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Adsorption Isotherms and Kinetics Studies on Adsorption of Malachite Green onto Activated Charcoal from Aqueous Solution

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ABSTRACT

The article presents low-cost activated charcoal as an adsorbent in the adsorption process for the removal of malachite green from aqueous solution by batch process. To find the optimum condition of the process, contact time, shaking rate, concentration of malachite green, and concentration of activated charcoal were examined. The malachite green was removed up to 98.9%. The adsorption isotherms were studied to check the performance of the adsorbent. Langmuir, Freundlich, Temkin, Hill De Boer, and Dubinin-Radushkevich adsorption isotherms were studied and compared to which one was suitable in the process. The adsorption process with the activated charcoal adsorbent followed suitably with the order of the Dubinin-Radushkevich > Langmuir > Hill De Boer> Temkin > Freundlich models. According to a kinetic study, the adsorption process was second order. In thermodynamic studies, we obtained negative values of ΔG, ΔS, and ΔH. The negative ΔH and ΔS values suggest that enthalpy contributes more than entropy in producing negative ΔG values. The negative ΔG values of malachite green adsorptions indicate that is a favorable and spontaneous process. The negative value of ΔH ensures the adsorption process is characterized as chemical adsorption and exothermic. The negative ΔS value indicates that randomness decreases at the solid–solution interface during the adsorption of MG by activated charcoal. The surface morphology of the Activated charcoal ensured the adsorption process. The results indicate that the adsorption process is exothermic, spontaneous, and favorable. So, activated charcoal might be useful for removing the malachite green dye from the aqueous solution.

1. Introduction

Water pollution becomes a prime issue to survive the living being. Without proper treatment of dye-containing industrial effluent is a severe problem in the Globe. About ten thousand dyes have been used in industries such as textiles, paper, leather, cosmetics, pharmaceuticals, and food & and beverage [1]. Malachite green dyes are low in cost and are usually used in paper, leather, and as coloring agents in the food and clothing industries [2]. Because of cost and efficiency, it is also used in aquaculture industries as a bactericide, fungicide, and parasiticide [3]. Malachite green is highly toxic and it is banned in the EU, USA, and China for use in aquaculture industries and tolerance level is 0.5-100µg/L [4]. It can cause carcinogenesis, make trouble in the lungs, liver, kidneys, gonads, intestine, etc. [4].

Half of the total dyes produced in the world go off during the dying process and it is discharged by the textile industries [5].

Therefore, to save the environment and living beings, the tolerance level of Malachite green should be removed from water bodies.

The textile industries are discharging dyes containing effluents to water bodies treatment. Focus on this problem of wastewater, the current investigation is aimed to examine the effectiveness of activated charcoal in the treatment of dye-containing aqueous solutions. Some dyes are highly visible even in small amounts (< 1ppm), not biodegrade, quite difficult to remove in aquatic environments which is undesirable. These dyes are also responsible for all kinds of skin diseases and even cancer [6-7]. Therefore, the removal of these types of dyes is extremely important before discharging the industrial effluents into water environments or environments.

Many methods have been used for many years for the removal of dyes from the wastewater like precipitation, flocculation filtration, adsorption, electrochemical processes, ion exchange, membrane separation, oxidation, etc. and occasionally also used in combination methods [8-9]. Every method has disadvantages and advantages. However, in literature, the adsorption methods are dominating for the removal of those dyes from industries effluents [10-11]. Due to simple operation technic, economical, and efficiency, the adsorption method is better than other methods [12]. There are many adsorbent materials used in adsorption methods. like biochar-based activated carbon. Commonly biochar activated carbon are prime choice for dye-contaminated wastewater treatment due to its superior sorption capability and physical properties [13]. We are finding an inexpensive material for the removal of these dyes from aqueous solution. One of the better possible candidates is activated charcoal. Activated charcoal is a common adsorbent to remove the color and odor, even trace quantities of impurities. Activated charcoal has capabilities as an adsorbent to extend its use in the treatment process in dyes containing industrial wastewater [14-15]. The cost-effective adsorbent activated charcoal is easily, and economically viable for large and small treatment units. Activated charcoal is a good adsorbent for the removal of dyes and suspended solids from polluted water, due to considerable surface area, porosity, and surface chemistry [16].

