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Adsorption of Methylene Blue on Prepared Charcoal from Molasses Waste

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ABSTRACT

Recently, important efforts have been made in an attempt to search for the cheapest and ecofriendly alternatives adsorbents. In the present work, waste molasses from Iraqi date palm (Zahdi) had been used as a provenance to produce charcoal for the removal of methylene blue (MB) dye from water. The optimum prepared charcoal was obtained at 150 C, by increasing temperature to 175 C, the charcoal had almost converted to ash. The obtained charcoal have been inspected for properties using scanning electron microscope (SEM), atomic force microscope (AFM), porosity and surface area. Adsorption data were optimized to Langmuir and Freundlich and adsorption parameters have been evaluated. The thermodynamic parameters like a change in Gipps energy (ΔG), enthalpy (ΔH) and entropy (ΔS). The effects of increasing temperature on adsorption capacity were investigated and the results indicate that pseudo-second-order kinetics model could be presented the adsorption dynamic data. The resultant values for the heat of adsorption and the free energy indicated that adsorption of methylene blue dye is preferred at low temperatures.

Keywords: Zahdi date, Methylene blue, molasses, dye removal

امتصاص الصبغة الزرقاء بواسطة الكاربون المحضر من مخلافات انتاج الدبس

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الخلاصة

مؤخرا اصبح من الواضح البحث عن الطرق الرخيصة و الصديقة للبيئة في عمل البحوث و السعي للحصول على احسن النتائج ومن ضمن المواضيح المهمة الامتصاص باستخدام مواد متوفرة و رخيصة. في هدا البحث تم استخدام فضلات عملية انتاج الدبس في صناعة الفحم بمواصفات عالية لامتصاص الصبغة الزرقاء بعد تجفيف الفضلات العملية انتاج الدبس يتم عملية الحرق بستخدام الفرن بدرجة حرارة 150 درجة مؤوية وكانت اعلى درجة يمكن الوصول اليها بدون تحول الى رماد. بعد الحصول على الفحم تم اجراء فحوص لمعرفة قابلية المادة للامتصاص و تكوين فكرة عن خواصها مثل فحص الالكتروني المصغر والحصول على صور للعينات بشكل مكبر و فحص الجزيئات و الذرات و اقطارها و معرفة الفراغات البينية و

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المساحة السطحية للعينات. وتم استخدام طرق المعايرة للنتائج ل لونكماير و فراندلج و معرفة احسن انتائج حيث كانت الافضل بستخدام معادلات الدرجة الثانية و عندما تكون درجات الحرارة اقل حيث استخدمت درجات الحرارة (25,30,45,65) و تم حساب الانثالبية و الانتروبية و طاقة كبس ورسم العلاقات لتوضيح فعالية المادة في الامتصاص.

1.INTRODUCTION

The draining of huge quantities of colored wastes (such as paper, plastics, textile, pharmaceutical industries, etc) into water has been considered as a worldwide problem **, Mulugeta, and Lelisa, 2014**. Globally, over than 10,000 commercial dyes being produced annually,**Mondalvol, 2008**. There is an estimation that about 10-15% of these produced dyes are lost and released with the effluent during the processes of dying, **Mohammed, et al., 2011**. Methylene blue is a well-known dye mostly used in wide range of industries involving textile, cosmetics, rubber, pharmaceutical as well as food industries , **Mohammed, et al., 2011**. MB can be considered as a typical example of relevant toxic dye with serious harmful effects on both human and aquatic environment ,**Ghorai, et al., ,2014**. Accordingly, it is momentously to handle these polluted wastewater using most effective and low-cost methods ,**Crini, 2006**. Adsorption is one of the different methods that have been experimented to eliminate dyes from wastewater and which found to be very effective in term of simplicity and economically low-cost, **Crini,2006, Khamparia, et al., 2015**. Adsorption is a physicochemical process in which variant types of molecules will depose on a surface**, Tehrani-Bagha, and Nikkar, 2013, Starch and Hart, 2014**. Variant kinds of carbons have been obtained from different agricultural as well as wood wastes and which is widely available and considered as environmentally friendly **Mulugeta and Lelisa 2014, Ekhlass, and Al-Taweil, 2015**. Waste molasses are produced from the extracted sugar syrup products that prepared from many types of dates palms and which considered as a well-known Iraqi meal especially in winter and one of the most abundant industry that is widely available in Iraq ,**Chechan and Mohyaddin, 2015**.

