Thermodynamic Study of Adsorption Cationic Methylene Blue Dye on the Plant Residue

Majida Hameed Obaid
Chemistry Department/ College of Education for Women/ University of Kufa

الخلاصة
تم دراسة سلوكية الأمتزاز لصبغة المثلين الزرقاء القاعدية من المحلول المائي باستخدام الفحم المنشط لنوى التمر ونشارة الخشب . كما تم التحقق عن طريق تجارب متنوعة من تأثير زمن الاتزان والدالة الحامضية وكمية المادة الممتزة ودرجة الحرارة. وأوضحت النتائج ان الايزوثيرمات هي من نوع S_4 على سطح الفحم المنشط لنوى التمر وS_3 على سطح نشارة الخشب وفقا لتصنيف كيلز . اما ايزوثيرمات الامتزاز تنطبق مع ايزوثيرم فرندلش ولانكماير على سطح نشارة الخشب .وفرندلش فقط على سطح الفحم المنشط لنوى التمر . كما تم حساب القيم الثرموديناميكية ΔS, ΔG, ΔH. دلت النتائج على ان الامتزاز على السطحين فحم نوى التمر ومخلفات الخشب جيدة لإزالة الصبغة من المياه الملوثة.

Abstract
Equilibrium adsorption isotherm for the removal of basic dye Methylene Blue from aqueous solution using dates seeds-activated carbon and sawdust wood were studied. The effects of various experimental parameters such as contact time, effect of pH and adsorbent dosage and temperature of dye solution on the adsorption capacities have been investigated. The result shows the isotherms were S_3 on dates seeds - activated carbon and S_4 on sawdust wood according to Giels classification. Adsorption data was better fitted to the Langmuir and Freundlish isotherm on sawdust and fitted to the Freundlish only on activated carbon. The thermodynamic parameters such as $\Delta H°$, $\Delta G°$ and $\Delta S°$ of adsorption were calculated. The result in this study indicated that activated carbon from dates seeds and sawdust wood were attractive candidate for removing cationic dyes from the dye wastewater.

Introduction

Organic dyes are used widely in many modern industries, such as food, paper, rubber, plastics, cosmetics and textile, in order to color their products. Dyes released by the industries can get into the water bodies and eventually contaminate. Dye-polluted water can besides the effect to the environment, can cause deterioration in human's health by allergy reactions, dermatitis, skin irritation, cancer and mutation both in babies[1].Although Methylene Blue is not considered to be a very toxic dye, it can reveal very harmful effects on living things. After in halation's symptoms such as difficulties in breathing, vomiting and diarrhea can occur in humans[2].In this study dates' seeds and sawdust wood low-cost and easily available biomaterial, can be efficiently used as an excellent sorbent for the removal of dyes from wastewater. It can be safely concluded that sawdust much economic- al and an be an alternative to more costly adsorbents. A number of workers have used agricultural waste materials. They have studied for their capacity to remove dyes from aqueous solution, such as peanut hulls[3], maize bran[4], rice husk[5], orange peel[6], banana pith[7], cotton waste[8] and egg shell [9].

Experimental

Materials and Apparatus

- Methylene blue was obtained from Fluka and used without further purification. It has molecular formula C16H18N3SCl (mol. wt. 319.86g/mol). The structure of methylene blue is Shawn as follows figure.1

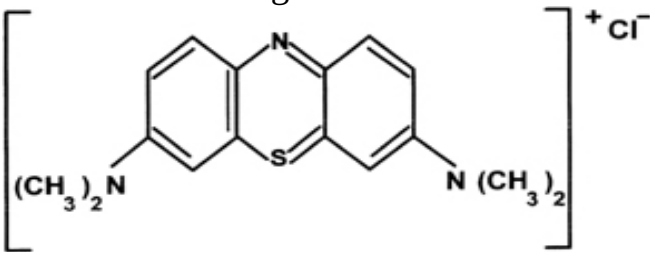

Figure 1: Chemical structure of Methylene blue.

-All spectral and absorbance measurements were carried out on ashimadzu Uv-Vis 1700 digital double beam recording spectrophotometer using 1cm glass cells.
-A digital pH meter 720WTW 82362 was used.
- The sawdust used in this experiment was collected from a local sawmill and washed repeatedly with distilled water and subsequently dried in sunlight until constant weight was maintained. It was sieved to500 μm size.
- Preparation of Activated Carbon
The dates seeds were first washed thoroughly with water to remove all foreign materials, mud and sticky sweet remnants of dates, then, dried in a drying oven at 100 C° to facilitate crushing and grinding. Activation ZnCl2 50g of the crushed dates seeds were soaked in (1M) ZnCl2 solution. The mixture was left overnight before carbonization. The seeds were carbonized in a Burning Furnace at 800 C° for 1 hour. The activated carbon was washed several times and dried in an oven at 100C° for 5 hour[10].

