

# EQUILIBRIUM AND THERMODYNAMIC PARAMETERS OF ADSORPTION OF METHYLENE BLUE ONTO RECTORITE

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## ABSTRACT

The effect of temperature on the equilibrium adsorption of Methylene Blue dye from aqueous solution using rectorite was investigated. The equilibrium adsorption data were analyzed using three widely applied isotherms; Langmuir, Freundlich, and Redlich-Peterson isotherm. A non-linear 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 Methylene Blue adsorption on rectorite was a spontaneous and endothermic process.

**KEYWORDS:** sorption; Methylene Blue; trial-and-error method; rectorite; thermodynamic parameters

## NOMENCLATURE

$q_e$  is the equilibrium adsorption capacity;

$\bar{q}_e$  is the average of  $q_e$ ;

$q_m$  is the maximum adsorption capacity;

$C_0$  is the initial concentration of Methylene Blue solution;

$C_e$  is the concentration of Methylene Blue at equilibrium;

$C_{Ac}$  is the amount adsorbed on solids at equilibrium;

$K_d$  is the distribution coefficient;

$K_a$  is adsorption equilibrium constant of Langmuir isotherm;

$K_F$  is adsorption value, one of empirical constant of Freundlich isotherm;

$n$  is empirical constant of Freundlich isotherm;

$A$ ,  $B$  and  $g$  are isotherm constants of Redlich-Peterson isotherm;

$K_R$  is a dimensionless separation factor;

$\Delta G^\circ$  is the Gibb's free energy change;

$\Delta H^\circ$  is the enthalpy change;

$\Delta S^\circ$  is the entropy change;

$R$  is the universal gas constant, 8.314 J/mol K;

$T$  is the absolute temperature, K;

$r^2$  is the coefficient of determination.

## INTRODUCTION

There are several methods which can be used to treat dye wastewater. The technologies can be divided into three categories: biological, chemical and physical [1]. Among those methods, adsorption is widely used for its maturity and simplicity. In different adsorbent materials, activated carbon is the most popular for the removal of pollutants from wastewater. However, its widespread use is restricted due to high cost [2]. As such, numerous alternative materials have been investigated to adsorb dyes from aqueous solution, using Methylene Blue as the model basic dye, such as guava leaf powder [3], dehydrated wheat bran carbon [4], diatomaceous silica [5], wheat shell [6], NaOH-treated pure kaolin [7], bamboo charcoal [8], silver fir (*Abies amabilis*) sawdust [9], and activated carbon from sugar beet molasses [10].

In the study of adsorption isotherm, linear regression is frequently used to determine the best-fitting isotherm. The linear least-squares method with linearly transformed isotherms has also been widely applied to confirm experimental data, and isotherms using coefficients of determination. However, such transformations of non-linear isotherms to linear forms implicitly alter their error structure, and may also violate the error variance and normality assumptions of standard least squares [11, 12]. It has been reported that bias results from deriving isotherm parameters from linear forms of isotherms, for example, Freundlich parameters producing isotherms which tend to fit experimental data better at low concentrations and Langmuir isotherms tending to fit the data better at higher concentrations [13]. Moreover, it has been also presented that using the linear regression method for comparing the best-fitting isotherms is not appropriate [12]. The advantage of using the non-linear method is that there is no

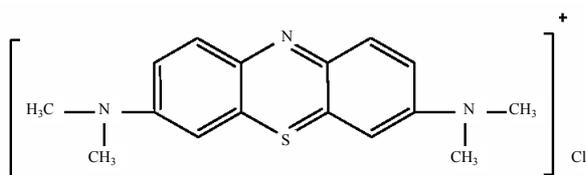
problem with transformations of non-linear isotherms to linear forms, and also they had the same error structures when the best-fitting isotherms are compared [14].

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 Methylene Blue adsorption onto rectorite. The thermodynamic parameters were also calculated.

## MATERIALS AND METHODS

### Materials

The dye used in this study, Methylene Blue, has many uses in different fields, such as biology, chemistry, and textile industry [3]. The relative molecular mass of Methylene Blue is 373.9, with three groups of water. The molecular formula is  $C_{16}H_{18}ClN_3S \cdot 3H_2O$ . The structure of Methylene Blue is shown as below:



The basic dye, Methylene Blue, was used without further purification. A stock solution of  $2000 \text{ mg L}^{-1}$  was prepared by dissolving a weighed amount of Methylene Blue 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 Yangzha ore deposit in Zhongxiang, Hubei Province, China. It was stored in the desiccator with silica gel and oven-dried at  $150^\circ\text{C}$  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 Methylene Blue solution with a concentration ranging from 90 to  $200 \text{ mg L}^{-1}$  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 Methylene Blue concentration by a spectrophotometer ( $\lambda_{\text{max}} = 664 \text{ nm}$ ).