In this study, we used a type of date called (Zahdi) for many reasons including it is wide availability and a very cheap, it is the ability to store for long periods of time and its high level of invert sugar ,**MATLOOB and Mohammed, 2014**. In the current study, waste molasses of (Zahdi) date was used to prepare charcoal which was used as an alternative cheap and effective adsorbent for methylene blue dye.

2.EXPERIMENTAL WORK

The raw materials, the date (Zahdi) were washed several times with distilled water for removing dust, dirt and other impurities then the nuclei have been removed, and the date was boiled to 85 °C. After that, the sugar liquid syrup was separated and the waste molasses were collected, then Drying process had been applied for 12 hours using the dryer at 100 °C to ensure that any humidity has been removed. After drying process, the resultant waste molasses had been applied in a furnace at 150 °C for 6 hours in order to convert a solid waste of molasses to charcoal. Charcoal properties have been checked by SEM, AFM, Porosity and surface area.

A (150 mg/L) stock solution of Methylene blue was made by dissolving the desired quantities of methylene blue dye in distilled water. The study was established using 500 ml conical flasks by mixing a previously weighed amount of dye (MB) with the 0.25-gram charcoal prepared from waste molasses. An agitation has been applied to the solution at 150 rpm with stirrer at a constant temperature for every run (25, 30, 45 and 65℃). After shaking, the mixtures were centrifuged and filtrate, using spectrophotometer. The time interval for reading was (5, 15,25,35,45,60,75,90 and ∞), the MB removal was checked by spectrophotometer using 665 nm as the absorbance wavelength.

The amount of Methylene blue adsorbed per weight of charcoal adsorbent (adsorption capacity) at equilibrium (q_e, mg/g) was calculated from Eq. 1.

$$q_e = \frac{V \times (C_o - C_e)}{m} \tag{1}$$

Where q_e is the adsorption capacity of the adsorbent (mg/g), C_o and C_e (mg/l) refer to initial and terminal (equilibrium) concentrations of Methylene blue in the adsorption solution, respectively, also V (l) is the volume of the adsorption solution and m (g) is the weight of charcoal adsorbent used.

3.RESULTS AND DISCUSSION

3.1 Adsorbent Characterization

The weight of date (Zahdi) that had been used in this experiment was 1 kg. After the production of waste molasses, the weight was also obtained and found to be 350 gm. The net weight of the resultant 124 gm. The surface characteristics have been checked using various techniques such as scanning electron microscope (SEM) this test important to see the shapes of particles **Fig.2**, atomic force microscope (AFM), porosity and surface area. The results of AFM test is shown in **Table 1** when the average diameter of the particles was 63.71 nm, three dimensions picture shown in **Fig.1** and Granularity accumulation distribution in **chart 1**.

Table 1. Diameter of particles using AFM test.

Percent of particles	**Diameter in (nm)**
10% of particles	**30.00 nm**
50% of particles	**60.00 nm**
90% of particles	**95.00 nm**