Malachite green dye is a triarylmethane type applied widely in textiles, food, health, paper, pigment, and fungi control industries. Because poisonous effects of Malachite green dye, such as genotoxic, mutagenic, carcinogenic, and teratogenic have been reported in living beings [17] and the presence of N (nitrogen) atom in its structure, makes it difficult the remove or make it bio-degradable [18-19]. In this research work, we used a batch process in the adsorption of malachite green onto activated charcoal from an aqueous solution. The investigation was under various parameters such as temperature, pH, and shaking time. Many types of adsorption isotherms were fitted with investigated data and kinetics models were studied to evaluate the efficiency of adsorbent and discussed.

2. Materials and methods

The dye malachite green [MW = 346] was purchased from Fluka and was used as it was. The known amount of the malachite green was mixed in double distilled water to prepare a stock solution. The adsorbent charcoal was activated by the heating process at 200^0C for 15 h and stored in a desiccator.

The percentages of moisture content in the adsorbent were calculated using the following equation [20].

$$\text{moisture content}=\frac{weight\ of\ moisture}{weight\ of\ sample}\times 100 \quad \textbf{(1)}$$

Thus, the percentage of moisture content was $= \frac{0.022}{2.73} \times 100 =$ 0.8%

2.2 Characterizations

AAS (atomic absorption spectroscopy) result, we determined the removal percentage of MO from the water. Residual activated charcoal was used for the image by using EDS. The XRD investigation was performed to determine the particle size of the activated charcoal. The adsorption isotherm model and kinetic studies were done to know the performances of the adsorbent.

2.3 Adsorption Isotherm Studies

To elucidate the working process of the adsorption, we fitted various adsorption isotherms with our investigated data points such as Langmuir, Freundlich, Temkin, Hill De Boer, and Dubinin–Radushkevich isotherm models. The important parameters are shown in **Table 1.**

Langmuir demonstrated a monolayer formation equation for the adsorbent surface. Langmuir [21] presumptions were as following equation:

$$q_e = \frac{q_{\max} K_l}{1+K_l C_e} \times C_e \quad \textbf{(2)}$$

Where, Ce = adsorbate concentration (mg/L) at equilibrium, qe = the MG adsorbed/gram of the activated charcoal at equilibrium (mg/g), qmax = monolayer formation capacity (mg/g) in maximum level, K_l = constant for Langmuir isotherm (L/mg).

The linear form of the Langmuir adsorption isotherm is as follows:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{(q_{max}K_l)\times C_e} \quad \textbf{(3)}$$

We can calculate the value of qmax and K_l by computing the $1/q_e$ versus 1/Ce plot in the Origin program. When $R_l > 1$, the process will be not suitable, when $R_l = 1$, then the process will be favorable, linear and it will be irreversible. Therefore, it may be concluded that when $0 < R_l < 1$, the process will be suitable.

Freundlich [22] proposed the following empirical equation in the adsorption of the heterogeneous surfaces of the adsorbent.

$$Q_e = K_f C_e^{\frac{1}{n}} \quad \textbf{(4)}$$

For data modeling, the log-based linear formula is found,

$$logQ_e = logK_f + \frac{1}{n} logC_e \quad \textbf{(5)}$$

Where, K_f = constant (mg/g) for the Freundlich adsorption model, n = the intensity of the process, Ce = concentration of MG at equilibrium, Qe = amount of MG absorbed / gram of acivated charcoal at equilibrium stage (mg/g). The value of K_f identifies the capacity of this process, while 1/n is a function of strength in an adsorption process. It assumes that when n=1, then the two phases partition is independent, when 1/n <1, then the process is normal, when 1/n>1, then the adsorption process is cooperative. The linear square method is widely used to describe n and K_f parameters. We used the Origin program to fit the linear data model.

Temkin Adsorption isotherm implies that the heat of adsorption of all molecules in the layer would not be decreased logarithmically but linearly by ignoring the extremely low and high concentration values.

Temkin Adsorption isotherm [23] expresses the adsorbate–adsorbate interactions in the adsorption process. In the implementation of this equation between absorbate and absorbent, adsorption is marked by homogeneous binding energies distribution, plotting Q_e against lnC_e show the capacity of maximum binding energy and the linear equation Temkin equation as follows:

$$Q_e = \frac{RT}{b} \ln{(A_T C_e)} \quad \textbf{(6)}$$

$$Q_e = \frac{RT}{b_T} lnA_T + \left(\frac{RT}{b}\right) lnC_e \quad \textbf{(7)}$$

Lets, $B = \frac{RT}{b_T}$

Therefore, the equation below shows the linear form:

$$Q_e = BlnA_T + BlnC_e \quad \textbf{(8)}$$

Here, $A_T =$ constant of Temkin isotherm binding energies, b_T = constant in Temkin isotherm, R= the molar gas constant, T= Kelvin temperature variable, B= heat sorption constant

