impact quantity was looked at a pH of 8, connecting time of 150 min and temperature of 303K onto the dye solute with a particular concentration of 60 mg/L by changing the adsorbent quantity from 1-6 g/L and the result is shown in Fig. 6.

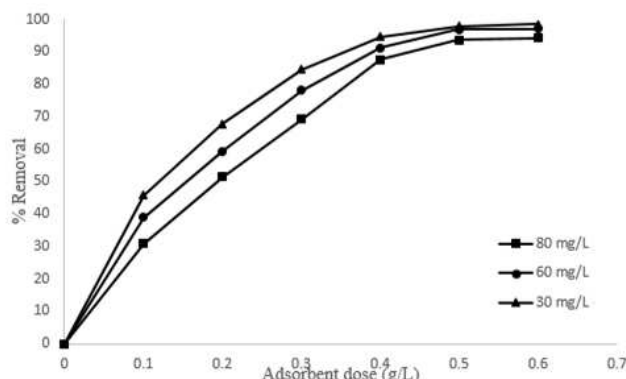


Fig 6: Adsorbent impact dose on the adsorption of dye

The outcomes indicated that when the quantity of adsorbent increases, the viability of dye removal also increases. The percentage of removal dye experienced a substantial increase, going from 38.93% to 96.84%, as the quantity of adsorbent material used was raised from 0.1 g/L to 0.5 g/L. Although, as the adsorbent dose continued to rise, the percentage removal remained relatively

constant. Hence 0.5 g/L of adsorbent dose was fixed for further adsorption experiments. The sites for adsorption were increased by the increase in adsorbent dosage, and as a result, the dye removal percentage increased.

3.5. Adsorption Isotherm Investigation

The interaction between the adsorbent and MG dye was investigated by examining adsorption isotherms, specifically Langmuir and Freundlich isotherms, at various temperatures (303K, 313K, and 323K).

3.5.1 Langmuir Isotherm

The graphs of C_e/q_e vs C_e were plotted at 303K, 313K, and 323K, which exhibited the linear trends as observed in Fig. 7.

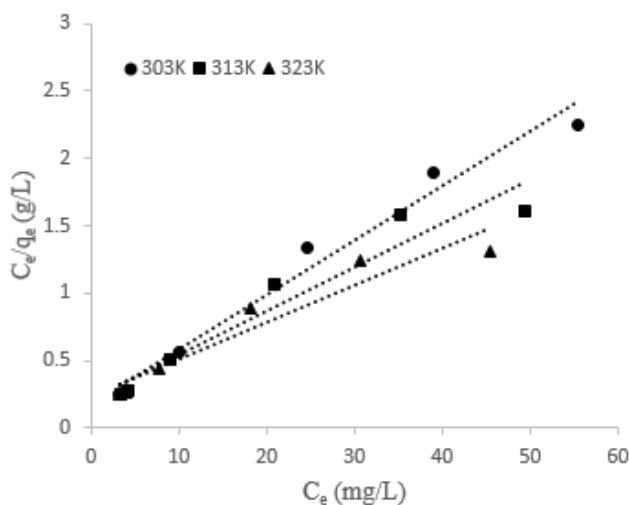


Fig 7: Langmuir isotherm for MG dye adsorption

Table 1: The removal's isotherm parameter of different temperatures for MG dye

Isotherms	Parameters	Temperatures (K)		
		303	313	323
Langmuir	$Q_{\max}$ (mg/g)	24.81	30.95	36.49
	k_L (L/mg)	0.2238	0.1435	0.1175
	R_L	0.0558	0.0870	0.1063
	R^2	0.92	0.91	0.93
Freundlich	k_F (mg/g(L/mg) ^{1/n})	10.92	9.76	9.14
	N	5.38	3.84	3.17
	R^2	0.97	0.93	0.92

The values of the correlation coefficient (R^2) acquired for the tested plots were as follows: 0.97 at 303K, 0.93 at 313K, and 0.92 at 323K. Such a large correlation coefficient value revealed the good fit of Langmuir's isotherm model which states the monolayer formation and uniform dispersion of dye at the adsorbent's surface [24]. The value of $Q_{\max}$ and k_L was obtained from slope and intercept of the graph and is reported in Table 1. The separation factor's numerical value, R_L , was evaluated and obtained to be 0.055, 0.087, and 0.10 at temperatures of 303K, 313K, and 323K respectively and it lies between 0 to 1. According to these findings, the adsorption of MG dye was advantageous inside the specified adsorption situations.

3.5.2 Freundlich Isotherm

The graphs of $\ln(q_e)$ vs $\ln(C_e)$ were plotted at 303K, 313K and 323K which shows linear trends as presented in Figure 8.