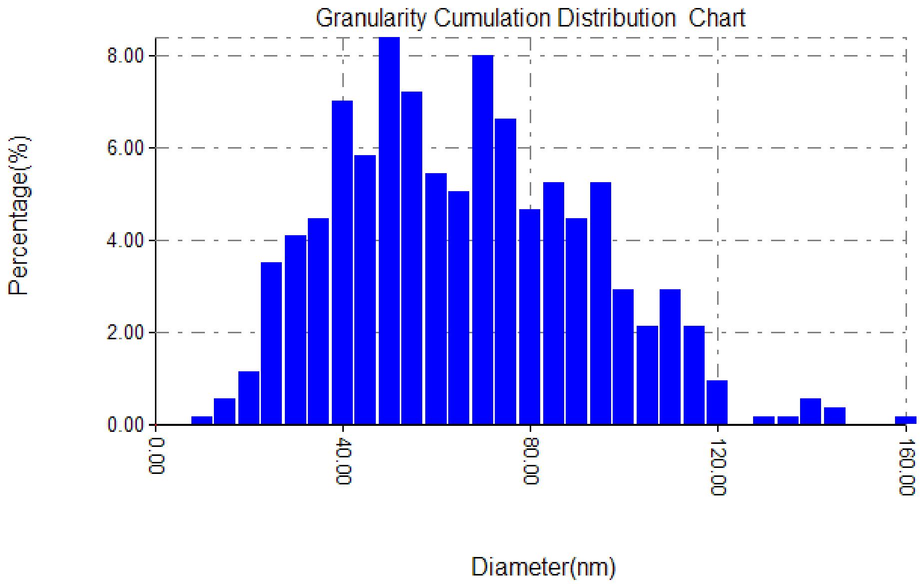

Chart 1. Granularity accumulation distribution chart.

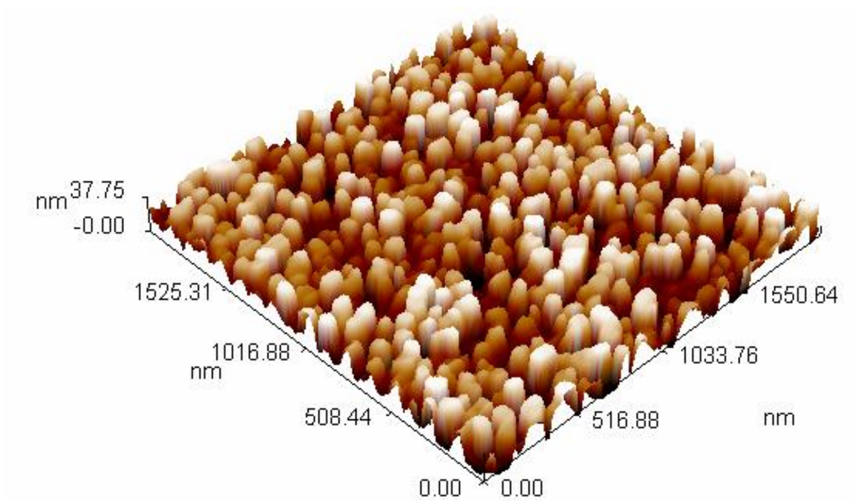

Figure 1. three dimension particular for AFM testing.

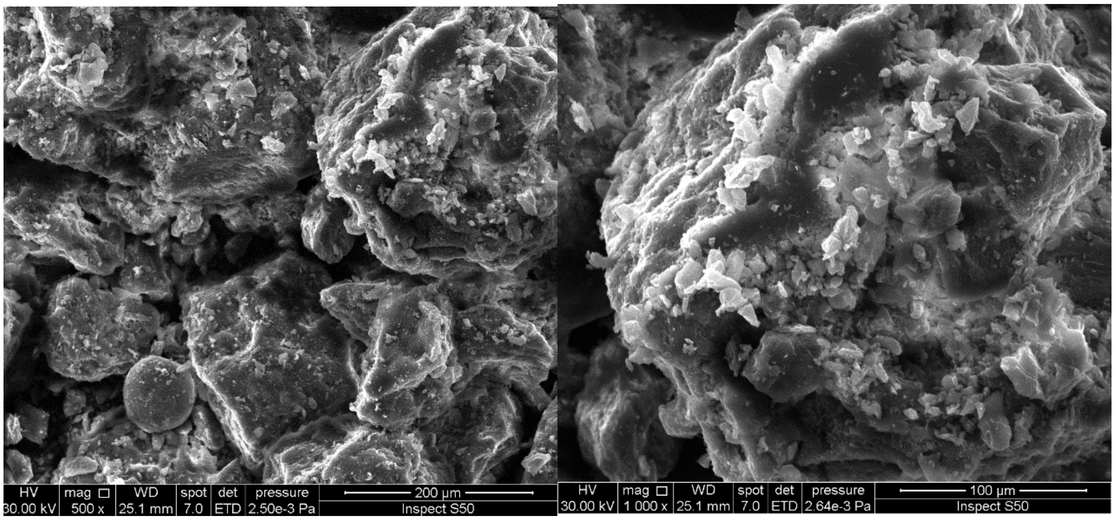

Figure 2. SEM electron images of the prepared charcoal.

