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## Adsorption of Malachite Green Dye on to Rectorite: Equilibrium and Thermodynamic Studies

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**Abstract** The effect of temperature on the equilibrium adsorption of Malachite green dye from aqueous solution using rectorite was studied. The equilibrium adsorption data were analyzed using three widely applied isotherms; Langmuir, Freundlich, and Redlich-Peterson isotherm. A nonlinear method was used for comparing the best fitting of the isotherms. Best fits were found to be Redlich-Peterson isotherm. Thermodynamic parameters, such as  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ , were calculated using adsorption equilibrium constant obtained from the Langmuir isotherm. Results suggested that the Malachite green adsorption on rectorite was an endothermic and spontaneous process.

**Keywords** Malachite green, isotherm, thermodynamics, rectorite, equilibrium

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### Introduction

Water is a vital commodity, one of the most important of all chemical substances with many remarkable and unique properties. Natural water includes rain water, spring water, river water, well water, lake water and sea water and these take over seventy per cent (70%) of the earth [1]. Water pollution is one of the most undesirable environmental problems in the world that requires urgent solution. Textile industries produce a lot of wastewater, which contains different contaminants, including acidic or caustic dissolved solids, toxic compounds and different type of dyes. These dyes are stable and fast, difficult to degrade, toxic, rendering the water unfit for its intended use. The greatest environmental concern with dyes is absorption and reflection of sunlight entering the water. Light absorption diminishes photosynthetic activity of algae and seriously affects the food chain. Many dyes and their breakdown products are carcinogenic [2]. Due to the damage effluents from factories and industries have caused to the sewer system. There is a need for the removal of these dyes because water must meet some certain basic requirements to make it fit for domestic uses through colour removal to make the effluent/waste water from industries safe for discharge into sewer systems [2].

An efficient removal of coloured substance is activated carbon through adsorption process but it is very expensive in its use commercially. For cost effectiveness and improved efficiency, environmental chemists have devised several methods for the removal of coloured substances (dyes) from wastewater using readily available and cost-effective agricultural wastes as an alternative to activated carbon for efficient removal of dyes using adsorption method. Furthermore, adsorption processes remove/minimize different pollutants; thus, it has a wide applicability in water pollution control. Lot of materials have been extensively investigated as adsorbents in water pollution control. Some of the important ones include silica gel [3], activated alumina [4], zeolite [5], rectorite etc. Agricultural materials particularly those containing cellulose, for example, cereals such as rice [7], maize [7] and corn [8] as well as sugarcane-bagasse [9] shows potential sorption capacity making them economical and eco-friendly due to their



unique chemical composition, availability in abundance, renewable nature, low ash content, reasonable hardness and low cost proffering a viable option for water and wastewater remediation. Several studies on the removal of toxic substances from aqueous solution by adsorption using low cost agro-wastes as alternatives to activated carbon abound in literature. A few of recent and relevant studies are on rubber seed coat [2], Cocoa shell [10], groundnut hull [7], unwanted barley and wheat straws [11], Cocoa pod husks [2], coconut husk [12] e.t.c.

Malachite green is traditionally used as a dye. Millions of kilograms of MG and related triarylmethane dyes are produced annually for this purpose [13]. It is used to combat the *Oomycete saprolegnia*, which infects fish eggs in commercial aquaculture, and other fungi, and its usage as a parasiticide and antibacterial [6]. MG has frequently been used to catch thieves and pilferers applied on money as bait, sprinkled with the anhydrous powder. The LD50 (oral, mouse) is 80 mg/kg. As a leuco-base dye, malachite green is retained in fish muscle much longer, most intake of malachite green would be in the leuco form, it has carcinogenic symptoms, but a direct link between malachite green and liver tumor has not been established [14]. In this study, rectorite, one kind of natural mineral material, was used as the adsorbent for its low-cost and convenient acquisition in local markets. A non-linear method of three widely used isotherms, the Langmuir, Freundlich and Redlich-Peterson, were compared in an experiment examining Malachite green adsorption onto rectorite. The thermodynamic parameters were also calculated.

