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# Thermodynamic Functions and Kinetic Models for Methelyne Blue Adsorption on Corn Straw Pulp.

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### THERMODYNAMIC FUNCTIONS AND KINETIC MODELS FOR -METHELYNE BLUE ADSORPTION ON CORN STRAW PULP دراسة ديناميكية ودوال الثرموديناميكا لامتزاز الميثيلين الأزرق باستخدام لب قش الذرة

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#### الملخص العربى

يهدف البحث الى تقييم عملية الامتزاز بواسطة لب قش الذرة كمادة حيوية مازة من خلال دراسة حركية امتزازه لصبغة المثيلين الأزرق ووصف عملية الامتزاز من خلال دراسة الدوال الثرموديناميكية وهى : الانثالييا (ΔΗ) العشوائية (ΔS) والطاقة الحرة (ΔG). وقد تم حساب معدل الامتزاز عند المتغيرات الموثرة على عملية الامتزاز وهى التركيز الابتدائى للصبغة؛ حجم حبيبات المادة المازة؛ كمية المادة المازة، رقم الأس الهيدروجينى وزمن العملية. وقد أوضحت النتائج أن عملية الامتزاز للصبغة تحدث تدريجيا ووجد أن معدل الامتزاز يكون مربع جدا في المرحلة الاولي من العملية (المتزاز للصبغة تحدث تدريجيا ووجد أن معدل الامتزاز يكون مربع جدا في المرحلة الاولي من العملية (ووسالة اتعانة المازة؛ كمية المادة المازة، رقم الأس الهيدروجينى مربع جدا في المرحلة الاولي من العملية (ووسالة rapid rate). وقد وجد أن النسبة المنوية لعملية الازالة مربع جدا في المرحلة الاولي من العملية (ومنان rate). وقد وجد أن النسبة المنوية لعملية الازالة مربع جدا في المرحلة الاولي من العملية (عمان الله الماذة المازة المستخدمة حيث وصلت الى حوالى ٩١ % عند درجة حرارة ٢٥ م<sup>0</sup> وعند رقم الأس الهيدروجينى من ٥-٩. وقد استخدمة حيث وصلت الى حوالى ٩١ % النتائج ومن ثم تم تقييم هذه النماذج من حيث أيهم أكثر تطابقا مع النتائج العملية وهى: -pseudo first وقد وجد أن النموذج الثاني ومن ثم تم تقييم هذه النماذج من حيث أيهم أكثر تطابقا مع النتائيج العملية وهى: معالجة ما النتائج ومن ثم تم تقييم هذه النماذج من حيث أيهم أكثر تطابقا مع النتائية العملية وهى: معالجة في معالجة ما النتائي ومن ثم تم تقييم هذه النماذج من حيث أيهم أكثر تطابقا مع النتائية العملية وهي: معاد معنوذج ما النتائي ومن ثم تم تقييم هذه النماذج من حيث أيهم أكثر تطابقا مع النتائية العملية وهى: معاد معنوذج ما النتائي معامل التصوذج المائية من حيث أيهم أكثر تطابقا مع النتائية العملية وهى: ما معاد أن النموذج النتائي ومن ثم تم تقييم هذه النماذج من حيث أيهم التائية العملية حمان التصحيح أعلى قيمة. ما النتائي معامل التصوذج النائي معلية أن عملية الامتزاز عملية تلقائية كما ألها ماصه للحرارة مما يتطبيق مع زيادة كفاءة عملية الامتزاز بزيادة درجة الحرارة المستخدمة من ٢٥ م م الى ٢٠ م<sup>0</sup> .