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The Hill-De Boer isotherm model explains both mobile adsorption as well as lateral interaction among adsorbed molecules [24-25]. The linear form of Hill-De Boer isotherm can be expressed by the following equation:

$$ln\left(\frac{C_e(1-\theta)}{\theta}\right) - \frac{\theta}{1-\theta} = -lnK_1 - \frac{K_2\theta}{RT} \quad \textbf{(9)}$$

whereK_1 = constant in Hill-Deboer isotherm and K_2 = the energetic constant of the interaction between adsorbed molecules. Equilibrium data from adsorption experiments can be analyzed by plotting $\ln[Ce(1-\theta)/\theta] - \theta/(1-\theta)$ versus θ [26].

Dubinin–Radushkevich model: This adsorption model expresses the distribution of the pores in adsorbents to follow Gaussian energy distribution. Dubinin-Radushkevich adsorption model is as follows:

$$lnq_e = lnq_m - K\mathcal{E}^2 \quad \textbf{(10)}$$

where K = the Dubinin-Radushkevich isotherm constant, qm = the saturation capacity of theoretical isotherms, and $\mathcal{E}$ is the Polanyi potential (J/mol) is calculated using

$$\mathcal{E} = RTln(1 + \frac{1}{C_e}) \quad \textbf{(11)}$$

To calculate the free energy of adsorption per adsorbate molecule, it is calculated using

$$E = \frac{1}{\sqrt{2K}} \quad \textbf{(12)}$$

2.3 Kinetics Studies

Intra-Particle Diffusion Model: Webber-Morris expressed an important adsorption process in which the uptake of adsorbates varies proportionally with the square root of time ($t^{1/2}$) [27]. The linear form of the model is as follows [28]:

$$q_t = K_{IPD} t^{\frac{1}{2}} + C \quad \textbf{(13)}$$

Here, K_{IPD} is the intra-particle diffusion constant, and C is the intercept. The intra-particle diffusion alone is the rate-determining step then a plot of qt vs $t^{1/2}$ appears as a linear graph.

Pseudo-Second order reaction equation: The expression of Pseudo-first order reaction is

$$\frac{dq_t}{dt} = k_n(q_e - q_t)^n \quad \textbf{(14)}$$

When n = 2, the expression is obtained for the pseudo-second-order reaction, which follows:

$$\frac{dq_t}{dt} = k_n(q_e - q_t)^2 \quad \textbf{(15)}$$

By integrating this equation, the conditions t = 0 and t = t give the following form:

$$q_t = \frac{q_e^2 \times k_2 t}{q_e k_2 t + 1} \quad \textbf{(16)}$$

The linear mathematical model of this equation is written in the following form

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_t} t \quad \textbf{(17)}$$

Where, q_e = the amount of adsorbate in the adsorbent at equilibrium, k_2=constant rate for the second order, t = contract time between solid and liquid.

Thermodynamics: In this process, thermodynamics parameters such as free energy of adsorption, the heat of the adsorption process, and standard entropy changes can be evaluated by the following equation

$$k_d = \frac{q_e}{C_e} \quad \textbf{(18)}$$

Where k_d is adsorption distribution coefficient. The k_d values are used to determine Gibbs's free energy at different temperature ranges. Thus, the Gibbs free energy is

$$\Delta G^0 = -RTlnK_d \quad \textbf{(19)}$$

Where, ΔG^0 = is the free energy of the adsorption process(kJ/mol), T= is the Kelvin temperature, R=is the universal gas constant (8.314 J/mol K)

The distribution constant of this process is determined by the term’s standard entropy changes and temperature changes function

$$lnK_d = \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad \textbf{(20)}$$

Where, ΔH^0 = is the heat of adsorption (kJ/mol), ΔS^0 = is the standard entropy changes (kJ/mol). The values of ΔH^0 and ΔS^0 are obtained by plotting 1/t vs ln k(l) in origin lab software.

4. Result and discussion

4.1. Particle size analysis

The XRD spectrum is shown in **Fig.1**, XRD peaks are very sharp and have high intensity which means particles are solid crystalline. We calculated the particle size using the Scherrer equation and the obtained size was 20.87843208 ≈ 20.88 nm. The particle size indicates that the brick sand particles are nanoparticles in size. The Scherrer equation which was used to estimate the average particle size of brick particles as follows:

$$D = \frac{K\lambda}{\beta cos\theta} \qquad \textbf{(21)}$$

Here, D = Crystalline Size (nm), β = Line Broadening at FWHM -Radians, θ (Bragg Angle) = Peak Position (Radians), λ = X-ray Wavelength K= Scherrer Constant, 2θ= 26.68542 degrees.