## Materials and Methods

### Materials

The dye used in this study was Malachite Green, it was cationic in nature (purity: 98.7%; colour: green; maximum wavelength of absorption: 618 nm. The cationic dye, Malachite green, was used without further purification. A stock solution of 2000 mg L<sup>-1</sup> was prepared by dissolving a weighed amount of Malachite green in 1000 ml distilled water. The experimental solution was prepared by diluting the stock solution with distilled water to different concentrations from 80-200 mg L, and each of them was stored in 500-ml reagent bottles, respectively. Rectorite used is a commercial product from the Yangzhaore deposit in Zhongxiang, Hubei Province, China. It was stored in the desiccator with silica gel and oven-dried at 150 °C for 2 h before experiments.

### Methods

The rectorite was determined by X-Ray Fluorescence Spectrometry (Bruker AXS S4 Pioneer), Laser Diffraction Particle Size Analysis (ZetaSizer 3000, Malvern), and Surface Area and Pore Size Analysis (Gemini V, Micromeritics). A 50-ml volume of Malachite green solution with a concentration ranging from 90 to 200 mg L<sup>-1</sup> was placed into 150-ml conical flasks. A weighed amount (0.1 g) of the rectorite was added to the solution. The conical flasks were then shaken at a constant speed of 150 rpm in a shaking water-bath with temperatures 288, 293, 298, 303, and 308 K, respectively. After shaking the flasks for 6 h, the rectorite was separated by centrifugation. The solution was analyzed for the remaining Malachite green concentration by a spectrophotometer ( $\lambda_{\max} = 618$  nm). The amount of Malachite green adsorbed onto rectorite was calculated by using the following expression:

$$q_e = (C_0 - C_e)V/m \quad (1)$$

where  $q_e$  is the equilibrium adsorption capacity of Malachite green adsorbed on unit mass of the rectorite (mgg<sup>-1</sup>);  $C_0$  and  $C_e$  are the initial Malachite green concentration (mg L<sup>-1</sup>) and Malachite green concentration (mg L<sup>-1</sup>) at equilibrium, respectively;  $V$  is the volume of the Malachite green solution (L); and  $m$  is the weight of the rectorite (g). A non-linear method of three widely used isotherms, the Langmuir, Freundlich, and Redlich-Peterson, were compared in an experiment examining Malachite green adsorption on to rectorite with a trial-and-error procedure, using the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel [15-16].

## Results and Discussion

### Properties of Rectorite

The result of XRF analysis is shown in Table 1. The particle size distribution is 720 – 883 nm (76.5%), 883 – 1058 nm (23.5%), and the average size is 827.2 nm. The BET surface area of rectorite is 28.69 m<sup>2</sup> g<sup>-1</sup>.



**Table 1:** Chemical compositions of rectorites

Composition	Percent (%)	Composition	Percent (%)
SiO <sub>2</sub>	44.89	SrO	0.143
Al <sub>2</sub> O <sub>3</sub>	37.09	V <sub>2</sub> O <sub>5</sub>	0.116
Fe <sub>2</sub> O <sub>3</sub>	2.89	ZrO <sub>2</sub>	0.084
TiO <sub>2</sub>	2.81	Cr <sub>2</sub> O <sub>3</sub>	0.07
SO <sub>3</sub>	2.79	Cl	0.0309
K <sub>2</sub> O	1.41	MnO	0.0219
Na <sub>2</sub> O	1.23	ZnO	0.0166
P <sub>2</sub> O <sub>5</sub>	0.478	CuO	0.0137
MgO	0.35	Y <sub>2</sub> O <sub>3</sub>	0.013
CaO	5.55	Nb <sub>2</sub> O <sub>5</sub>	0.011