#### ABSTRACT

Methylene Blue (MB) in aqueous solutions was subjected to color removal by the adsorption technique onto corn straw pulp (CSP) as a biosorbent waste agricultural material. Results obtained indicate that the removal efficiency of Methylene Blue at 25°C exceeds 91% and that the adsorption process is highly pH-dependent. The optimum pH lies between 5 and 9. The amount of Methylene Blue adsorbed from the aqueous solution increases with the increase of the initial Methylene Blue concentration and temperature. Smaller adsorbent particles help in increasing the percentage removal of Methylene Blue. The results fit the BET model for adsorption of Methylene Blue on corn straws pulp, verify the assumption that the adsorbate molecules could be adsorbed in more than one layer thick on the surface of the adsorbent. A comparison of kinetic models (pseudo first-order, the pseudo secondorder, Elovich and intraparticle diffusion kinetic models) at different conditions showed that the pseudo second-order kinetic model correlate the experimental data well. Van't Hoff equation was used to evaluate the thermodynamic parameters ( $\Delta H$ ,  $\Delta S$ and  $\Delta G$ ) for the interpretation of the adsorption process. The values of the thermodynamic parameters indicate that all adsorption processes are endothermic, and this is in agreement with the increasing adsorption capacity with temperature. The process of removal of MB by Corn straw pulp is a spontaneous one.

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#### P. 16 M. M. El-Halwany

#### 1. INTRODUCTION

Cationic dyes, such as MB, were used initially for dyeing of silk, leather, plastics, paper, and cotton mordant with tannin, as well as for the production of ink and copying paper in the office supplies industry [1]. In the textile sector, an estimated 10–20% of dyes (active substance) used is lost in residual liquors through the exhaustion and washing operations [2]. The releasing of dyes to the environment can cause acute and/or chronic effects on the exposed organisms, adsorb or reflect sunlight entering into water, and thus result in change of food chain [3].

Previous studies found MB that molecules existed as dimer or 28 aggregates at the surface, as well as a protonated form depending on the concentration and the surface properties [4]. Such extensive use of dyes and pigments often poses problems in the form of colored wastewater that require pre-treatment for color removal prior to disposal into receiving water bodies or publicly owned treatment works [5]. The problem main for dvestuff manufactureres and users is the removal or reducing the quantity of color in effluent and water sources [6].

At the present time there is no single process capable of adequate treatment [7]. Most of the existing processes include adsorption, usually with activated carbon (AC) [8]. The adsorption of the cationic dye, MB, has been used for a long time for the evaluation of the adsorption properties of AC, and in monitoring the production and quality of AC prepared from coal, in fluidized bed [9, 10]. Adsorption from dilute aqueous solutions onto solid surfaces is a highly attractive separation technique for many applications, such as wastewater

treatment, liquid mixture separation and purification, or polar organic solutes recovery from biotechnology processes [11, 12]. In particular, adsorption provides a technique of great interest to remove dyes from municipal and industrial wastewater [13, 14]. This can be achieved by using adsorbents with a high adsorptive capacity and selectivity [15].

The adsorption process can be either physical or chemical in nature, and frequently involves Physical both. adsorption involves the attraction by electrical charge differences between adsorbent and the adsorbate. Chemical adsorption is the product of a reaction between the adsorbent and the adsorbate [16]. In recent vears. stringent government regulations have made it mandatory to stop such effluents, unless they are treated properly; hence, the removal of color from the effluent discharge has become environmentally important [17, 18].

# 2. MATERIALS AND METHODS

#### 2.1. Preparation of Corn Straws Pulp

The corn straws pulp was rinsed a few times with distilled water and then airdried. The washed corn straws pulp were lightly ground in a mortar and sieved through 0.5 mm and 0.05 mm diameter by means of a test sieve shaker.

#### 2.2. Batch adsorption studies

Batch experiments with corn straws pulp were conducted to investigate the parametric effects of initial adsorbate particle size and concentration, adsorption time, pH, temperature on MB adsorption. All reagents used were of AR grade (Sigma-Aldrich, Germany). MB samples were prepared by dissolving a known quantity of the dye in distilled water and used as a stock solution and

diluted the required initial to concentration (range: 25 to 125 mg/l). 50 solution ml of MB of known concentration  $(c_0)$  was taken in a 100 ml conical flask with the required amount of adsorbent and was shaked for different time intervals in a shaker at different pH values and different temperatures. Then, the solution was filtered through a filter spectrophotometer paper. UV-visible PHTOMECH  $301 - D^{+}$ was (model employed to determine the remaining concentrations of MB in the filtrate.