Experimental methods of adsorption

Adsorption experiments were carried out in thermostat shaker with speed 120rpm and 25 C° using conical flask containing 30ml of known initial concentration 3-18 ppm and (0.05,0.2)g amounts of adsorbents to dates seeds- activated carbon and sawdust wood respectively. Analytical determinations of Methylene blue in solution after equilibration 30min were estimated by measuring absorbance at maximum wavelength 663nm figure 2. using a spectrophotometer shimadzuTRUV754.

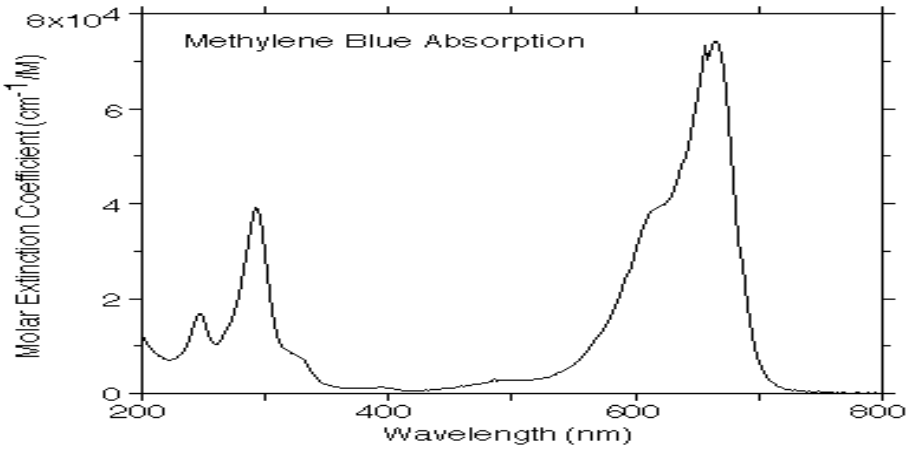

Figure 2: Spectrum of methylene blue.

The experiment were repeated at different temperatures (298,208,218,228)k . The amount of dyes adsorbed were calculated by the following equation :

$Qe= (C_\circ - Ce).V_{sol} / M$ ……..(1)

Factors affecting adsorption such as initial dye concentration ,pH, adsorbent dose, temperature and contact time were evaluated .

Result and Discussion

The equilibrium adsorption of MB dye was studied as a function of concentration. The amount of dye adsorbed Qe plotted against the equilibrium concentration Ce for MB, is given in figure 3. The equilibrium adsorption of MB increases with the increase of initial dye concentration, showing the adsorption process to be dependent on the initial concentration. A schematic of the interaction between the methylene blue molecule and sawdust wood surface is shown in figure 4.

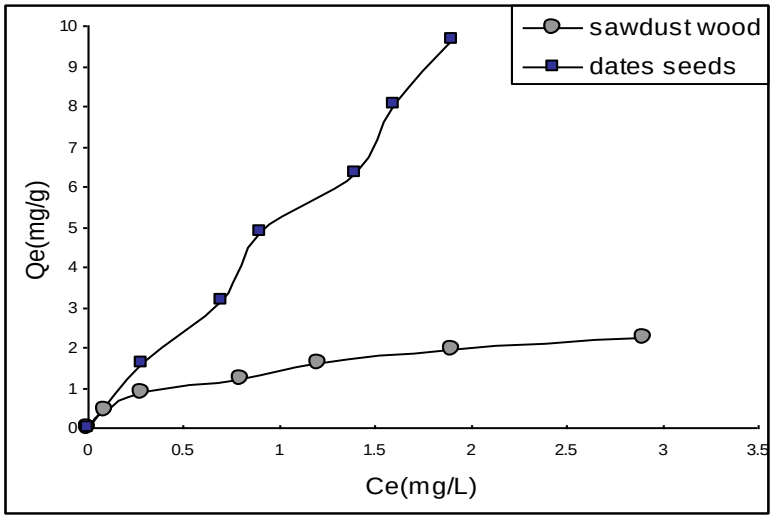

Figure 3: Equilibrium isotherms for MB adsorption by sawdust wood and activated carbon from dates seeds at pH=7