The **Fig.2** represents the effect of time, shaking rate, concentration of MG, and concentration of activated charcoal during the adsorption process. From **Fig.2,** it is clear that 25 min and 200 rpm were suitable conditions for this adsorption process. On the other hand, the effect of concentration of both adsorbent and adsorbate showed that 3.7 mg/L of malachite green and 50 mg/L of activated charcoal had a better performance in this separation process as shown in **Fig.2.** The maximum removal percentage of malachite green was 98.9 and the range was 86 to 98.9 %.

The adsorption isotherm explains how the adsorbate molecules absorb in the adsorbent surface at an equilibrium state between the liquid and the solid phases in the adsorption process. The investigated data were analyzed by fitting them into Langmuir, Freundlich, Temkin, Hill De Boer, and Dubinin-Radushkevich adsorption isotherm models is an important step to find the suitable model that can be used for the design process. The adsorption isotherm models were used to describe the equilibrium adsorption, respectively.

From the **Fig.3,** the calculated value of R_l was 0.0334 which was less than 1. According to the Langmuir isotherm if, $0 < R_l < 1$, the nature of adsorption is favorable. Moreover, R^2 was 0.933 which was indicating the adsorption process was favorable in this process. The Langmuir adsorption isotherm was linearly fitted with the experimental data.

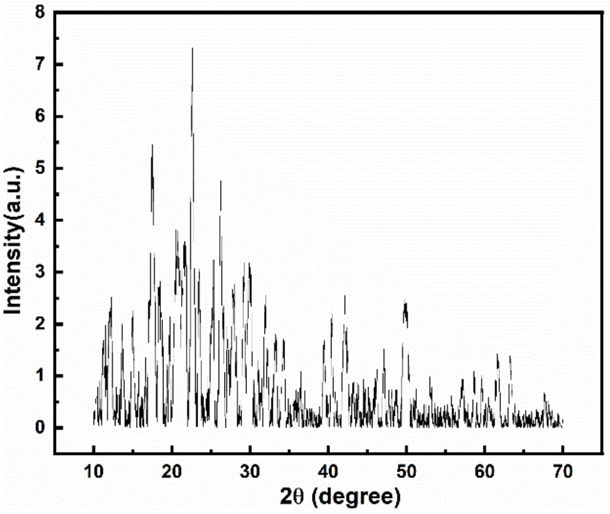

Figure 1. XRD spectrum of activated charcoal.

Freundlich adsorption isotherm is represented in **Fig.4.** According to Freundlich isotherm, the process is controlled by 1/n value. The adsorption process is either favorable (0.1 <1/n < 0.5) or unfavorable (1/n > 2). In our investigation the 1/n value was 0.16957 which was greater than 0.1. So. the adsorption was favorable. Compared to the Langmuir isotherm, the Langmuir isotherm is better fitted with experimental data. Because the value of linear regression coefficient R^2 was greater than that of Freundlich isotherm as shown in **Fig.3** & **Fig.4** and **Table 1.**

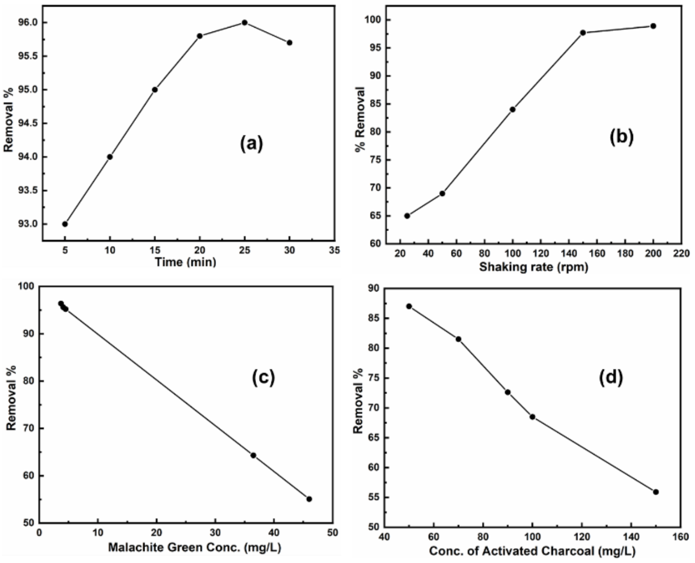

Figure 2. Effect of time, shaking rate, concentration of MG and concentration of activated charcoal.

