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Hemicellulose-Based Absorbent Toward Dye: Adsorption Equilibrium and Kinetics Studies

J. Zhang[1, 2], H. Xiao[2,* 3], and Y. Zhao[3]

[1]*Liaoning Key Laboratory of Pulp and Paper Engineering, Dalian Polytechnic University, Dalian 116034, China*
[2]*Department of Chemical Engineering, University of New Brunswick, Fredericton E3B 5A3, Canada*
[3]*School of Environmental Science & Engineering, North China Electric Power University, Baoding 071003, China*

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ABSTRACT. Exploitation of biomaterials derived from renewable resources as absorbents for the removal of dyes from industrial effluents is of great importance. In this work, the efficiency of the hemicellulose-based absorbent for the adsorption of methylene blue dyes was systematically examined. It was found that the hemicellulose-based absorbent removed the dyes from aqueous solution very effectively. The study on the kinetics of methylene blue onto hemicellulose-based absorbent showed that experimental data followed a pseudo-second-order model, suggesting that the adsorption process was controlled by chemical-sorption. The equilibrium data was also fitted to the two isotherm models, Langmuir and Freundlich ones; and it was found that Langmuir model presented the best fit, showing the maximum adsorption capacity of 39.22 mg/g at 25 °C. The thermodynamic parameters, including the standard enthalpy, entropy and free energy obtained from this work, indicated that the adsorption of methylene blue onto hemicellulose based absorbent is an endothermic and spontaneous process. Overall, the adsorption process of methylene blue to hemicellulose-based absorbent is a combination of chemical-sorption and physical-sorption.

Keywords: hemicellulose, methylene blue, adsorption, kinetics, equilibrium, thermodynamic

1. Introduction

Dyes as organic pollutants, form a major class of environment contaminants. The complex structures and xenobiotic properties of dyes make them extremely difficult to degrade (Parida et al., 2011). Dyes are harmful to flora and fauna, and some of the organic dyes and their products have a mutagenic or carcinogenic influence on human beings (Aksu, 2005). The growing concern over the environmental issues raised by the release and use of dyes have led to the research on exploring methods of treatment, and developing novel materials that are able to tackle these environmental problems (Demirbas et al., 2008).

Methylene blue (MB), an organic dye, has wide applications (Sheng et al., 2009). Due to its known strong adsorption onto solids, MB often serves as a model compound for studying the removal of dyes and organic contaminants from aqueous solution (Hameed et al., 2007). Although not strongly poisonous, MB still possesses some harmful effects on human beings (Hajjaji and El Arfaoui, 2009). Owing to these harmful effects on humans, it is necessary to remove MB from aqueous solution.

Hemicelluloses are a class of hetero-polysaccharides present in the cell wall of wood and annual plants together with cellulose and lignin. Hemicelluloses, comprising the noncellulose cell-wall polysaccharides of plants, are the second most abundant polysaccharide in nature, representing about 20 to 35% of lignocellulosic biomass (Coviello et al., 2007; Peng et al., 2011). Recently, the importance of hemicellulose-based macromolecules and materials has been increasingly emphasized (Petzold et al., 2006; Schwikal et al., 2006). Due to their inherent hydrophilicity, low toxicity, biodegradability, and biocompatibility, the formation of latex is a potential area of application for hemicelluloses and their derivatives (Ebringerova, 2006; Coviello et al., 2007). These functional derivatives are found to be widely used in the food exploration, paper, textile, heavy metal removal and paint industries (Methacanon et al., 2003; Heinze and Koschella, 2005; Chen et al., 2009). Our preliminary results indicated that the efficiency of hemicellulose-containing latex for the removal of MB from aqueous solutions was good.

In this regard, in order to develop more efficient processes for preparing functional hemicellulose-based adsor- bent, the present work focused on the investigation of the equilibrium, thermodynamics and kinetics of MB adsorption from aqueous solution using hemicellulose-based latexes as adsorbents.

* Corresponding author. Tel.: +1 506 4533532; fax: +1 506 4533591.
E-mail address: hxiao@unb.ca (H. Xiao).