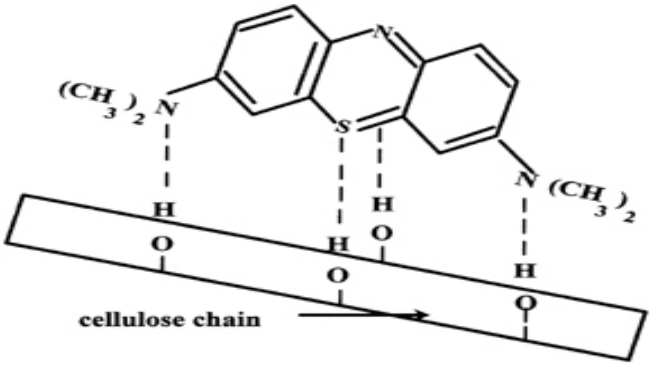

Figure 4: interaction of Methylene blue and sawdust wood

The Langmuir and Freundlich are the most frequently employed models to describe the equilibrium characteristics of adsorption isotherm . The linearised from of the Freundlich equation[11]is as follows :

$\log Qe = \log K_F + 1/n \log Ce$……..(2)

and the Langmuir equation[12] as follows :

$Ce / Qe = Ce /Q_m + 1/ (K_a . Q_m)$…….(3)

where Q_m (mg/g) and K_a (L/mg) are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The constants Q_m and K_a can be calculated from the plot between Ce/Qe versus Ce equation 3. Ce (mg/L) and Qe (mg/g) are the equilibrium concentration, and the amount of dye adsorbed at equilibrium, respectively figure 5. Similarly the Freundlich isotherm constants K_F and 1/n can be calculated from the plot log Qe versus log Ce equation 2. K_F(mg/g) , 1/n(L/g) and n are the Freundlich constants which are indicators of adsorption capacity and adsorption intensity, respectively[13] figure 6. The R^2 values goodness of fit criterion computed by linear regression for the two types of isotherms are presented in table 1. The data in table. 1 indicate that the Freundlich isotherm is best suited for adsorption of MB by Sawdust wood and Dates seeds respectively. The surface of dates seeds contain Carbone that don't bonding with the dye formed only interaction. But the surface of sawdust wood containing OH group that formed H-bond with the dye as in figure 4.

Table1: Freundlich and Langmuir parameters of adsorption isotherms for removal of MB

Adsorbents	Methylene blue					
	Freundlich Con.			Langmuir Con.		
	K_F	n	R^2	K_a	Q_m	R^2
Dates seeds	5.033	1.079	0.9845			0.1353
Sawdust wood	1.431	2.126	0.9915	1.476	3.976	0.9727