# 3. ADSORPTION ISOTHERMS STUDY

Equilibrium studies that give the capacity of the adsorbent and adsorbate are described by adsorption isotherms, which is usually the ratio between the quantity adsorbed and that remained in solution at equilibrium fixed temperature. at Freundlich, Langmuir and BET isotherms are the earliest and simplest known relationships describing the adsorption equation [19-21]. Adsorption isotherms have been classified into six characteristic types. Microporous adsorbents produce adsorption isotherms of Type 1 (which has a convex shape) and is also associated with it monomolecular layer adsorption. Types II and III depict adsorption for multimolecular layer formation while Types IV and V describe the adsorption process of multi-molecular layer formation and in pores. condensation Type VI represents surface phase transition of a monomolecular layer on a homogeneous surface [22].

#### 3.1. Langmuir Isotherm

The Langmuir equation is used to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface and is expressed by:

$$q_{e} = \frac{(q_{\max} K_{I} C_{e})}{(1 + K_{I} C_{e})}$$
(1)

The linearized form of the above equation after rearrangement is given by:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}K_i} + \frac{C_e}{q_{\max}}$$
(2)

The experimental data is then fitted into the above equation for linearization by plotting  $C_e/q_e$  against  $C_e$ .

### 3.2. Freundlich Isotherm

The Freundlich model named after Freundlich (1926) is an empirical equation used to estimate the adsorption intensity of the sorbent towards the adsorbate and is given by:

$$q_e = \frac{K_F C_e}{n} \tag{3}$$

Also, the value of n indicates the affinity of the adsorbate towards the adsorbent. The above equation is conveniently used in linear form as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{4}$$

A plot of  $ln C_e$  against  $ln q_e$  yielding a straight line. The constants l/n and  $ln K_F$  can be determined from the slope and . intercept, respectively.

#### 3.3. BET Isotherm

The BET (Brunauer, Emmeth and Teller) derived an adsorption isotherm based on the assumption that the adsorbate molecules could be adsorbed in more than one layer thick on the surface of the adsorbent. Their equation, assumed that the energy of adsorption holds the first monolayer but that the condensation energy of the adsorbate is responsible for adsorption of successive layers. The equation, known as the BET equation, is commonly written as follow:

$$\frac{x}{m} = \frac{ACX_m}{\left(C_s - C\right)\left(1 + \frac{(A-1)C_s}{C}\right)}$$
(5)

or

$$\frac{1}{\left(C_{x}-C\right)\left(\frac{x}{m}\right)}=\frac{1}{AX_{m}}+\frac{\left(A-1\right)}{AX_{m}}\left(\frac{C}{C_{x}}\right)$$
(6)

Thus, plotting  $[C/(C_s-C)]/(x/m)$  against  $C/C_s$  will give rise to straight lines with slope  $(A-1)/AX_m$  and intercept  $1/AX_m$  for adsorption processes that conform BET equation.

#### 4. ADSORPTION DYNAMICS STUDY

The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solidsolution interface. Kinetics of (MB) adsorption on the CSP were analysed using pseudofirst-order (Lagergren, 1898), pseudo second-order (Ho et al., 2000), Elovich (Chien and Clayton, 1980; Sparks, 1986) and intraparticle diffusion (Srivastava et al., 1989; Weber and Morris, 1963) kinetic models [23].

#### 4.1. The pseudo first-order model

The pseudo first-order equation (Lagergren, 1898) is generally expressed as follows:

$$\frac{dq_i}{dt} = k_1 (q_e - q_i) \tag{7}$$

At t=0 to t=t and  $q_i=0$  to  $q_i=q_i$ , the integrated form of Equation (7) becomes:

$$(\log q_e - \log q_t) = \log(q_e) - \frac{k_1}{2.303}t$$
 (8)

where  $k_l$  and  $q_e$  can be determined from the slope and intercept of the plot.