### Equilibrium Isotherm

The isotherm usually describes the adsorption system with some important information from which we can develop an equation representing the results and we can use the equation for certain purposes. In order to investigate the adsorption isotherm, three equilibrium isotherms were analyzed: the Langmuir, the Freundlich, and the Redlich-Peterson isotherms. The Langmuir adsorption isotherm is perhaps the best known of all isotherms describing adsorption [17]. The theoretical Langmuir isotherm is often used to describe adsorption of a solute from a liquid solution as follows [17-18]:

$$q_e = q_m K_a C_e / (1 + K_a C_e) \quad (2)$$

where  $q_e$  is the equilibrium adsorption capacity ( $\text{mg g}^{-1}$ ),  $C_e$  is the equilibrium liquid phase concentration ( $\text{mg L}^{-1}$ ),  $q_m$  is the maximum adsorption capacity, ( $\text{mg g}^{-1}$ ),  $K_a$  is adsorption equilibrium constant, ( $\text{L mg}^{-1}$ ).

The Freundlich isotherm is the earliest known relationship describing the adsorption isotherm [19]. This fairly satisfactory empirical isotherm can be used in adsorption from diluted solutions. The ordinary adsorption isotherm is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \quad (3)$$

where  $C_e$  is the equilibrium concentration in the solution ( $\text{mg L}^{-1}$ ),  $q_e$  is the equilibrium adsorption capacity ( $\text{mg g}^{-1}$ ),  $K_F$  and  $1/n$  are empirical constants.  $K_F$  is the adsorption value, the amount adsorbed at unit concentration, that is, at  $1 \text{ mg L}^{-1}$ . It is characteristic for the adsorbent and the adsorbate adsorbed. The Redlich-Peterson isotherm contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms [20]. It can be described as follows:

$$q_e = AC_e / (1 + BC_e^g) \quad (4)$$

It has three isotherm constants, namely,  $A$ ,  $B$ , and  $g$  ( $0 < g < 1$ ).

### Error Analysis

Due to the inherent bias resulting from linearization, alternative isotherm parameter sets were determined by nonlinear regression. This provides a mathematically rigorous method for determining isotherm parameters using the original form of the isotherm equation [21-22]. To compare the three isotherms, a trial-and-error procedure was applied to obtain the isotherm parameters. The method is using an optimization routine to maximize the coefficient of determination  $r^2$ , between the experimental data and isotherms in the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel [14, 23]. The coefficient of determination  $r^2$  was as follows:

$$r^2 = \frac{\sum (q_m - q_e^-)^2}{[\sum (q_m - q_e^-)^2 + \sum (q_m - q_e)^2]} \quad (5)$$

where  $q_m$  is the equilibrium capacity obtained from the isotherm model,  $q_e$  is the equilibrium capacity obtained from experiment, and  $q_e^-$  is the average of  $q_e$ .

### Effect of Temperature on Equilibrium Isotherm

In order to assess different isotherms and their ability to correlate with experimental results, the theoretical plots from each isotherm have been shown with the experimental data for adsorption of Malachite green on rectorite at



five various temperatures from 288 to 308 K in Fig. 1. The graph is plotted in the form of Malachite green adsorbed per unit mass of rectorite,  $q_e$ , against the concentration of Malachite green remaining in solution,  $C_e$ . A comparison of coefficient of determination for three isotherms has been made and listed in Table 2. Redlich-Peterson isotherm was most suitable for the data, followed by Langmuir and then Freundlich isotherm. The Langmuir and the Redlich-Peterson isotherms have best fitted for the adsorption of Malachite green on rectorite at various temperatures, but Redlich-Peterson might be the better fitting isotherm because of its higher  $r^2$  value. However, at 293 K, the coefficients of determination of Redlich-Peterson and Langmuir isotherm is the same ( $r^2 = 0.97$ ).