3.2 Adsorption Results

According to the present work, equilibrium adsorption capacity (q_e) versus equilibrium concentration (Ce) of MB could be represented to obtain the behavior of adsorption capacity progresses process. **Fig. 3** Illustrates the directly proportional relation. As the Ce of the MB increased q_e increasing. The rate of removal of the adsorbate is higher in the beginning due to the increased surface area of the adsorbent available for the adsorption of ions dye

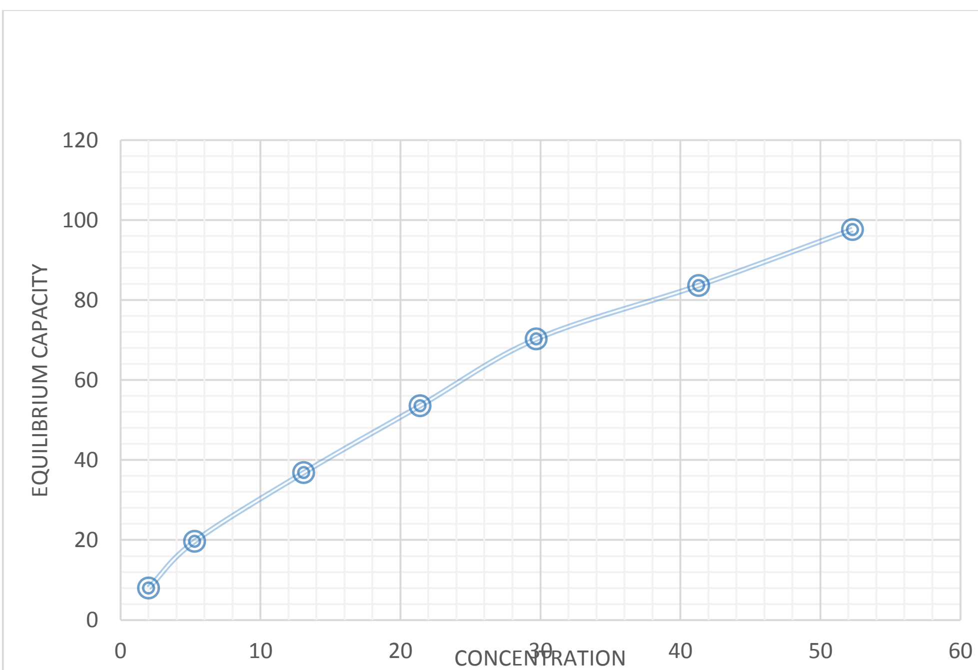

Figure 3. Equilibrium Methylene blue removal versus initial concentration after 24 h of adsorption at 25 °C.

3.3 Adsorption isotherms models

A simulated solution containing 150 mg/l of Methylene blue (150 mg of methylene blue per one liter of water) at 25 °C used to examine the adsorption isotherms. Most popular two-parameter isotherms were selected to describe the adsorption of Methylene blue on Charcoal **, Foo and Hameed, 2010, and Dada, et al., 2012**. These isotherms models are Langmuir and Freundlich.

3.3.1 Langmuir adsorption isotherm model

Langmuir isotherm model is an empirical model assuming that adsorption can only occur at a fixed Methylene blue of definitely contained sites without lateral interaction between the adsorbed molecules, **Abbas and Hussien, 2017**. According to this model, the adsorbed layer is one molecule in thickness or monolayer adsorption. Langmuir isotherm refers to a homogeneous process, which each molecule has constant enthalpy and sorption activation energy without transmigration of the adsorbate throughout the surface. The linear form of the Langmuir adsorption isotherm represented in Eq. (2).

$$\frac{1}{q_e} = \left[\frac{1}{q_m K_L}\right]\frac{1}{C_e} + \frac{1}{q_m} \qquad \textbf{(2)}$$

Where $q_m$is the maximum adsorption capacity in mg/g and $K_L$is the Langmuir isotherm constant energy or net enthalpy of adsorption in l/mg.

By plotting $\frac{1}{q_e}$ versus$\frac{1}{C_e}$, a straight line obtained with slope of $\left[\frac{1}{q_m K_L}\right]$ and intercept equal$\frac{1}{q_m}$, as shows in **Fig 4**. The determine value of slope was 0.2364 and the intercept was 0.0068 with 0.9992 correlation coefficient (R^2) value. Thus, the maximum value of adsorption capacity (q_m) was 147.06 mg/g and $K_L$was 0.02876 l/mg.