The amount of Methylene Blue adsorbed onto rectorite was calculated by using the following expression:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where  $q_e$  is the equilibrium adsorption capacity of Methylene Blue adsorbed on unit mass of the rectorite ( $\text{mg g}^{-1}$ );  $C_0$  and  $C_e$  are the initial Methylene Blue concentration ( $\text{mg L}^{-1}$ ) and Methylene Blue concentration ( $\text{mg L}^{-1}$ ) at equilibrium, respectively;  $V$  is the volume of the Methylene Blue 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 Methylene Blue adsorption onto rectorite with a trial-and-error procedure, using the solver add-in with Microsoft's spreadsheet, Microsoft Excel [14, 15].

## 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  $28.69 \text{ m}^2 \text{ g}^{-1}$ .

TABLE 1 - Chemical compositions of rectorites.

Composition	Percent (%)	Composition	Percent (%)
SiO <sub>2</sub>	44.9	SrO	0.143
Al <sub>2</sub> O <sub>3</sub>	37.1	V <sub>2</sub> O <sub>5</sub>	0.116
CaO	5.56	ZrO <sub>2</sub>	0.0839
Fe <sub>2</sub> O <sub>3</sub>	2.89	Cr <sub>2</sub> O <sub>3</sub>	0.071
TiO <sub>2</sub>	2.81	Cl	0.0309
SO <sub>3</sub>	2.78	MnO	0.0219
K <sub>2</sub> O	1.4	ZnO	0.0166
Na <sub>2</sub> O	1.24	CuO	0.0137
P <sub>2</sub> O <sub>5</sub>	0.477	Y <sub>2</sub> O <sub>3</sub>	0.0127
MgO	0.349	Nb <sub>2</sub> O <sub>5</sub>	0.0111

### 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 [16]. The theoretical Langmuir isotherm is often used to describe adsorption of a solute from a liquid solution as follows [16, 17]:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (2)$$

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 [18]. 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 [19]. It can be described as follows:

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (4)$$

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 non-linear regression. This provides a mathematically rigorous method for determining isotherm parameters using the original form of the isotherm equation [12, 20]. 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, 21].

The coefficient of determination  $r^2$  was as follows:

$$r^2 = \frac{\sum (q_m - \bar{q}_e)^2}{\sum (q_m - \bar{q}_e)^2 + \sum (q_m - q_e)^2} \quad (5)$$

where  $q_m$  is the equilibrium capacity obtained from the isotherm model,  $q_e$  is the equilibrium capacity obtained from experiment, and  $\bar{q}_e$  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 Methylene Blue on rectorite at five various temperatures from 288 to 308 K in Fig. 1. The graph is plotted in the form of Methylene Blue adsorbed per unit mass of rectorite,  $q_e$ , against the concentration of Methylene Blue 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 Methylene Blue 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

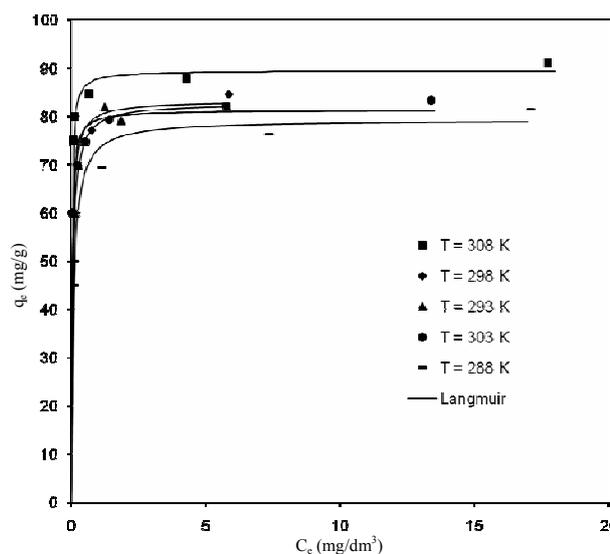


FIGURE 1 - Langmuir isotherms obtained using the non-linear method for the adsorption of Methylene Blue onto rectorite at different temperatures.

TABLE 2 - Isotherm parameters obtained using the non-linear method for the adsorption of Methylene Blue onto rectorites at different temperatures.