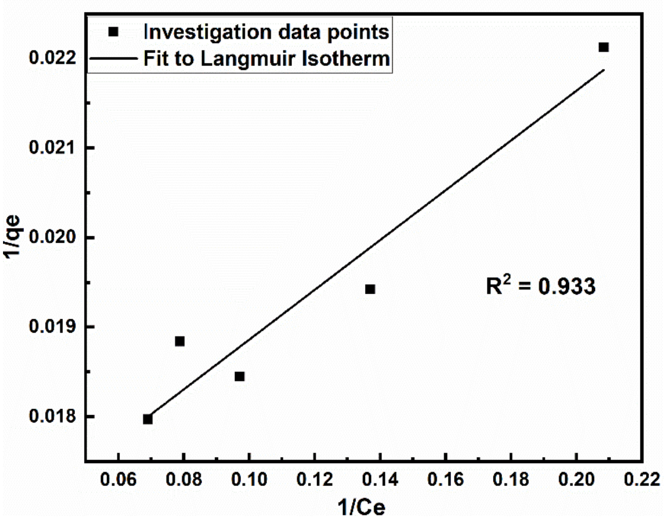

Figure 3. Fitting of investigated data with Langmuir adsorption isotherm model.

The Temkin adsorption isotherm expresses the adsorbate-adsorbate interactions in the adsorption process [29]; and also assumes that the adsorption of heat of all molecules in the layer decreases linearly as a result of increased surface coverage. After fitting the Temkin isotherm, we calculated BT and A_T values which are shown in **Table 1**. The fitting experimental data points with the Temkin adsorption model reveal that the adsorption is favorable as shown in **Fig.5**. The Langmuir isotherm is better than Temkin isotherm because the R^2 value was greater than Temkin isotherm.

Fig.6 represents the Hill De Boer isotherm model. The Hill De Boer isotherm assumes the binding of different species onto homogeneous substrates. This model assumes that adsorption is a cooperative phenomenon with adsorbates at one site of the adsorbent influencing different binding sites on the same adsorbent. According to Hill De Boer isotherm, the K_2 is the energetic constant of the interactions between adsorbed molecules (kJ/mol), and in this investigation, K_2 is 0.0433 KJ/mol (which was greater than 0), which means attraction between absorbed molecules occurred.

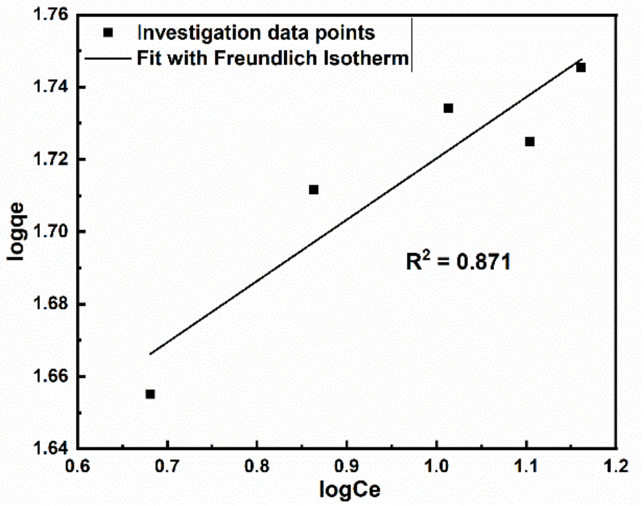

Figure 4. Fitting of investigated data with Freundlich adsorption isotherm model

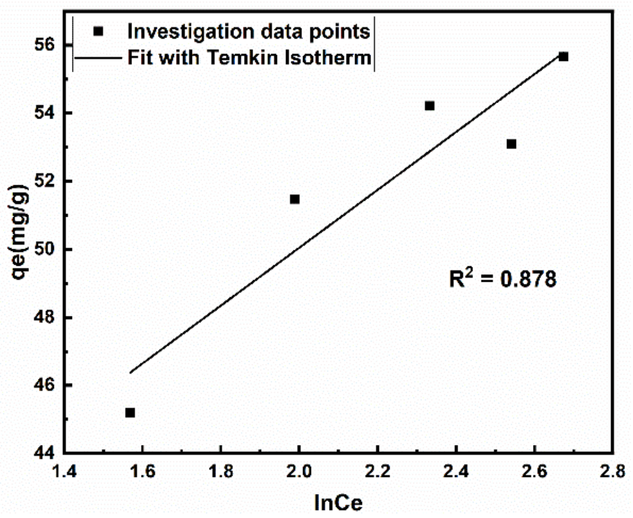

Figure 5. Fitting of investigated data with Temkin adsorption isotherm model

The Dubinin-Radushkevich [30] isotherm is derived from the pore structure or adsorbent which has a heterogeneous surface and also expresses adsorption-free energy. D-R model, we need to convert qe into the form of lnqe value and examine for the ε^2 value which is used for data fitting the model as shown in **Table 1**.