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2. Experimental

2.1. Preparation of Hemicellulose-Based Adsorbent

Hemicellulose used in this work was the one isolated from pre-hydrolysis liquor (PHL) of the kraft-based dissolving pulp production process (Liu et al., 2011). All chemicals and reagents used for experiments and analysis were analytical grade and purchased from Sigma Chemical Reagent Co. Ltd., Canada. 3 g Hemicellulose were mixed with 0.3 g sodium dodecyl sulfate for 1 h, and then heated to 65 °C; followed by the addition of monomer (3 g butyl acrylate and 12 g acrylamide) and initiator (0.2 g ammounium persulfate) while N_2 was purged through the flask. The polymerization in the presence of hemicellulose proceeded for 2 h under constant stirring with the rate of 500 rpm at 70 °C. The hemicellulose-based absorbent was obtained after dried in an oven at 90 °C for 24 h and kept in tightly closed bottles for further analysis.

2.2. Adsorption Procedure

The cationic dye, MB (Sigma-Aldrich, Germany) was used as an adsorbate. A series of stock solutions of MB (100 mg/L) were prepared and further diluted to the required concentration (50 and 100 ppm) prior to use. Batch adsorption was performed in a set of 20-mL vials containing 10 mL of MB solution with various initial concentrations. The amount of 0.01 g hemicellulose-based adsorbent was added and equilibrated at different temperatures (25, 35 and 45 °C) in a temperature-controlled water bath shaker at 120 rpm. After adsorption equilibrium was achieved, the final concentration of MB in the solution was measured using an UV-visible spectrophotometer (Geneys 10S, Thermo Electron C_o) at 664 nm. The adsorbed capacity (Q_e) and the removal efficiency (R) of MB adsorbed onto diatomite were calculated according to the following equations:

$$Q_e = \frac{(C_0 - C_e) \times V}{M} \tag{1}$$

$$R = \frac{(C_0 - C_e) \times 100}{C_0} \tag{2}$$

where Q_e is the adsorption capacity at equilibrium, mg/g; R is the removal efficiency, %; C_0 and C_e are the initial and equilibrium concentrations of MB in the solution, mg/L; V is the volume of solution, L; M is the mass of adsorbent, g (Liu et al., 2012).

2.3. Adsorption Kinetics

Kinetic studies were carried out in vial which contained the fixed amount of adsorbent (0.01 g) and 10 mL of MB solution with different concentrations (100 and 50 ppm) at 25 °C. The prediction of adsorption rate is important for designing batch adsorption systems. In order to clarify the adsorption kinetics of MB onto hemicellulose-based adsorbent, the pseudo-first-order (Malash and El-Khaiary, 2010), pseudo-second-order (Han et al., 2009) and intraparticle diffusion (Mahmoodi et al., 2012) models were used to understand the adsorption dynamics in relation to time for the MB and adsorbent system. These models can be described as follows:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \tag{3}$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^{\,2}} + \frac{1}{Q_e} t \tag{4}$$

$$Q_t = K_i t^{1/2} + C \tag{5}$$

where Q_t is the amount of adsorbed MB onto adsorbent at t moment, mg/g; K_1 (1/min), K_2 (g/(mg·min)), K_i (mg/(g·min$^{1/2}$)) are the rate constants of the adsorption in pseudo-first-order (Equation (3)), pseudo-seconde-order (Equation (4)) and intraparticle diffusion (Equation (5)), respectively.

2.4. Adsorption Isotherm

Isotherm studies were carried out in vials where a fixed mass 0.01 g of adsorbent was introduced into 10 mL of MB solution with different concentrations at 25, 35 and 45 °C.

Adsorption isotherms are used to express the surface properties and affinity of the adsorbent and can also be used to compare the adsorption capacities of the adsorbent for MB in aqueous solutions. In this study, the two well-known adsorption isotherm models, Langmuir and Freundlich (Shawabkeh and Tutunji, 2003) models were selected to fit the equilibrium data. The parameters obtained from the different models provide important information on the sorption mechanisms. The Langmuir model (Equation (6)) (Langmuir, 1918) and Freundlich model (Equation (7)) (Freundlich, 1932) are as follows:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{Q_{\max} K_L} \tag{6}$$

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{7}$$

where Q_{max} is the maximum adsorption capacity, mg/g; K_L is a Langmuir constant relate to the affinity of the binding sites and energy of adsorption, L/g; K_F is a Freundlich constant related to adsorption capacity, L/g; 1/n is an empirical parameter related to adsorption intensity.