3.3.2 Freundlich adsorption isotherm model

Freundlich isotherm model is an empirical formula for multilayer, heterogeneous adsorption states describing the non-ideal and reversible adsorption process, **Freundlich, 1960**. The Freundlich equation is commonly given by the linear form shown in Eq. (3).

$$\ln q_e = \ln K_F + \frac{1}{n} ln\, C_e \qquad \textbf{(3)}$$

Where K_F is a Freundlich constant indicative of the relative adsorption capacity of the adsorbent (mg/g), and n is the intensity or the heterogeneity factor.

By plotting $\ln q_e$ versus $ln\, C_e$, a straight line obtained with slope of $\left[\frac{1}{n}\right]$ and intercept equal to $\ln K_F$, as shows in **Fig. 5**. The determine value of slope was 0.7606, consequently the relative adsorption capacity is 1.7022 mg/g. The intercept value was 1.63 therefore the intensity

(n) is 1.3147. The model correlation coefficient (R^2) value was 0.9959. When n = 1 so the partition between phases are independent of the concentration. If amount of n is above one (our finding) it will be a good indication for the normal adsorption. On the other hand, n being less than one meaning that cooperative adsorption occurs.

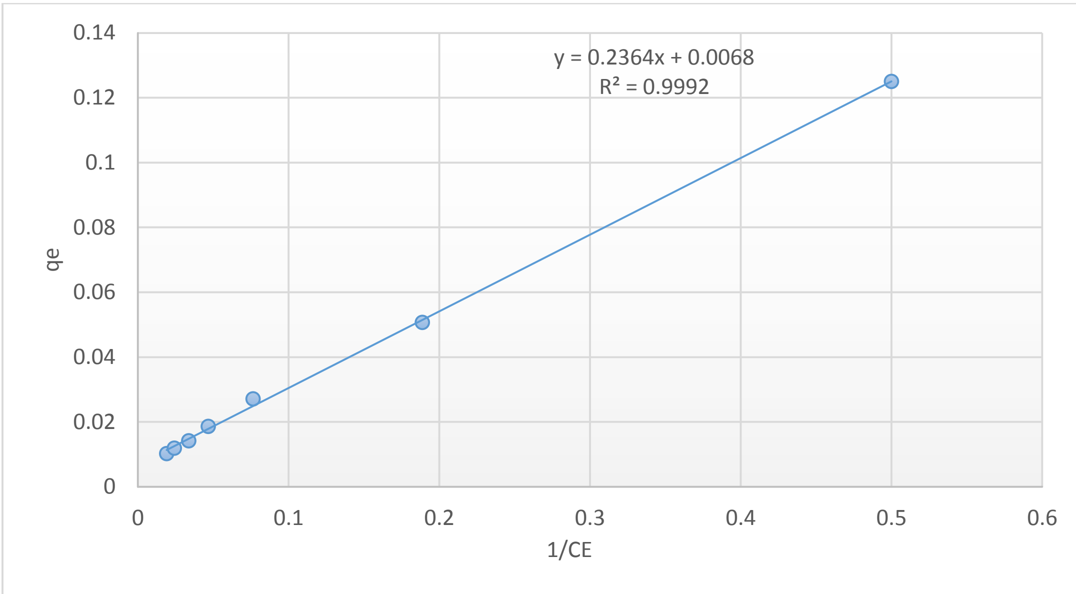

Figure 4. Langmuir isotherm model for adsorption of MB on Charcoal.