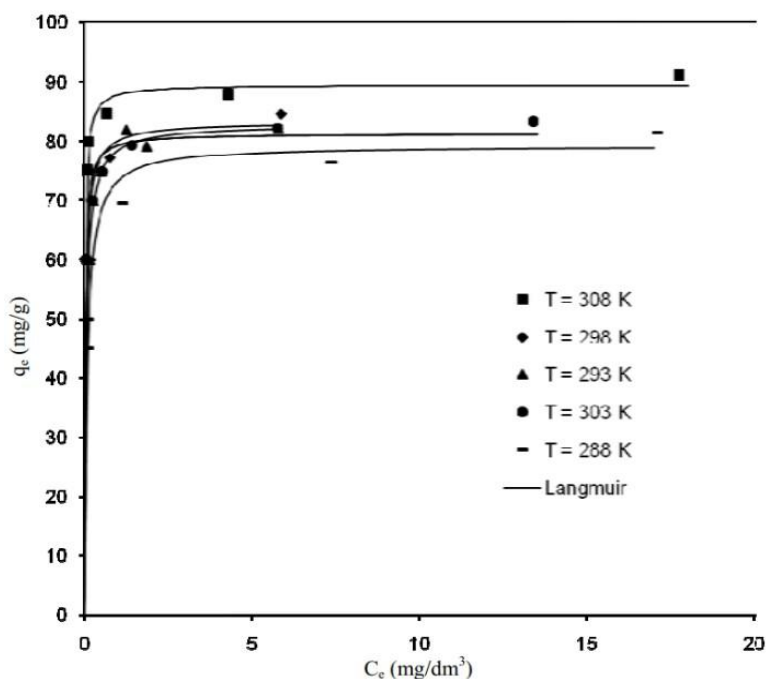


Figure 1: Langmuir isotherms obtained using the non-linear method for the adsorption of Malachite green onto rectorite at different temperatures

**Table 2:** Isotherm parameters obtained using the non-linear method for the adsorption of Malachite green onto rectorites at different temperatures

Isotherm	T(K)	288	293	298	303	308
Langmuir	$q_m$ , mg/g	79.29	82.77	83.26	81.22	89.44
	$K_a$ , $\text{dm}^3/\text{mg}$	11.89	17.89	25.51	40.12	51.2
	$AG^0$ , KJ/mol	-20	-21.3	-22.8	-24.09	-25.39
	$r^2$	0.95	0.97	0.953	0.918	0.934
Freundlich	$1/n$	0.11	0.086	0.085	0.061	0.036
	$K_F$ , $(\text{mg/g})(\text{dm}^3/\text{mg})^{1/n}$	63.3	74.6	77.32	74.59	83.7
	$r^2$	0.897	0.841	0.89	0.904	0.92
Redlich-Peterson	G	0.97	1	0.96	0.97	0.98
	$B(\text{dm}^3/\text{mg})^g$	17.9	18	51.8	80.11	93.49
	$A, \text{dm}^3/\text{g}$	1326	1484	4157	6244	8119
	$r^2$	0.96	0.97	0.98	0.99	0.97

Figure 2 shows the plots comparing the theoretical Langmuir, empirical Freundlich, and the Redlich-Peterson isotherm with the experimental data for the adsorption of Malachite green onto rectorite at a temperature of 293 K. The Redlich-Peterson and Langmuir isotherms overlapped and seemed to be the best fitting isotherms for the



experimental results. By using non-linear method, there was no problem with transformation of non-linear isotherm equation to linear forms, and also they had the same error structures [21]. The adsorption capacity of Malachite green increases with temperature which is typical for the adsorption of most dyes from their solution. When the system is in a state of equilibrium, the distribution of Malachite green between the rectorite and the Malachite green solution is of fundamental importance in determining the maximum adsorption capacity of rectorite for the Malachite green from the isotherm. The Langmuir, Redlich-Peterson, and Freundlich isotherm constants are shown in Table 2. The maximum adsorption capacity,  $q_m$ , and the adsorption equilibrium constant,  $K_a$ , were found to increase from 79.29 to 89.44  $\text{mg g}^{-1}$  and 11.89 to 51.2  $\text{L mg}^{-1}$  for an increase in the solution temperatures from 288 to 308 K, respectively. The increase in  $K_a$  values with temperature indicates a higher heat of adsorption with increasing temperature. It is clear that the adsorption of Malachite green on rectorite is an endothermic process. In addition, the values of  $g$  were close to unity ( $>0.960$ ), which means that the isotherms are approaching the Langmuir form and not the Freundlich isotherm.