2.5. Adsorption Thermodynamics

Thermodynamic parameters including the change in the standard free energy (ΔG), the standard enthalpy (ΔH) and the standard entropy (ΔS) were calculated using the follow-

ing equations (Hsu et al., 2008):

$$\Delta G = -RT \ln K_L \tag{8}$$

$$\Delta G = \Delta H - T\Delta S \tag{9}$$

$$\ln K_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{10}$$

where ΔG is the standard free energy, kJ/mol; R is the universal gas constant, 8.314 J/(mol·K); T is the absolute solution temperature, K; ΔH is the standard enthalpy, kJ/mol; ΔS is the standard entropy, J/K.

3. Results and Discussion

3.1. The Efficiency of MB Adsorption onto the Hemicellulose-Based Adsorbent

The effect of the hemicellulose-based adsorbent dosage on MB adsorption at 25 °C was investigated and the results are depicted in Figure 1.

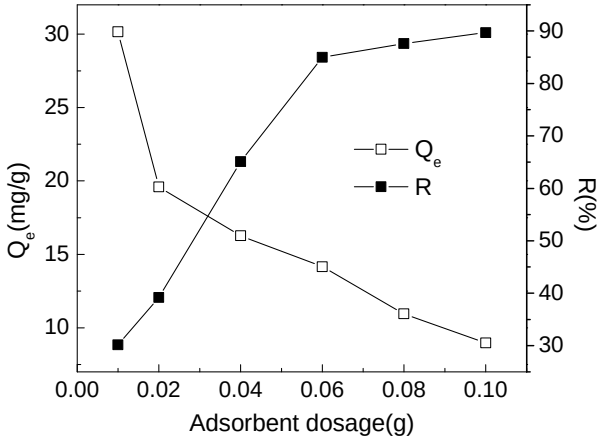

Figure 1. Effect of absorbent dosage on MB adsorption.

Figure 1 shows that the MB removal efficiency increased while the adsorption capacity (Q_e) decreased with the increase of the hemicellulose-based adsorbent dosage. The maximum capacity and removal efficiency were 30.16 mg/g and 89.68%, respectively. It is attributed to more surface area and active sites provided by hemicellulose-based adsorbent at a relatively high dosage. In the current system, the MB amount in aqueous solution was fixed, so that the adsorption capacity in terms of per gram absorbent deceased to some extent with the increase of the dosage of hemicellulose-based absorbent.

3.2. Adsorption Kinetics

Kinetic studies are important to understand the dynamic of the adsorption in terms of order of the rate constant (Cazetta et al., 2011). In order to examine the controlling mechanism of the adsorption process, pseudo-first-order model, pseudo-second-order model and intraparticle diffusion model were applied to analyze the experimental data at two levels of initial MB concentrations (50 and 100 ppm). The corresponding plots at both concentrations are shown in Figures 2, 3 and 4, respectively. The kinetic parameters obtained from kinetic plots and model equations (Equations (3) to (5)) are presented in Table 1.

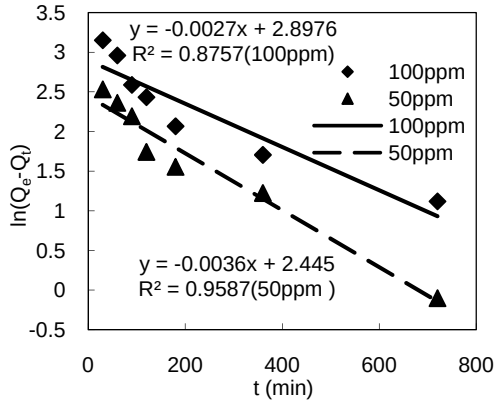

Figure 2. Pseudo-first-order kinetic plots.

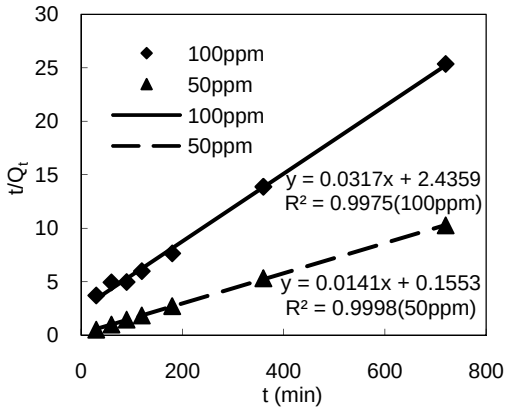

Figure 3. Pseudo-second-order kinetic plots.