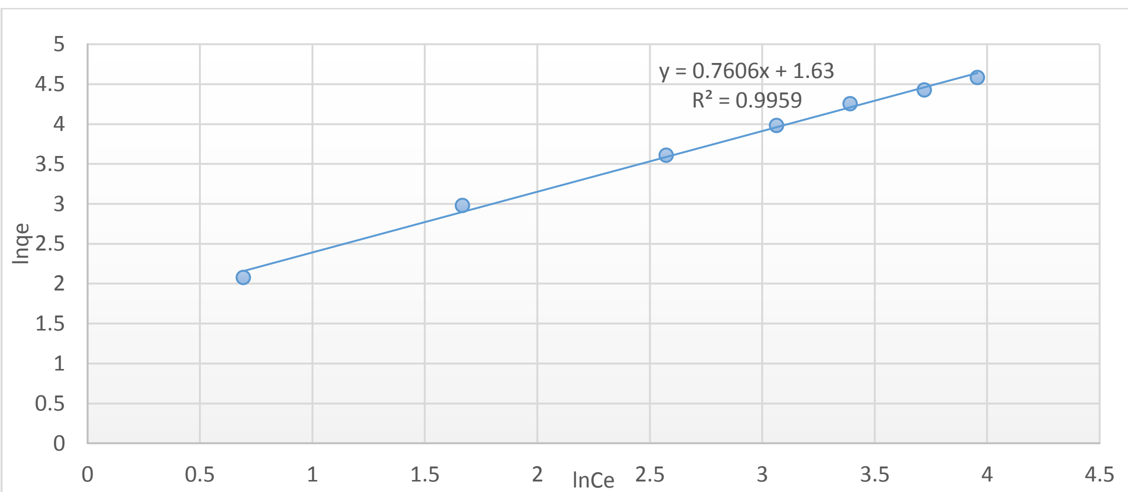

Figure 5. Freundlich isotherm model for adsorption of MB on Charcoal.

Table 2. Constants for different isotherm models.

Isotherm model	Model parameters	Parameter value	R^2
Langmuir	q_m, mg/g	147.06	0.9992
	K_L, l/mg	0.02876	
Freundlich	K_F, mg/g	1.7022	0.9959
	n, -	4.4308	

3.4 Kinetics of adsorption

The total removal of the Methylene blue was increasing sharply with the time during first 15 minutes and tend to unchanged very high after 35 minutes. This behavior was repeated for all experiments at different studied temperatures (25, 30, 45 and 65 °C), as shown in Figure 5. Also, Figure 6 shows that the adsorption capacity of Methylene blue was growing very fast from the beginning to 15 minutes, after that the adsorption capacity has a tendency to unaffected with time more than 35 minutes.

The MB removal was decreasing with temperatures. After 35 minutes, the lowest value of the total Methylene blue removal was 58.8% at 65 °C, while, the highest total MB removal value was 62.7% at 25 °C, **Fig. 5.** The drop in MB removal value was due to the decreasing of the Charcoal adsorption capacity from 156.7 to 147.0 mg/g when the temperature increasing from 25 to 65 °C, as shown in **Fig. 6**.

The adsorption capacity versus time data was used to examine the best adsorption models that represented the adsorption data of MB on Charcoal. Three kinetic models were used, namely; pseudo-first order [S. Lagergren1898], pseudo-second order **,Ho and McKay, 1999**, and intra-particle kinetic model, **Weber and Morris, 1963**. The linear form of these models (Equation 7 to 9) were solved by linear regression, **Tan and Hameed, 2017,** based on the least squares criterion, **Montgomery, et al., 2012,** to obtain the adsorption rate constants for each model at the different temperatures.

Pseudo-first order kinetic model: $ln(q_e - q_t) = lnq_e - k_1 t$ **(7)**

Pseudo-second order kinetic model: $\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e}$ **(8)**

Intra-particle kinetic model: $q_t = k_3 t^{\frac{1}{2}} + C$ **(9)**

Where q_e and q_t (in mg/g) are the adsorption capacity of Methylene blue at equilibrium and any time (t), respectively. k_1 (1/min), k_2 (g/mg.min) and k_3 (mg/g.min$^{1/2}$) are the adsorption rate constants for pseudo-first order, pseudo-second order and intra-particle kinetic model, respectively. Whereas C is an arbitrary constant. **Table 3** summarized the obtained rate constants at different temperature by least square technique.