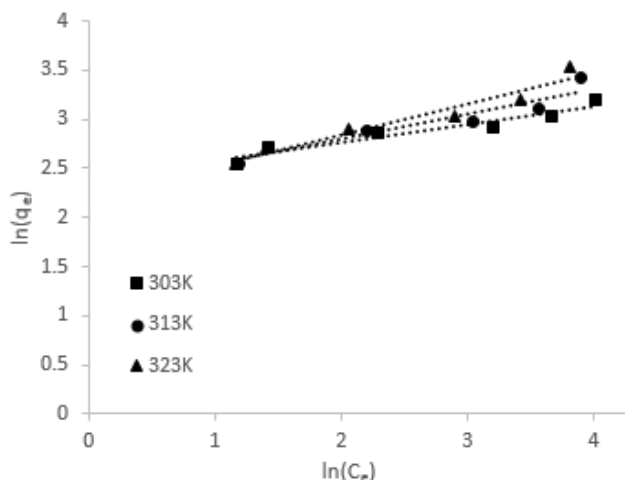


Fig 8: The Freundlich isotherm for MG dye adsorption

The correlation coefficient (R^2) values were found to be 0.92, 0.91, and 0.93 at 303K, 313K, and 323K respectively. Such elevated correlation coefficient values demonstrate the good fit of the Freundlich model [25]. The Freundlich constant n and k_f were estimated based on the slope and intercept of the graph, and their values are reported in Table 1. The values of n , greater than 1, elucidate that the dye adsorption exhibits both favorability and heterogeneity

3.6. Kinetic Adsorption

The adsorption constant rate (k_1) of MG dye using TDH was found using Lagergren's first-order kinetics. The graph of $(-\ln(q_e - q_i))$ vs t was plotted at 303K as shown in Fig. 9. The graph shows linear trends.

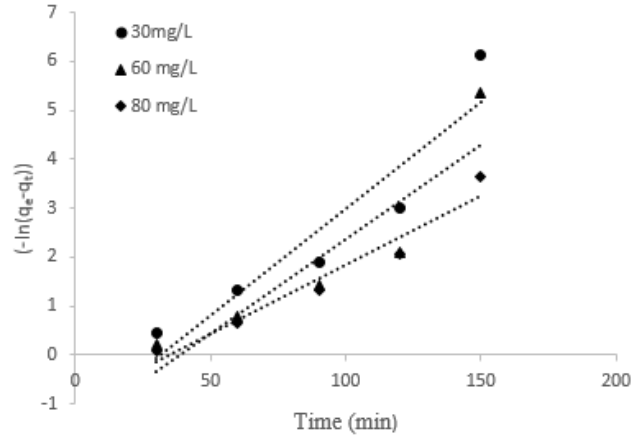


Fig 9: Lagergren's pseudo first order kinetics for adsorption of MG dye

The coefficient of correlation (R^2) was determined to be 0.87, 0.82, and 0.94 for dye concentrations 30mg/L, 60mg/L, and 80 mg/L. The value of k_1 was assessed from the graph's slope and intercept and is documented in Table 2.

Table 2: Comparing the calculated q_e values for the initial concentration of MG dye (C_0) and the first- and second-order pseudo system reactions' rate constants

C_0 (mg/L)	Pseudo-first-order kinetics			Pseudo-second-order kinetics			Interparticle diffusion		
	q_1	k_1	R^2	q_2	k_2	R^2	k_i	C	R^2
	(mg/g)	(min ⁻¹)		(mg/g)	(g.mg/min)		(mg/g.min ^{0.5})	(mg/g)	
30	2.71	0.0387	0.82	7.24	0.003624	0.99	0.3515	1.52	0.93
60	3.93	0.0436	0.87	16.23	0.000917	0.99	0.8528	0.80	0.98
80	4.50	0.0283	0.94	22.32	0.000557	0.99	1.1855	0.073	0.97

To study Ho's model for the kinetics at second order, a graph plotting t/q_t vs. t was created as presented in Figure 10 and the correlation coefficient (R^2) was estimated to be 0.99, 0.99, 0.99 for 30, 60, and 80 mg/L dye solution consequently.

The coefficients of correlation for Ho's model were more than those for Lagregen's model, demonstrating that the procedure of adsorption conforms to the model for kinetics of pseudo-second order. The findings demonstrating that chemisorption is likely the step that establishes the general rate in the adsorption of MG dye [26].

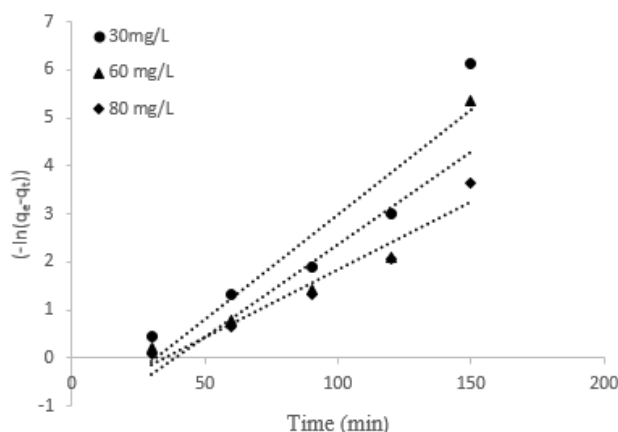


Fig 10: Ho's pseudo second order kinetic model for adsorption of MG dye

3.7. Interparticle Diffusion Study

The graph of q_t vs. $t^{0.5}$ was plotted for 30, 60, and 80 mg/L dye solution at 303K as represented in Figure 11. If the graph is a linear trajectory that goes through the point of origin, it suggests that interparticle diffusion is important in the adsorption in a process. However, if this line doesn't intersect the origin, it suggests that other processes, in addition to interparticle diffusion, may be influencing the rate of adsorption.