#### 4.2. The pseudo second-order model

The pseudo second-order kinetic rate equation is expressed as (Ho et al., 2000):

$$\frac{dq_1}{dt} = k_2 (q_c - q_1)^2 \tag{9}$$

At t=0 to t=t and  $q_t=0$  to  $q_t=q_t$ , the integrated form of Equation (9) becomes:

$$\frac{1}{(q_e - q_i)} = \frac{1}{q_e} + kt$$
(10)

Equation (4) can be rearranged to obtain Equation (11), which has a linear form:

$$\frac{t}{q_{t}} = \frac{1}{k_{2}q_{e}^{2}} + \frac{1}{q_{e}}t$$
 (11)

If the initial adsorption rate,  $h \pmod{g}$ . min) is:

$$h = k_2 q_e^2 \tag{12}$$

then Equations (11) and (12) become:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \tag{13}$$

The plot of  $(t/q_t)$  and t of Equation (11) should give a linear relationship from which  $q_e$  and  $k_2$  can be determined from the slope and intercept of the plot, respectively.

## 4.3. The Elovich model

The Elovich model equation is generally expressed as:

$$\frac{dq_i}{dt} = \alpha \exp(-\beta q_i) \tag{14}$$

To simplify the Elovich equation, Chien and Clayton (1980) assumed  $\alpha\beta t >> t$  and by applying the boundary conditions t=0to t=t and  $q_t=0$  to  $q_t=q_t$ , Equation (14) becomes:

$$q_{t} = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$$
 (15)

A plot of  $q_i$  vs. ln(t) should yield a linear relationship with a slope of  $(1/\beta)$  and an intercept of  $(1/\beta) ln(\alpha\beta)$ .

4.4. The intraparticle diffusion model

The intraparticle diffusion model is expressed as (Weber and Morris, 1963)

$$R = k_{\mu}(t)^{\sigma} \tag{16}$$

A linearized form of the equation is obtained as:

$$\log R = \log k_{ul} + a \log(t) \tag{17}$$

If (MB) adsorption fits the intraparticle model, a plot of log R vs. log t should yield a linear relationship with a slope of a and an intercept of  $log k_{id}$ .

# 5. RESULTS AND DISCUSSION 5.1. Adsorption Isotherms

The results of this study show that CSP was effective, in adsorbing MB as its reached 91% at 25°C. removal Adsorption of MB was highly pHdependent and the results showed that the optimum pH for the removal was found to be (5-9), at which MB exists mostly as the most easily adsorbed form aqueous solution increases as the initial MB concentration. Also on increasing temperature, smaller adsorbate particle were found to increase the percentage removal of MB. The Experimental data were applied in the three isotherms, which results indicate that the adsorption of MB on CSP fits the BET model (Fig. 1), verifying the assumption that the adsorbate molecules could be adsorbed in more than one layer thick on the surface of the adsorbent.

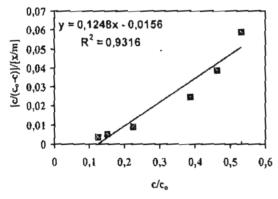


Fig. (1): Plot of BET isotherm

# 5.2. Adsorption Dynamics

5.2.1. Effect of adsorbate concentrations The removal of MB by adsorption on CSP was found to increase with time and attained a maximum value at 150 min. On changing the initial concentration of MB solution from 25 to 125 mg/l, the amount adsorbed increased at 25 °C, pH 7.5 and particle size of 0.05 mm. The experimental results correlate with the theoretically predicted curves. Results obtained show good compliance with the pseudo second-order kinetic model (Fig. 2), with values of correlation coefficient,  $r^2 > 0.969$ .

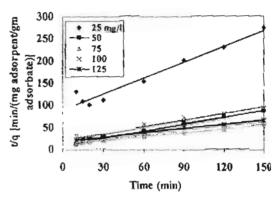


Fig. (2): Plot of pseudo second-order equation at different adsorbate concentrations

#### 5.2.2. Effect of adsorbent particle size

The batch adsorption experiments were carried out using adsorbent with different particle sizes, (blew 0.05 to over 0.5 mm) at pH 7.5, 25°C, and initial concentration of 25 mg/l. The removal of MB increased with the decrease in particle size. The relatively higher adsorption with smaller adsorbent particle may be attributed to the fact that smaller particles yield large surface areas. The data obtained separately for each of the kinetic models from the slopes of plots, show a good compliance with the pseudo second-order equation (Fig. 3), the  $r^2$  values for the linear plots being > 0.9644.