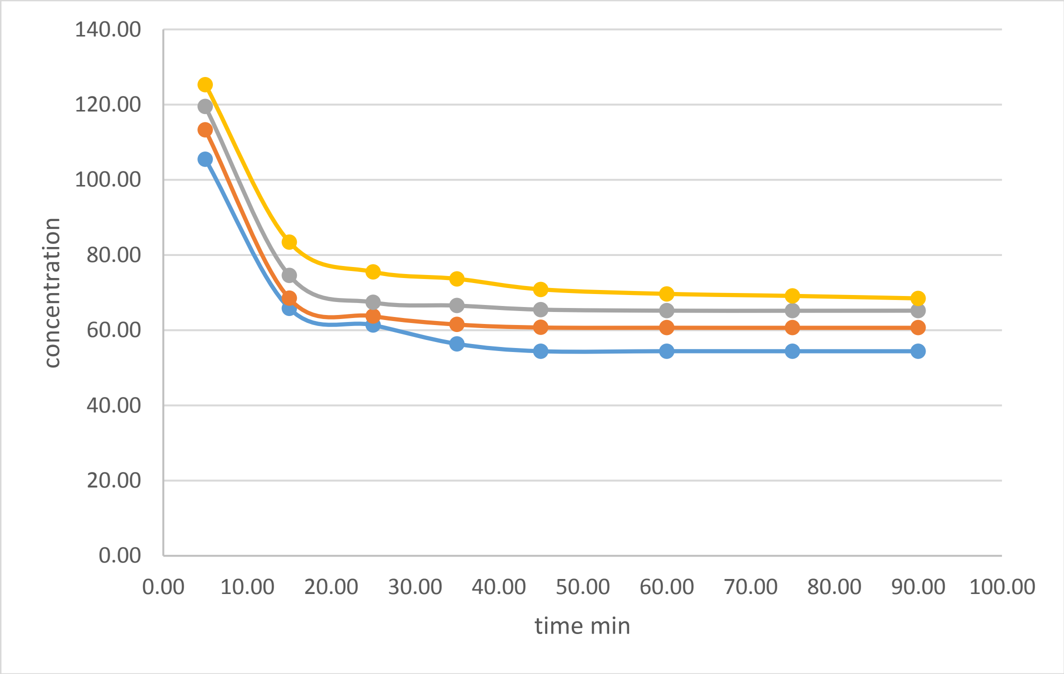

Figure 6. The effect of time on the MB removal at different temperatures.

Table 3. Rate constant values for adsorption of MB on Charcoal.

Adsorption kinetic model	Model rate constant	Model parameter value at temperature			
		25 °C	30°C	45 °C	65 °C
Pseudo-first order	k_1, (1/min)	4.5819	4.504	4.4462	3.7532
	q_e, (mg/g)	1.102	1.04	1.03	1.014
	R^2	0.47-0.7525			
Pseudo-second order	k_2, (g/mg.min)	3.81	3.86	4.81	7.63
	q_e, (mg/g)	26.46	24.45	18.9	11.81
	R^2	0.9981	0.9957	0.9931	0.9918
Intra-particle	k_3, (mg/g.min$^{1/2}$)	51.627	47.298	41.022	31.368
	R^2	0.5451-06532			

The values of the correlation coefficient calculated for the kinetic models with the obtained parameters indicate that the kinetic of organic removal by adsorption on Charcoal was superior behave as pseudo-second-order model (high R^2 for all temperatures) but did not fit well to the pseudo-first-order and intra-particle kinetic model. Environmentally, the pseudo-second-order kinetic model has frequently success to describe the adsorption data of organic substances from the aqueous solution. **, Guo, et al., 2009, Tan and Hameed 2017, Abbas and Hussien, 2017, Khenniche and Benissad-Aissani, 2010.**

Thermodynamic of Methylene blue adsorption on Charcoal

Thermodynamic behavior of the organic adsorption on CHARCHOL was investigated by estimation of different thermodynamic parameters. These parameters were the change in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS), and might found based on Equations 10 and 11 .

$$\Delta G = -\, RT\, ln(K_d) \quad \textbf{(10)}$$

$$\Delta G = \Delta H - T\Delta S \quad \textbf{(11)}$$

Where R is the gas constant (8.314 J/mol K) and T (K) is the absolute temperature of the adsorption process. Though K_d is the distribution coefficient for the adsorption of adsorbate (MB) at the adsorbent (Charcoal) surface and was calculated by Eq. 12.

$$K_d = \frac{q_e}{C_e}\left(\frac{m}{V}\right) \quad \textbf{(12)}$$

Where q_e is the adsorption capacity of the adsorbent (mg/g), C_e (mg/l) is equilibrium concentrations of MM in the adsorption solution, V (l) and m (g) are the volumes of the adsorption solution and the weight of Charcoal adsorbent used.