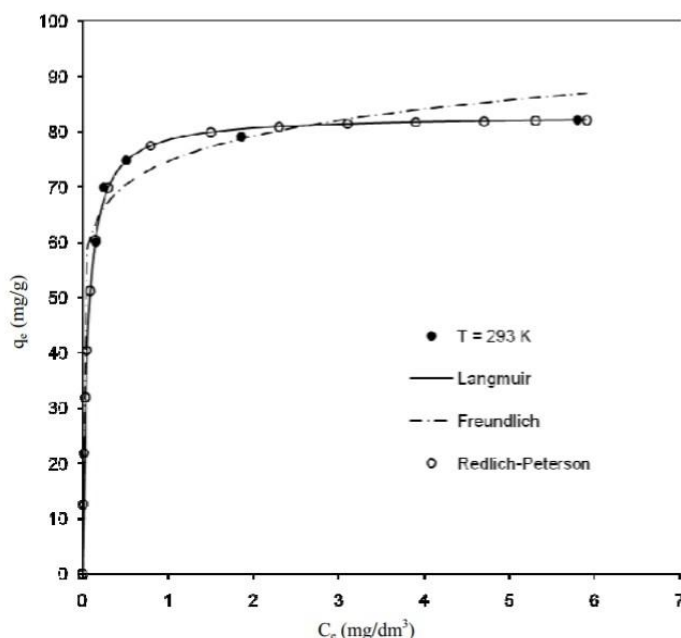


Figure 2: Isotherms obtained using the non-linear method for the adsorption of Malachite green onto rectorite at a temperature 293 K.

The effect of isotherm shape can be used to predict whether an adsorption system is “favourable” or “unfavourable” both in fixed-bed systems [24] as well as in batch processes [25]. According to Hall *et al* [26], the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter  $K_R$ , which is defined by the following relationship:

$$K_R = 1/1 + K_a C_0 \quad (6)$$

where  $K_R$  is a dimensionless separation factor,  $C_0$  is initial concentration ( $\text{mg L}^{-1}$ ) and  $K_a$  is Langmuir constant ( $\text{L mg}^{-1}$ ). The parameter  $K_R$  indicates the shape of the isotherm accordingly:

Value of $K_R$	Type of Isotherm
$K_R > 1$	Unfavourable
$K_R = 1$	Linear
$0 < K_R < 1$	Favourable
$K_R = 0$	Irriverssible

A figure with a relationship between  $K_R$  and  $C_0$  was presented to show the essential features of the Langmuir isotherm [18]. Figure 3 shows the values of  $K_R$  for Malachite green at different temperatures. The  $K_R$  values indicate



that adsorption is more favourable for the higher initial dye concentration and higher temperature than the lower ones.