The fitting of the model with the experimental data is presented in Fig.7. From the fitting data, the K value is obtained to calculate *E* value. After fitting the D-R isotherm, calculate the free energy at 298K was 706.65 KJ/mol. According to Dubinin-Radushkevich isotherm model $8 < E < 706.65$ kJ/mol, the adsorption model is chemical adsorption process [31]. The larger pore volume impact on highest maximum binding energy value. The fitting data of D-R model shown high correlation coefficient value which was is ($R^2 > 0.9587$).

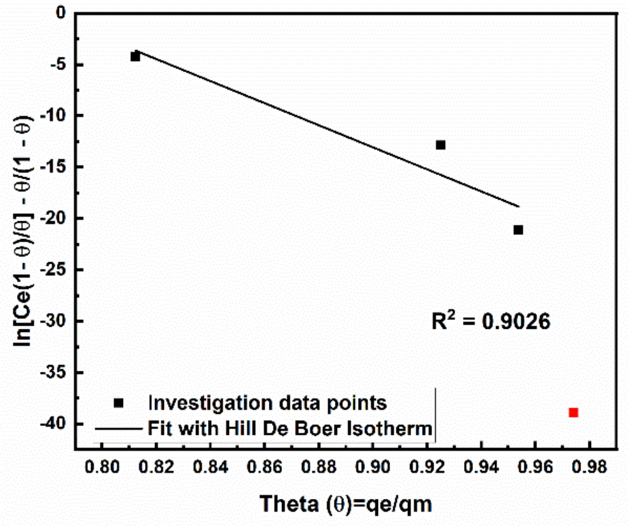

Figure 6. Fitting of investigated data with Hill De Boer adsorption isotherm model

Table 1 Parameters of Langmuir, Freundlich, Temkin, Hill De Boer and D-R isotherm model equations.

Isotherms	Parameters	Value
Langmuir	qmax(mg/g)	62.19
	K_L	0.0334
	R^2	0.933
Freundlich	1/n	0.16957
	K_f	35.54
	R^2	0.871
Temkin	BT	8.499
	A_T	48.824
	R^2	0.878
Hill De Boer	K_1	2.00E+36
	K_2	0.0433
	R^2	0.9026
Dubinin-Radushkevich	K(mol^2/K^2J^2)	1.00E-06
	E (KJ/mol)	706.65
	R^2	0.9587

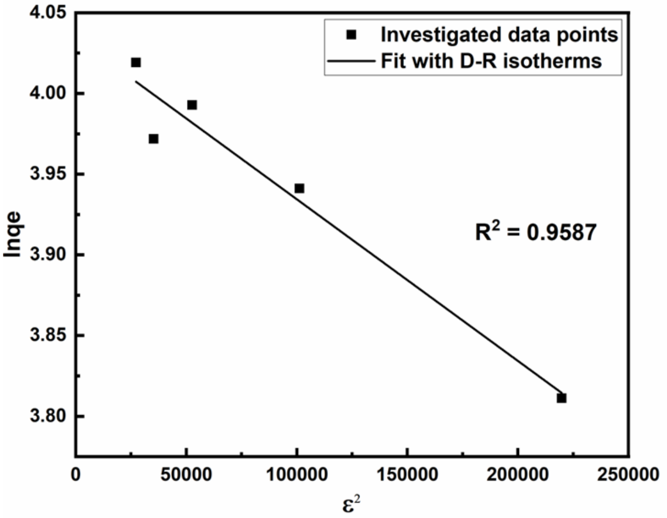

Figure 7. Fitting of investigated data with D-R isotherm model.

Therefore, D-R adsorption isotherm model is well fit Langmuir, Freundlich, Temkin and Hill De Boer model have same assumption that adsorption process occurs by forming a monolayer without the presence of adsorbate-adsorbent lateral interactions [31].with the investigation result.

Besides assuming the adsorption is monolayer, the adsorption system with the CPS adsorbent is also assumed to have adsorption by forming a multilayer. This is confirmed because it fits the D-R model. The adsorption process with the activated charcoal adsorbent followed suitable with the order of the Dubinin-Radushkevich > Langmuir > Hill De Boer> Temkin > Freundlich models.