The calculated values of K_d (Eq. 12), then the values of ΔG (Eq. 10) were calculated, and finally the plot of ΔG versus T **see Fig. 7**, used to obtained ΔH (the intercept) and ΔS (negative value of the slop). The numerical values obtained summarized in **Table 4**.

Table 4. Numerical values obtained of the distribution coefficient and thermodynamic parameters versus temperature.

Temperature, K	K_d	Thermodynamic parameters			R^2
		ΔG, J/mol	ΔH, J/mol	ΔS, J/mol K	
298	1.762	-1404.0	1855.7	10.96	0.9978
303	1.797	-1477.2			
318	1.846	-1621.2			
338	1.933	-1851.4			

The negative value of ΔH (exothermic process) and the increase in ΔG with the temperature indicate that the adsorption process is more favorable at low temperature. However the negative value of ΔS realizing the decreasing in the randomness at the solution/solid interface during the adsorption of MB onto Charcoal, **Guo, et al., 2009, Abbas and Hussien, 2017, and Reddy and Dunn, 1986**.

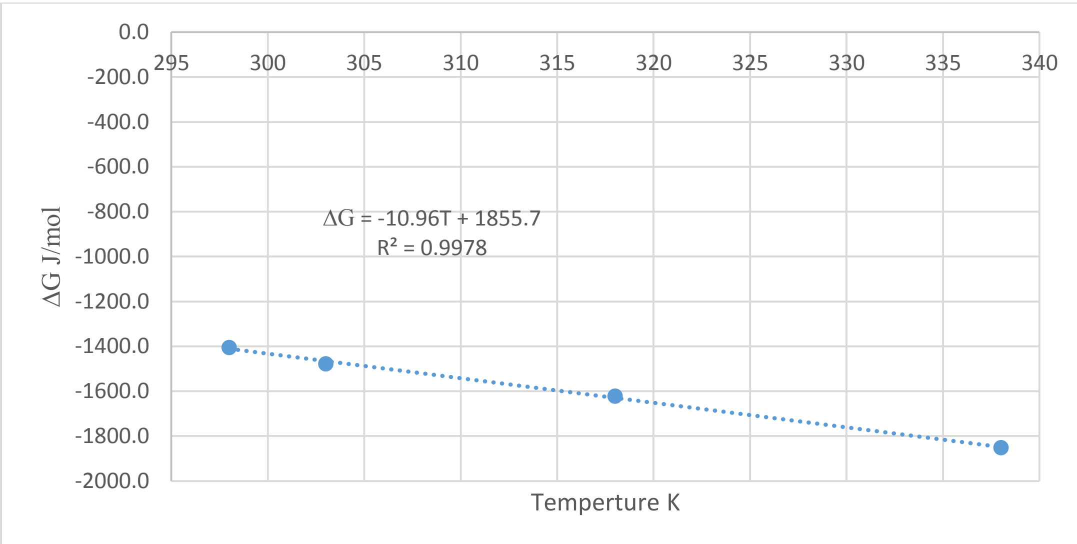

Figure 7. Plot of change in Gibbs free energy versus adsorption temperature.

4.CONCLUSION

Adsorption method may be one of the best techniques of separation processes due to its high efficiency and low-cost and environmentally friend to remove Methylene blue pollutants from industrial wastewater using bio-adsorbents Charcoal. The present results showed that the Charcoal which is obtained from waste molasses has the ability to remove Methylene blue from wastewater effectively. The equilibrium adsorption data could be represented by the Langmuir isotherm having (147.07 mg/g) maximum adsorption capacity. The adsorption process of MB on Charcoal was relatively fast during first 15 minutes. The MB adsorption process obviously followed the pseudo-second-order model. Thermodynamic results from the present work indicated that the adsorption of MB on Charcoal can be considered as spontaneously exothermic process and satisfactory at low temperature. The outcome from the current experiment revealed that the prepared charcoal from waste molasses has good properties in term of surface areas, porosity as well as adsorptive capacity. Furthermore, the result of the present work clarified that the adsorption process was relatively acceptable in different temperature, but the optimum adsorption magnitude was obtained at low temperature.

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