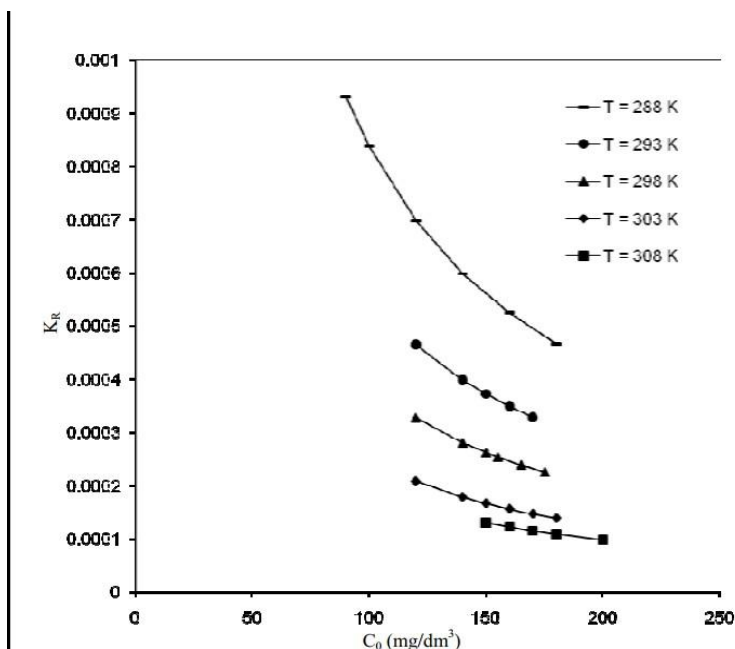


Figure 3: Plot of  $K_R$  against initial Malachite green concentration at various temperatures

### Thermodynamic Studies

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. Gibb's free energy change,  $\Delta G^\circ$ , is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if  $\Delta G^\circ$  is a negative value. The thermodynamic parameters of Gibb's free energy change,  $\Delta G^\circ$ , enthalpy change,  $\Delta H^\circ$ , and entropy change,  $\Delta S^\circ$ , for the adsorption processes are calculated using the following equations:

$$\Delta G^\circ = RT \ln K_a \quad (7)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (8)$$

where  $R$  is universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the absolute temperature in K. The thermodynamic parameter, Gibb's free energy change,  $\Delta G^\circ$ , is calculated using  $K_a$  obtained from Langmuir Eq. (2) and shown in Table 2. A plot of Gibb's free energy change,  $\Delta G^\circ$ , versus temperature,  $T$ , was found to be linear (Fig. 4). The enthalpy change,  $\Delta H^\circ$ , and the entropy change,  $\Delta S^\circ$ , for the adsorption processes were obtained from the intercept and slope of Eq. (8) and found to be  $54.8 \text{ kJ mol}^{-1}$  and  $0.260 \text{ kJ mol}^{-1} \text{ K}^{-1}$ , respectively. The negative values of  $\Delta G^\circ$  confirm the feasibility of the process and the spontaneous nature of adsorption with a high preference of Malachite green by rectorite. The decrease in the negative value of  $\Delta G^\circ$  with an increase in temperature indicates that the adsorption process of Malachite green on rectorite becomes more favorable at higher temperatures [27]. There are consistencies with the adsorption of Malachite green by other adsorbents, for example, guava leaf powder [28], dehydrated wheat bran carbon [29], diatomaceous silica [30], wheat shell [31], and NaOH-treated pure kaolin [32]. However, a negative value for  $\Delta S^\circ$  was also reported for the adsorption of Methylene Blue by cereal chaff [33] and fallen phoenix tree's leaves [34]. In most cases, adsorption of Malachite green is found to have negative values of  $\Delta G^\circ$  (Table 3). The positive value of  $\Delta H^\circ$  indicates that the adsorption reaction is endothermic. Entropy has been defined as the degree of chaos of a system. The positive value of  $\Delta S^\circ$  suggests that some structural changes occur on the adsorbent, and the randomness at the solid/liquid interface in the adsorption system increases during the adsorption process [35].