The correlation coefficient (R^2) values were discovered to be 0.93, 0.98, and 0.97 for 30mg/L, 60 mg/L and 80 mg/L dye solution. The values of C and k_i were established based on the gradient and intercept of the graph and are provided in Table 2. The graph is a line that is straight and does not cross over the source which demonstrates that interparticle diffusion represents more

than just the step that limits the rate. The values of C for all dye solutions were obtained to be positive which indicating that the experimental values must be fitted with a diffusion model external.

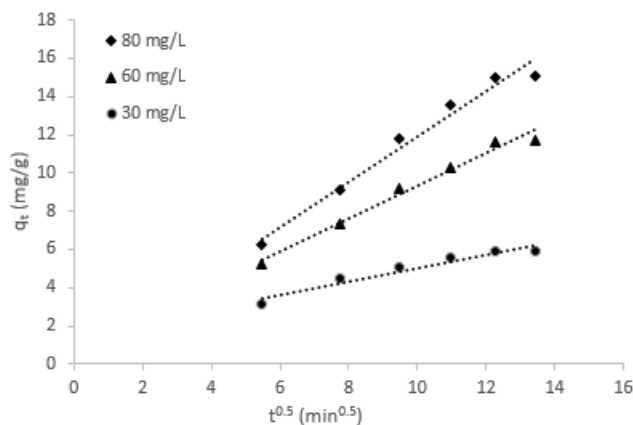


Fig 11: A model of diffusion applied to the adsorption of MG dye

3.8. Adsorption Thermodynamics

The thermodynamic characteristics, such as changes in entropy, enthalpy, and Gibbs free energy (ΔS , ΔH , and ΔG), were determined using equations (8) and (9). Fig. 12 shows the graph of $\ln(KD)$ against $1/T$, from which the values of ΔH and ΔS were obtained by analyzing the y-intercept and slope.

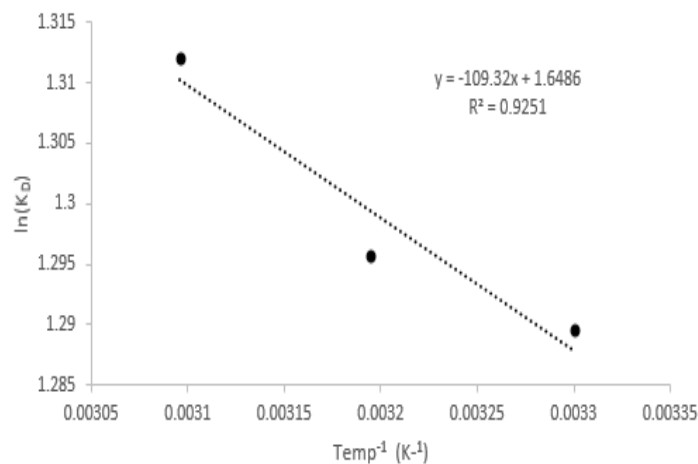


Fig 12: Graph of $\ln(KD)$ vs $1/T$ for MG dye adsorption

The values of ΔG were evaluated to be -3.244, -3.381, and -3.518 KJ/mol at 303K, 313K, and 313K consecutive. The values of ΔH and ΔS were discovered to be 908.88 J/mol K and 13.70 J/mol consecutive. The ΔH value is positive suggesting that the adsorption procedure of MG dye is characterized as endothermic [27]. The value of ΔS was positive which elucidates that the process of adsorption of MG dye occurs due to energy re-distribution between dye and TDH.

4. CONCLUSION

TDH was effectively utilized as form of MG dye hazardous waste removal adsorbent for synthetic wastewater. The characterization results elucidated that the TDH adsorbent possessed significant adsorption sites to perform of MG dye adsorption. The dye's adsorption increased with the build in pH, temperature and adsorbent dose. The data in equilibrium was examined utilizing the Langmuir and Freundlich models of isotherms. The highest possible monolayer adsorption capability was obtained as 24.81 mg/g, 30.95 mg/g, and 36.49 mg/g at 303K, 313K and 323K respectively. The value of separation factor was estimated and it lies in between 0 to 1 which stated that adsorption of dye was favorable under given adsorption study. The data followed Ho's kinetic model which demonstrated pseudo second order kinetics. The study of interparticle model of diffusion elucidated that interparticle not just diffusion was a rate limiting process. The thermodynamic parameter values (ΔG , ΔH , ΔS) showed that the adsorption procedure is both spontaneously and absorbs heat (endothermic). Thus, Tur Dal Husk (TDH) carbon-based activated can be effectively employed as a sorbent for removing malachite green dye.

DECLARATION

The authors assert that they do not have any conflicts of interest.

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