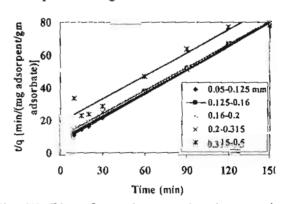


Fig. (3): Plot of pseudo second-order equation at different adsorbent particle size

P. 19

# P. 20 M. M. El-Halwany

#### 5.2.3. Effect of Temperature

Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. In addition, changing temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate. The experimental data were obtained at pH 7.5, particle size blew 0.05 mm, and initial concentration of 25 mg/l. The increasing adsorption rate of MB on the surface of CSP may be explained by considering more conversion of the dimer species to monomers. The data obtained for each of the kinetic models from the slopes of plots (Fig. 4) show a good compliance with the pseudo second-order equation, with values of correlation coefficient,  $r^2 > 0.9994$ .

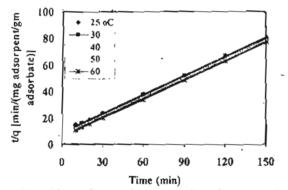


Fig. (4): Plot of pseudo second-order equation at different temperatures

#### 5.2.4. Effect of adsorbent dose

MB uptake was studied using different doses of CSP by using 50 ml of solution at pH 7.5, 25°C, particle size blew 0.05 mm and initial concentration of 25 mg/l. The concentrations used were 0.5, 0.75, 1, 1.25 and 1.5gm adsorbent/ liter adsorbate, keeping the batch experimental volume the same in all cases. The results indicated that the percent adsorption increased with the increase in CSP dose. The curves (Fig. 5), showed good compliance with pseudo second-order model with values of correlation coefficient,  $r^2 > 0.985$ .

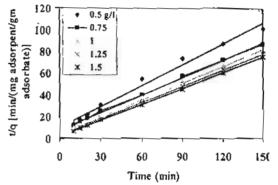


Fig. (5): Plot of pseudo second-order equation at different adsorpent dose

#### 5.2.5. Effect of pH

The removal of MB was studied at different pHs in the range 2.2-11.1 by CSP at initial MB concentration of 25 mg/l, and a temperature of 25°C, particle size blew 0.05mm. The variation in adsorption capacity in this pH range is largely due to the influence of pH on the adsorption characteristics of the CSP which indicates the adsorption capacity of the that adsorbent is clearly pH dependent. The optimum removal (91%) was observed in the pH range 5-9. Results also showed that adsorption reaction the can he approximated with the pseudo secondorder kinetic model (Fig. 6), with values of correlation coefficient,  $r^2 > 0.9917$ . The rate values of correlation constants and coefficient are represented in table 1.