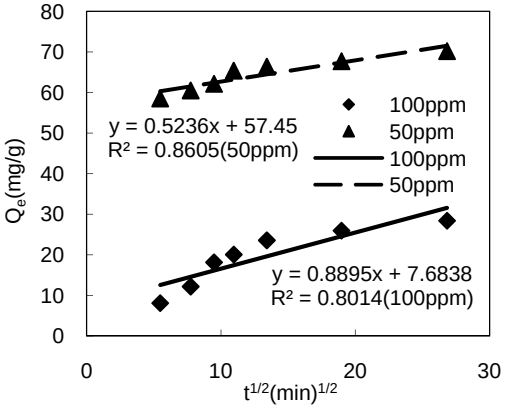

Figure 4. Intraparticle diffusion kinetic plots.

Table 1. Adsorption Kinetic Parameters of MB on Absorbent

MB concentration		50 ppm	100 ppm
Pseudo-first-order	Q_e exp. (mg/g)	71.10	30.16
	Q_{e1} cal. (mg/g)	11.53	18.13
	K_1 (1/min)	0.0036	0.0027
	R_1^2	0.9587	0.8757
Pseudo-second-order	Q_{e2} cal. (mg/g)	70.92	31.54
	K_2 (g/(mg·min))	0.0013	0.0004
	R_2^2	0.9998	0.9975
Intraparticle diffusion	K_i (mg/(g·min$^{1/2}$))	0.5236	1.0748
	C	57.45	4.57
	R_3^2	0.8605	0.8485

As can be seen from Figure 2 and Table 1, the experimental Q_e is not in agreement with calculated Q_{e1} and the coefficients of determination R_1^2 (0.9587 and 0.8757) are low. Accordingly, the adsorption of MB onto the adsorbent did not follow the pseudo-first-order kinetic model. However the R_2^2 values were in range of 0.9975 to 0.9998 and the theoretical Q_{e2} values were closer to the experimental Q_e values, shown in Figure 3 and Table 1. The results demonstrated that the adsorption followed the pseudo-second-order kinetic model well. Figure 4 shows the plots of Q_t versus $t^{1/2}$. The data obtained from Figure 4 showed the two stage of adsorption. The first stage is the instantaneous adsorption, was completed within the first 3 h. The second stage is the gradual adsorption where the intraparticle diffusion is the rate limiting. Both the linear lines did not pass through the origin which suggested that the intraparticle diffusion was not the only limiting mechanism in the adsorption process (Morris and Weber, 1962). The R_3^2 values shown in Table 3 were lower than those for pseudo-first-order and pseudo-second-order models. Base on these results, it can be concluded that the pseudo-second-order kinetic model provided a good correlation for the adsorption of MB onto the adsorbent in contrast to the pseudo-first-order model and intraparticle diffusion model. This also suggested that the rate of the adsorption process was preferably controlled by chemical-sorption (Ho et al., 2000; Tan et al., 2008).

3.3. Adsorption Isotherm

The adsorption isotherms show how the adsorbates are distributed between the solution and the absorbent at the equilibrium conditions. Moreover, the adsorption isotherms can reveal the effect of equilibrium concentration on the adsorption capacity at different temperatures as well (Hameed et al., 2008).

The effect of MB equilibrium concentration on the adsorption capacity of the hemicellulose-based absorbent was carried out at 25, 35 and 45 °C and the results are shown in Figure 5.

It is clear that the absorption capacity of the hemicellulose-based adsorbent increased as the temperature increased (Figure 5). This is attributed to the increasing rate of diffusion of the MB molecules, partly owing to the decrease in the viscosity of the solution (Al-Ghouti et al., 2003). The equilibrium adsorption amount was of MB also affected by temperature, which was increased from 32.8 to 46.5 mg/g when the temperature was raised from 25 to 45 °C. The increase of absorption amount of MB onto hemicellulose-based absorbent with the increase of temperature suggests that the adsorption is endothermic.