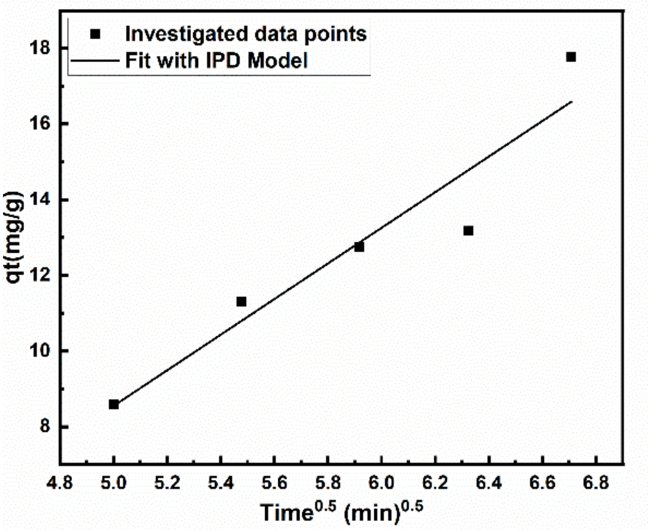

Figure 8. Fitting of investigated data with Intra-particle Diffusion model

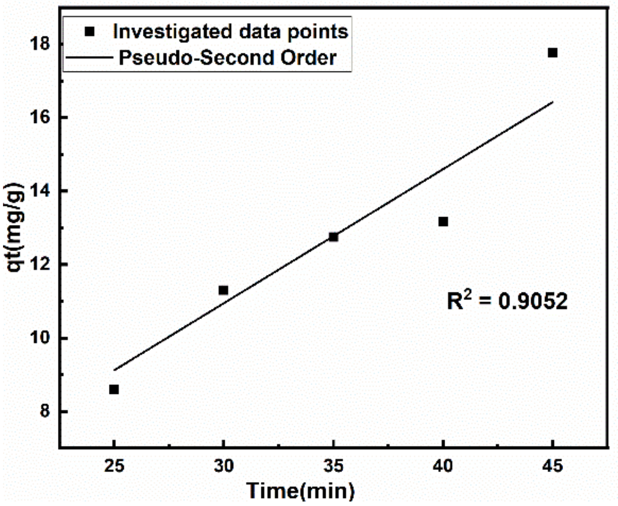

Figure 9. Fitting of investigated data with Pseudo-Second Order model

The intra-particle diffusion is the rate-determining step and plotted qt vs t 1/2 by using equation (13) which was appear as a linear graph as shown in Fig.8. The plotted line did not pass through the origin which expressing the intraparticle diffusion was not only the rate-limiting step, but also a multiple steps diffusion or other processes take place [32].

The kinetics parameter for removal of MG using activated charcoal as an adsorbent is shown in Table 2 and Fig.9. In the charcoal particles K_2 value is 2.58E-10, which is positive. The value of R^2 is 0.9052. The R^2 values indicate that activated charcoal are better performed.

The **Fig. 10** is representing the Van’t Hoff plot fitting with experimental data, from which ΔG, ΔH and ΔS values were calculated as shown in **Table 2.**

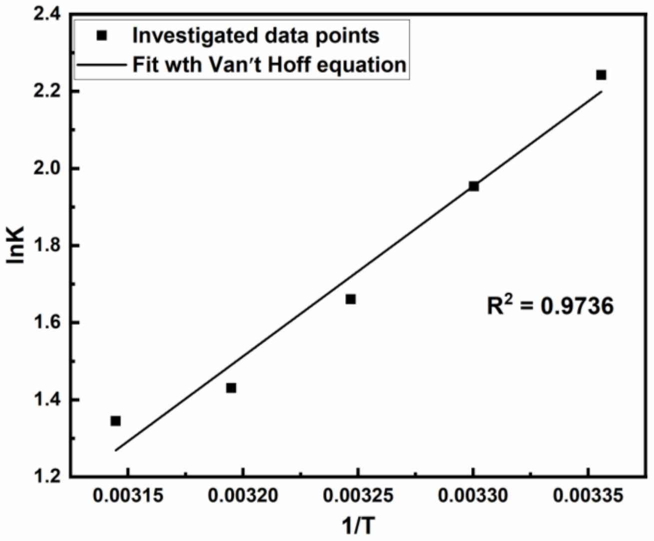

Figure 10. Fitting of investigated data with Van’t Hoff equation.