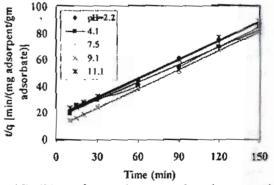


Fig. (6): Plot of pseudo second-order equation at different pH values

		Table (1): The adsorption kinetic model rate constants for CSP										
First order		Second order El		Elc	ovich model		Intraparticle diffusion					
Paran	neter	k <sub>i</sub>	r <sup>2</sup>	k <sub>2</sub>	h	$\mathbf{R}^2$	β	α	<b>г</b> <sup>2</sup>	k <sub>id</sub>	a	r
	2	0.028	0.993	6.977	2.117	0.999	2.098	0.122	0.956	8.63	0.474	0.972
<b>[</b>	5	0.039	0.992	7.368	2.264	0.992	1.916	0.123	0.923	8.25	0.495	0.960
Hd	7.5	0.044	0.969	5.026	2.124	0.999	2.242	0.227	0.976	16.24	0.362	0.942
	9	0.039	0.996	4.689	2.085	0.999	2.345	0.257	0.811	18.02	0.339	0.952
	12	0.039	0.995	7.211	2.122	0.995	2.060	0.115	0.955	7.62	0.498	0.959
[	0.08	0.026	0.976	3.921	2.069	0.997	2.791	0.539	0.975	1.90	1.429	0.961
l ≞ Ê	0.1	0.034	0.993	4.420	2.081	0.999	2.506	0.528	0.970	2.01	1.330	0.971
particle size (mm)	0.2	0.036	0.994	4.780	2.104	0.999	2.327	0.327	0.963	2.21	1.247	0.936
E B	0.315	0.042	0.974	5.026	2.124	0.999	2.242	0.234	0.91	2.30	1.211	0.942
S: _	0.5	0.025	0.967	7.461	2.126	0.964	2.140	0.120	0.69	3.32	0.838	0.845
20	0.5	0.016	0.983	3.915	1.571	0.985	3.957	0.444	0.954	21.45	0.235	0.978
Adsorbent dose (mg/l)	0.75	0.029	0.992	4.004	1.886	0.998	2.935	0.386	0.948	22.45	0.272	0.982
25	1	0.031	0.992	2.959	1.958	0.999	3.518	1.788	0.976	35.43	0.194	0.959
0 Ad	1.25	0.047	0.994	2.562	2.030	0.999	4.892	1.105	0.964	41.93	0.171	0.958
	1.5	0.041	0.996	1.877	2.072	0.999	3.692	2.837	0.834	56.40	0.116	0.957
Temperature (°C)	25	0.036	0.994	4.800	2.104	0.999	2.327	0.254	0.976	17.65	0.344	0.936
T a	30	0.036	0.996	4.520	2.096	0.999	2.409	0.296	0.950	19.73	0.322	0.942
pera (°C)	40	0.030	0.986	4.219	2.114	0.999	2.475	0.364	0.976	22.36	0.301	0.934
	50	0.030	0.989	4.064	2.128	0.999	2,525	0.417	0.902	24.44	0.284	0.950
Ĕ	60	0.034	0.985	3.440	2.104	0.999	2.783	0.673	0.971	29.77	0.245	0.936
5	25	0.023	0.994	7.169	0.841	0.995	5.672	0.027	0.976	3.78	0.668	0.936
_ af	50	0.029	0.992	4.004	1.886	0.998	2.935	0.386	0.910	2.45	0.272	0.982
centra (mg/l)	75	0.027	0.990	8.862	3.399	0.997	1.303	0.182	0.463	6.16	0.499	0.958
E C	100	0.017	0.921	7.110	1.961	0.969	2.371	0.115	0.852	3.62	0.481	0.883
Concentration (mg/l)	125	0.019	0.997	9.621	3.010	0.992	1.508	0.135	0.849	3.53	0.523	0.986

Table (1): The adsorption kinetic model rate constants for CSP

#### 5.3. Determination of Thermodynamic Parameters

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**5.3.1. Determination of**  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$  and  $\Delta G^{\circ}$ The values of the thermodynamic parameters, enthalpy variation ( $\Delta H$ ) and entropy variation ( $\Delta S$ ), were calculated from the curve relating the distribution coefficient ( $K_D$ ) as a function of temperature (Fig. 7) using the equation:

$$\ln K_{D} = \left(\frac{\Delta S^{\circ}}{R}\right) - \left(\frac{\Delta H^{\circ}}{RT}\right) \quad (18)$$

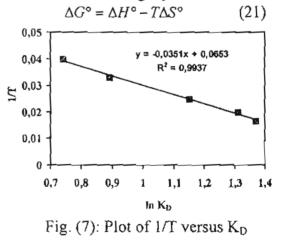
where  $K_D$  is the distribution coefficient (cm<sup>3</sup>.g<sup>-1</sup>), defined as:

$$K_{D} = \frac{Q}{C_{e}}$$
(19)

with Q the amount adsorbed (mg adsorbate/g adsorbent) described by the equation:

$$Q = \frac{V(C - C_e)}{m} \tag{20}$$

where C and  $C_e$  are the initial and equilibrium concentrations of the solute, respectively (mg.cm<sup>-3</sup>). The calculated data for  $K_D$  and Q are shown in table 2. The free energy change ( $\Delta G^{\circ}$ ) parameter was calculated using equation 21:



P. 21

# P. 22 M. M. El-Halwany

Table 2: Q and K<sub>D</sub> parameters at different temperatures

Temperature (°C)	Q	KD
25	7.488	2.103
30	7.58	2.445
40	7.714	3.174
50	7.78	3.705
60	7.804	3.941

From figure 7 the values of  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$  were determined from the slopes and intercepts of the curves, respectively as well as the calculated values of  $\Delta G^{\circ}$  and are listed in table 3. Investigation of the obtained values of the thermodynamic parameters shows that the adsorption process is endothermic. This is in accordance with increasing adsorption rate with increasing temperature.