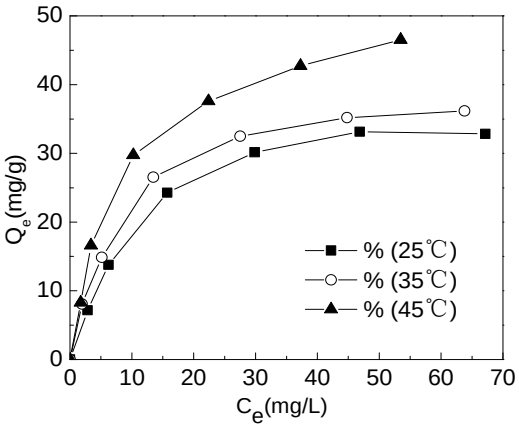

Figure 5. Adsorption isotherms for methylene blue onto the hemicellulose-based absorbent.

Langmuir and Freundlich isotherm models were used to fit the experimental data. Based on the Equations (6) and (7), the values of the models constants in addition to the values of the correlation coefficient were calculated by plotting $\ln Q_e/C_e$ versus Q_e and $\ln Q_e$ versus $\ln C_e$ from the slope and intercept at different temperatures. Figures 6 and 7 show the linear fits of Langmuir model and Freundlich model, respecttively. The isotherm parameters are shown in Table 2.

The Langmuir model assumes that the adsorption is a process which occurs in a homogeneous surface (Kumar et al., 2010). Figure 6 showed the linear Langmuir isotherm plot and the R_L^2 values at different temperatures were in range of 0.99 39 to 0.9982. The results indicated that the adsorption of the MB onto the hemicellulose-based adsorbent fitted the langmuir model well with the characteristic of the monolayer coverage of MB at the outer surface. The separation factor (D_L =

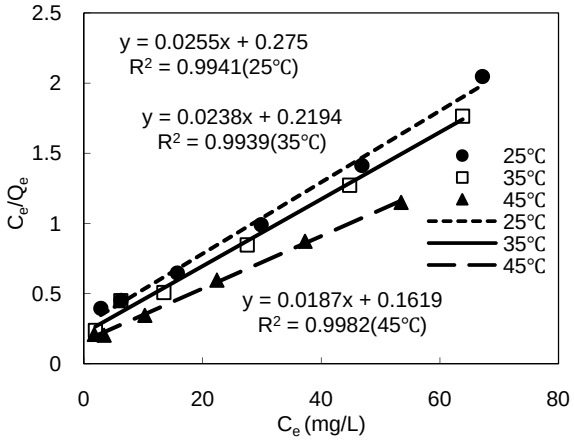

Figure 6. Linear fits of Langmuir model.

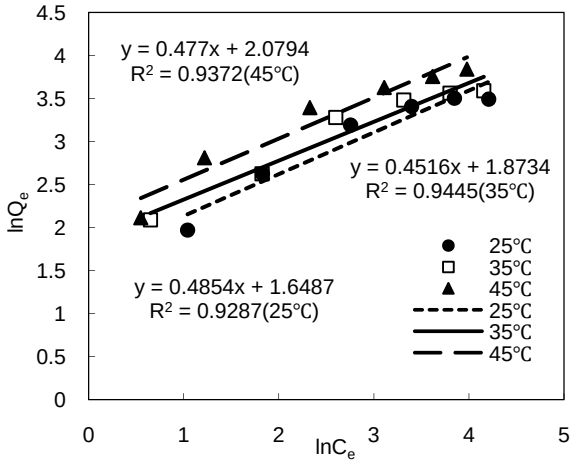

Figure 7. Linear fits of Langmuir model.

$1/(1 + K_LC_e)$) is an important parameter of the Langmuir isotherm that can be used to verify if the adsorption in the system is unfavorable ($D_L > 1$), linear ($D_L = 1$), favorable ($0 < D_L < 1$) or irreversible ($D_L = 0$) (Weber and Chakravo, 1974). The D_L values were in the range of 0.7967 to 0.9734, indicating that the adsorption system is favorable.