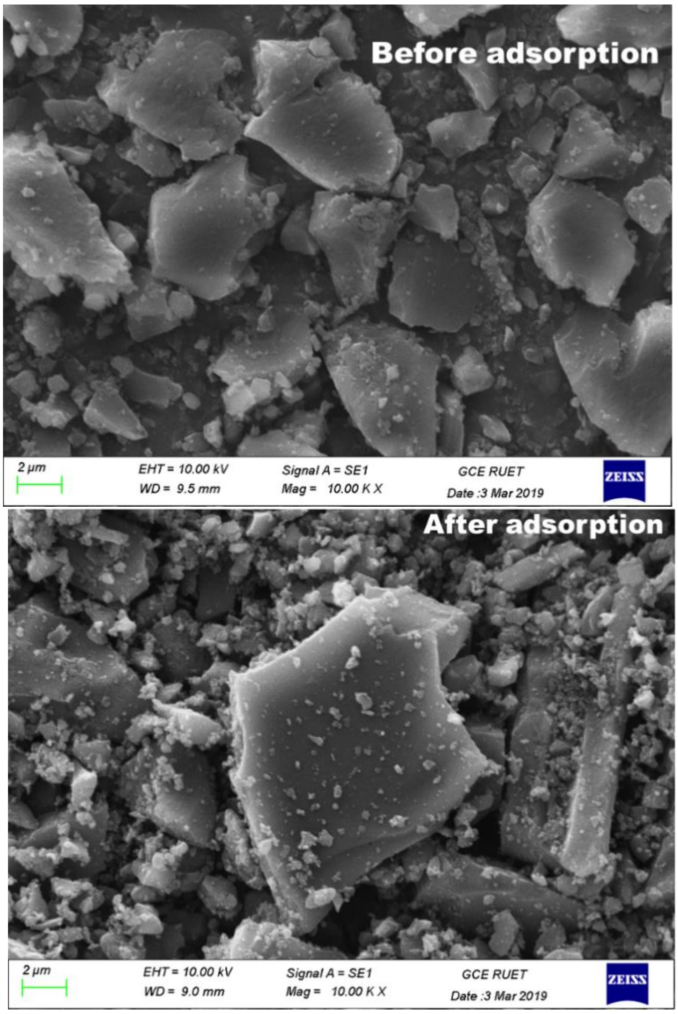

Figure 11. The surface morphology of activated charcoal (before and after the adsorption process).

The van't Hoff equation was satisfied with the coefficient of correlation value 0.9736. The ΔG value is assume as the fundamental thermodynamic criterion to characteristic adsorption process. The negative ΔG values of MG adsorptions indicate that is a favorable process and spontaneous [33].

The negative value of ΔH ensure the adsorption process characterize as chemical adsorption and exothermic in nature [33]. The negative ΔS value indicates that randomness decreases at the solid–solution interface during the adsorption of MG by activated charcoal. The negative ΔH and ΔS values suggest that enthalpy contributes more than entropy in producing negative ΔG values.

The **Fig. 11** represents the surface morphology of activated carbon before and after the adsorption process. After adsorption, the surface of the activated charcoal showed deposited some particles of MG. The surface morphology confirmed the adsorption was done.

Table 2 Thermodynamics parameter in the treatment of malachite green dye. [using $R = 8.316\ Jmol^{-1}K^{-1}$].

Temp. (K)	**K_L**	**ΔG^0 ($KJmol^{-1}$)**	**ΔH^0 ($KJmol^{-1}$)**	**ΔS^0 ($JK^{-1}\ mol^{-1}$)**	**R^2**
298	9.417	-5.5559	-36.64	-104.673	0.9736
303	7.052	-4.9207			
308	5.263	-4.2526			
313	4.179	-3.7218			
318	3.838	-3.5558			

5. Conclusions

To remove malachite green dye from an aqueous solution, we studied low-cost activated charcoal as an adsorbent. To check the performance of adsorbent, different parameters were studied. The adsorption process with the activated charcoal adsorbent followed suitable with the order of the Dubinin-Radushkevich > Langmuir > Hill De Boer> Temkin > Freundlich models. The kinetics and thermodynamics studies revealed that it was second order, chemical adsorption, exothermic, favorable, and spontaneous process. By optimizing the condition, it can remove 96% of malachite green from aqueous solution. Therefore, activated charcoal might be a better adsorbent for the removal of malachite green.

Acknowledgment: Department of Applied Chemistry and Chemical Engineering, University of Rajshahi, Rajshahi 6205, Bangladesh.

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