Table 3: Thermodynamic parameters at different temperatures

untere	at temper	atures
45	1	(keal/mol

ΔH	ΔS	ΔG (kcal/mol)					
kcal/mol	kcal/mol. K	25 °C	30 °C	40 °C	50 °C	60 °C	
0.0695	0.1293	-3.16	-3.81	-5.1	-6.39	-7.69	

# 5.3.2. Determination of Mean Free Energy (E)

The mean free energy of adsorption (E) is the free energy change when one mole of ions is transferred to the surface of the membrane from infinity in the solution and it is calculated from:

$$\bar{z} = -(2K_{D}R)^{\frac{1}{2}} \tag{22}$$

The mean free energies (E) were calculated and documented in table 4.

Table	4:	Free	Energy	(E)	at	different
temperatures						

Temperature (°C)	KD	E, kj/mol
25	2.103	2.885807
30	2.445	3.111623
40	3.174	3.545284
50	3.705	3.830379
60	3.941	3.950489

The magnitude of E is useful for estimating the type of sorption reaction, since E < 8kJ. mol<sup>-1</sup>, physical forces such as diffusional processes may affect the sorption mechanism [24]. So, the adsorption of dyes seems to be a complex phenomenon, where diffusion and chemical bonding occur at different temperature ranges, this may support that the monolayer capacity  $(q_{max})$  increases with increasing temperature.

#### 6. CONCLUSION

- Corn straw pulp could be used as an alternative low cost adsorbent of dyes from industrial wastewater discharged from dying units.
- The adsorption process fits the BET model, corroborating the assumption that the adsorbate molecules could be adsorbed in more than one layer thick on the surface of the adsorbent.
- The kinetics of MB adsorption on the CSP was found to follow a pseudo second-order rate equation.
- The mean free energies (E) revealed that, adsorption of dyes on corn straw pulp seems to be a complex phenomenon, where diffusion and chemical bonding occur at different temperature ranges.
- The values of thermodynamic parameters indicate that all adsorption processes are endothermic, and this is in agreement with the increasing adsorption capacity with temperature.
- Thermodynamic studies are performed and the values of the parameters suggest that the process of removal of MB by corn straw pulp is a spontaneous one.

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#### 8. NOMENCLATURE

- A Constant describing the energy of interaction between solute and adsorbent surface;
- C Initial concentration (mg/l);
- C<sub>e</sub> Concentration equilibrium (mg/l);
- C<sub>s</sub> Saturation concentration of solute (mg/l);
- K<sub>F</sub>&n Freundlich constants;
- m Weight of adsorbent (mg);
- k<sub>1</sub> Rate constant of pseudo first-order adsorption (l/min);
- k<sub>2</sub> Rate constant of pseudo secondorder adsorption (g/mg. min);
- $K_D$  Distribution coefficient (cm<sup>3</sup>.g<sup>-1</sup>)
- $k_{id}$  Intraparticle diffusion rate constant (min<sup>-1</sup>)
- $K_L$  Constant related to the adsorption /desorption energy (1 g<sup>-1</sup>);
- q<sub>c</sub> Adsorption capacity at equilibrium, (mg of dye/g adsorbate);
- q<sub>max</sub> Maximum sorption (mg of dye/g adsorbate);

 $q_t$ 

Adsorption capacity at time *t*, (mg of dye/g adsorbate);

R universal gas constant (j/mole. K)

- P. 24 M. M. El-Halwany
- R Percent (MB) adsorbed;
- t Contact time (min)
- V Volume of the solution
- x Amount of solute adsorbed (mg);
- X<sub>m</sub> Amount of solute adsorbed in forming a complete mono layer (mg of dye/g adsorbate);
- α Initial adsorption rate (mg of dye/g adsorbate. min);
- β Desorption constant (g/mg) during any experiment;