The Freundlich model assumes a hetegeneous adsorption surface (Cazetta et al., 2011). Figure 7 indicated the linear Freundlich isotherm plot and the R_F^2 values were lower than 0.9500, revealing that the adsorption system did not follow the Freundlich model. The heterogeneity factor (n) showed whether the adsorption process is linear (n = 1), chemical (n < 1) or physical (n > 1). According to the results shown in Table 2, the values of n were all higher than 2 at different temperatures, indicated that the adsorption is physical. Moreover the values of K_F and n increased as the temperature increased, indicating that the adsorption was favorable at high temperature (Sharma, 2010).

3.4. Adsorption Thermodynamics

The thermodynamic parameters of the adsorption process of MB onto the adsorbent are the changes in standard enthalpy, entropy and free energy. The standard enthalpy and standard entropy parameters are calculated from the slope and intercept of the plot of $\ln K_L$ versus 1/T yields, respectively (Figure 8).

The values of these parameters were calculated using Equations (8), (9) and (10) at various temperatures and are shown in Table 3.

The positive ΔH (8.70 KJ/mol) means that the adsorption process was carried out as endothermic at 25 to 45 °C. The positive value of ΔS (0.0670 KJ/mol) indicated the increased randomness at the solid-liquid interface and the affinity of the adsorbent for the MB (Nasuha and Hameed, 2011). The values of ΔG were all negative at difference temperatures, indicating that the adsorption was spontaneous. In general, the values of ΔG between 0 and -20 KJ/mol indicated that the adsorption process is physical-sorption, while the value in between -400 and -80 KJ/mol correspond to chemical-sorption (Weng et al., 2009; Fernandes et al., 2010). The values of ΔG suggested the adsorption is a physical-sorption process. The increase in negative ΔG value parallel to temperature revealed that adsorption of MB onto the adsorbent became more favorable at higher temperature. This was previously confirmed by the isotherm experiments at different temperatures.

Table 2. Isotherm Parameters of MB onto the Hemicellulose-Based Absorbent

T/°C	Langmuir			Freundlich		
	Q_{max} (mg/g)	K_L	R_L^2	K_F	n	R_F^2
25	39.22	0.0927	0.9941	5.2002	2.06	0.9287
35	42.02	0.1085	0.9939	6.5104	2.21	0.9445
45	53.48	0.1155	0.9982	7.9997	2.10	0.9372

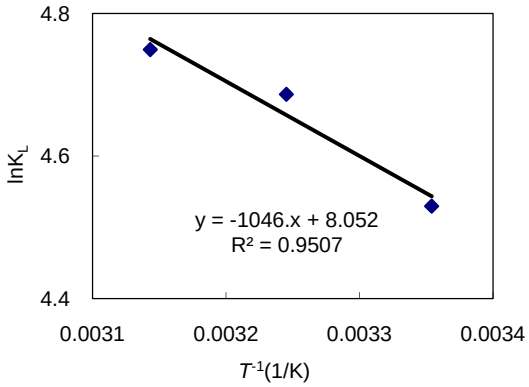

Figure 8. Plot of $\ln K_L$ versus 1/T.

Table 3. Adsorption Thermodynamics Data of MB onto the Absorbent

T/°C	⊿H (KJ/mol)	⊿S (KJ/mol)	⊿G (KJ/mol)
25	8.70	0.0670	-11.26
35			-11.93
45			-12.60

4. Conclusions

In this study, the hemicellulose-based absorbent for the removal of MB was developed along with the investigation of the adsorption equilibrium as well as the thermodynamic and the kinetics of adsorption using a batch system. The results showed that the as-prepared hemicellulose-based adsorbent presented very efficient absorption toward MB. The kinetic analysis demonstrated that the adsorption process follows the pseudo-second-order model well, which suggests that the process was controlled by chemical-sorption. Based on the linear models of Langmiur and Freunlich, the Langmuir isotherm model was better fitted to the experimental data, showing the maximum monolayer adsorption capacity of 39.22 mg/g at 25 °C. The thermodynamic parameters indicated that the adsorption of MB onto the hemicellulose-based adsorbent was an endothermic and spontaneous process. The values of ΔG suggested the adsorption is a physical-sorption process. The above results confirmed that the hemicellulsoe-based adsor-

bent is very promising absorbent for the removal of the dyes like MB from contaminated aqueous solutions; and the adsorption process combines physical-sorption and chemical-sortion.

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