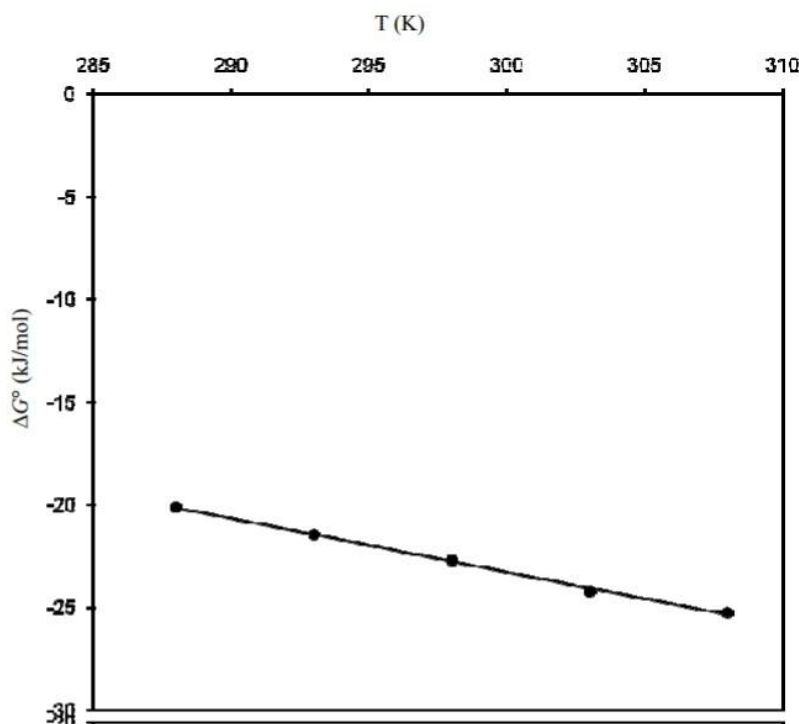


Figure 4: Plot of Gibbs free energy change,  $\Delta G^\circ$ , versus temperature,  $T$

**Table 3:** A comparison of thermodynamic parameters for the adsorption of Malachite green by different adsorbents

Adsorbent	$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/molK)	References
Guava leaf powder <sup>a</sup>	Negative	33.2	0.193	[28]
Dehydrated wheat bran carbon <sup>a</sup>	Negative	53.24	0.272	[29]
Dehydrated peanut hull <sup>a</sup>	Negative	20.05	0.155	[36]
Fallen phoenix tree's leaves <sup>b</sup>	Negative	7.77	-0.04	[34]
Cereal chaff <sup>b</sup>	Negative	2.41	-0.034	[33]
Diatomaceous silica <sup>b</sup>	Negative	9.61	0.0376	[30]
Wheat shell <sup>a</sup>	Negative	33.41	0.185	[31]
NaOH-treated pure kaolin <sup>b</sup>	Negative	6.03	0.0697	[32]

Thermodynamic parameter  $\Delta G^\circ$  calculated from <sup>a</sup>:  $K_d$ , adsorption equilibrium constant of Langmuir isotherms (Eq. 2) <sup>b</sup>:  $K_d$ , the distribution coefficient.  $K_d = C_{Ae}/C_e$ , where  $C_{Ae}$  is the amount adsorbed on solids at equilibrium and  $C_e$  is the equilibrium concentration [26].

### Conclusion

Malachite green in aqueous solutions can be adsorbed by rectorite. The removal of Malachite green using rectorite is affected by the temperature: The adsorption capacity increases with rising temperature. By comparing coefficient of determination, using the non-linear method, the Redlich-Peterson and the Langmuir isotherms have higher coefficients of determination than that of Freundlich isotherm. The Redlich-Peterson coefficient of determination might be the best fitting isotherm. By utilizing the adsorption equilibrium constant obtained from Langmuir isotherm, thermodynamic parameter  $\Delta G^\circ$ , was calculated to tell the spontaneity of the adsorption reaction. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were also obtained from a slope and intercept of the relationship between  $\Delta G^\circ$  and reaction temperature. The negative values of  $\Delta G^\circ$  and the positive value of  $\Delta H^\circ$  indicate the spontaneous nature of adsorption with a high preference of Malachite green on rectorite, and that the adsorption reaction is endothermic,



respectively. During the adsorption of Malachite green on rectorite in the aqueous solution, the positive value of  $\Delta S^\circ$  explains the increasing randomness at the solid/liquid interface

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