Isotherm	T (K)	288	293	298	303	308
Langmuir	$q_m$ , mg/g	79.3	82.8	83.2	81.2	89.4
	$K_a$ , $\text{dm}^3/\text{mg}$	11.9	17.9	25.5	40.1	51.2
	$\Delta G^\circ$ , kJ/mol	-20.1	-21.4	-22.8	-24.1	-25.4
	$r^2$	0.946	0.973	0.953	0.918	0.936
Freundlich	$1/n$	0.108	0.0859	0.0850	0.0605	0.0356
	$K_F$ , $(\text{mg/g})(\text{dm}^3/\text{mg})^{1/n}$	63.2	74.6	77.3	74.6	83.7
	$r^2$	0.897	0.841	0.886	0.904	0.920
Redlich-Peterson	$g$	0.965	1.000	0.959	0.970	0.984
	$B$ , $(\text{dm}^3/\text{mg})^g$	18.0	17.9	51.8	80.1	93.5
	$A$ , $\text{dm}^3/\text{g}$	1326	1484	4157	6243	8118
	$r^2$	0.957	0.973	0.980	0.991	0.974

of determination of Redlich-Peterson and Langmuir isotherm is the same ( $r^2 = 0.973$ ). Figure 2 shows the plots comparing the theoretical Langmuir, empirical Freundlich, and the Redlich-Peterson isotherm with the experimental data for the adsorption of Methylene Blue onto rectorite at a temperature of 293 K. The Redlich-Peterson and Langmuir isotherms overlapped and seemed to be the best-fitting iso-therms 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 [12]. The adsorption capacity of Methylene Blue 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 Methylene Blue between the rectorite and the Methylene Blue solution is of fundamental importance in determining the maximum adsorption capacity of rectorite for the Methylene Blue 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 79.3 to 89.4  $\text{mg g}^{-1}$  and 11.9 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 Methylene Blue on rectorite is an endothermic process. In addition, the values of  $g$  were close to unity ( $>0.959$ ), which means that the isotherms are approaching the Langmuir form and not the Freundlich isotherm.

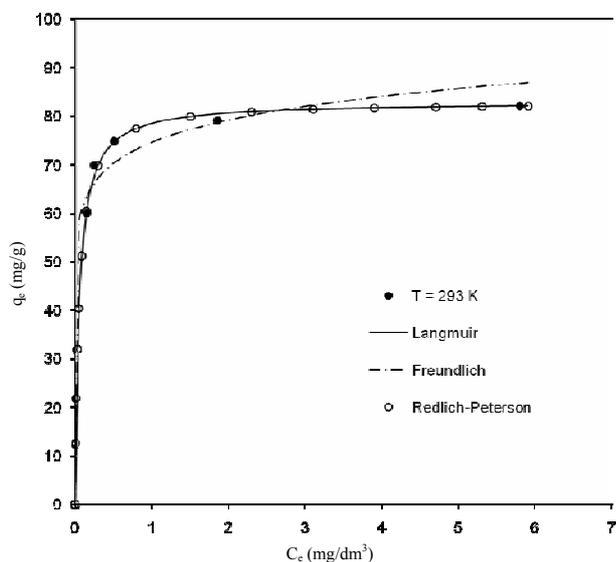


FIGURE 2 - Isotherms obtained using the non-linear method for the adsorption of Methylene Blue onto rectorite at a temperature 293 K.

The effect of isotherm shape can be used to predict whether an adsorption system is “favourable” or “unfavourable” both in fixed-bed systems [22] as well as in batch processes [23]. According to Hall et al. [24], 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:

$$K_R = \frac{1}{1 + K_a C_0}; \quad (6)$$

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:

Values of $K_R$	Type of isotherm
$K_R > 1$	Unfavourable
$K_R = 1$	Linear
$0 < K_R < 1$	Favourable
$K_R = 0$	Irreversible

A figure with a relationship between  $K_R$  and  $C_0$  was presented to show the essential features of the Langmuir isotherm [17]. Figure 3 shows the values of  $K_R$  for Methylene Blue 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.

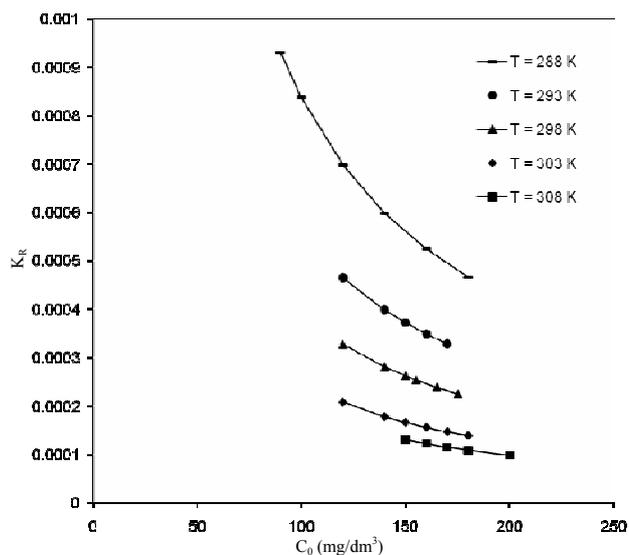


FIGURE 3 - Plot of  $K_R$  against initial Methylene Blue concentration at various temperatures.

#### 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:

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

and

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

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 Methylene Blue by rectorite. The decrease in the negative value of  $\Delta G^{\circ}$  with an increase in temperature indicates that the adsorption process of Methylene Blue on rectorite becomes more favorable at higher temperatures [25]. There are consistencies with the adsorption of Methylene Blue by other adsorbents, for example, guava leaf powder [3], dehydrated wheat bran carbon [4], diatomaceous silica [5], wheat shell [6], and NaOH-treated pure kaolin [7]. However, a negative value for  $\Delta S^{\circ}$  was also reported for the adsorption of Methylene Blue by cereal chaff [26] and fallen phoenix tree's leaves [27]. In most cases, adsorption of Methylene Blue is found to have negative values of  $\Delta G^{\circ}$  (Table 3). The positive value of  $\Delta H^{\circ}$  indicates that the ad-

sorption 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 [28].

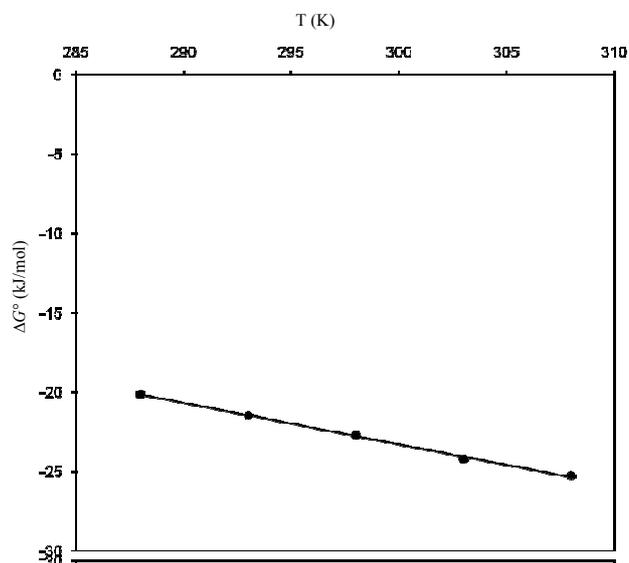


FIGURE 4 - Plot of Gibbs free energy change,  $\Delta G^{\circ}$ , versus temperature,  $T$ .

TABLE 3 - A comparison of thermodynamic parameters for the adsorption of Methylene Blue by different adsorbents.

Adsorbent	$\Delta G^{\circ}$ (kJ/mol)	$\Delta H^{\circ}$ (kJ/mol)	$\Delta S^{\circ}$ (kJ/mol K)	References
Guava leaf powder <sup>a</sup>	Negative	33.20	0.193	[3]
Dehydrated wheat bran carbon <sup>a</sup>	Negative	53.24	0.272	[4]
Dehydrated peanut hull <sup>a</sup>	Negative	20.05	0.155	[29]
Fallen phoenix tree's leaves <sup>b</sup>	Negative	7.77	-0.040	[27]
Cereal chaff <sup>b</sup>	Negative	2.41	-0.034	[26]
Diatomaceous silica <sup>b</sup>	Negative	9.61	0.0376	[5]
Wheat shell <sup>a</sup>	Negative	33.41	0.185	[6]
NaOH-treated pure kaolin <sup>b</sup>	Negative	6.03	0.0697	[7]

Thermodynamic parameter  $\Delta G^{\circ}$  calculated from a:  $K_a$ , adsorption equilibrium constant of Langmuir isotherms (Eq. 2)

b:  $K_d$ , 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

The Methylene Blue in aqueous solutions can be adsorbed by rectorite. The removal of Methylene Blue 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 using 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 Methylene Blue on rectorite, and that the adsorption reaction is endothermic, respectively. The positive value of  $\Delta S^{\circ}$  suggests increasing randomness at the solid/liquid interface during the adsorption of Methylene Blue on rectorite in the aqueous solution.

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**Received:** January 18, 2010

**Revised:** March 30, 2010

**Accepted:** May 19, 2010

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