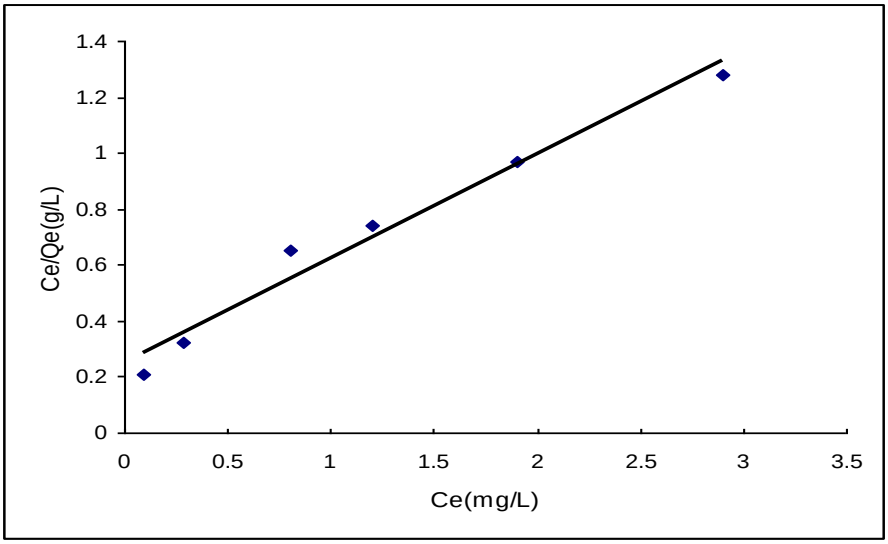

Figure 5: Langmuir adsorption isotherm of methylene blue onto sawdust wood

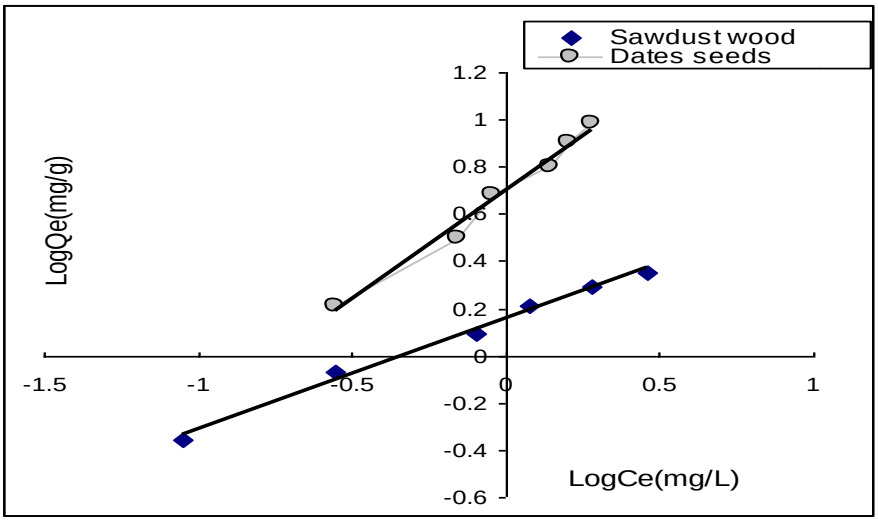

Figure 6: Freundlich adsorption isotherm of methylene blue onto sawdust wood and activated carbon from dates seeds at pH=7

Effect of initial solution pH

The effect of initial pH on two adsorbents of dye was examined over a range of pH values from3 to 11 and the results are presented in figure 7. Change of pH affects the surface charge of the adsorbents as well as the degree of ionization of different pollutants. The hydrogen ion and hydroxyl ions are adsorbed quite strongly and therefore the adsorption of other ions is affected by the pH of the solution. As the pH increases, it is usually expected that the cationic dye adsorption also increases due to increasing of the negative surface charge of adsorbents[14]. With increasing pH values the adsorption of MB on sawdust wood tends to increase, which can be explained by the electrostatic interaction of cationic MB species with the negatively charged hydrolyzed sawdust wood composite surface. A similar behavior for adsorption MB on wheat shells[15]. From the figure 7, it is evident that the maximum removal of MB color by activated carbon is observed at pH 7.

Similar trend of pH effect was observed for the adsorption of MB on activated carbon prepared from ricinus communes[16]. Low pH value leads to an increase in hydrogen ion H+ concentration in the system and the surface of the activated carbon acquires positive charge by absorbing H+ ions. On the other hand, increase of the pH value 7 led to increase of the number of negatively charged sites. As the dates seeds- activated carbon surface is negatively charged at high pH, a significantly strong electrostatic attraction appears between the negatively charged carbon surface and cationic dye molecule leading to maximum adsorption of dyes[17] from waste water.

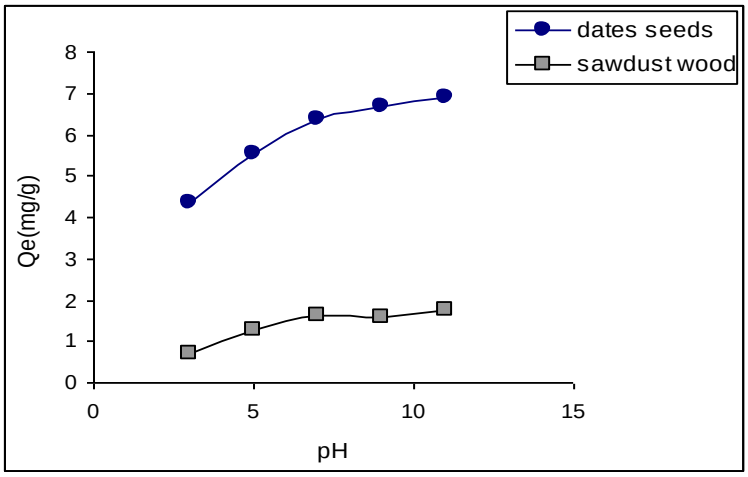

Figure 7: Influence of different pH on the adsorption of MB onto sawdust wood And activated carbon from dates seeds at pH=7

Effect of Temperature and Thermodynamic Parameters

The adsorption of MB on sawdust wood and activated carbon from dates seeds at four different temperatures has been carried out. MB adsorption decreased with increase in temperature because the adsorption is an exothermic process. This may also be explained on the basis that the solubility of the dyes is increased at higher temperature and adsorbate-adsorbent interactions decreased resulting into decreased adsorption. The general shapes of the dye adsorption on the two surfaces are given in figure 8and 9.

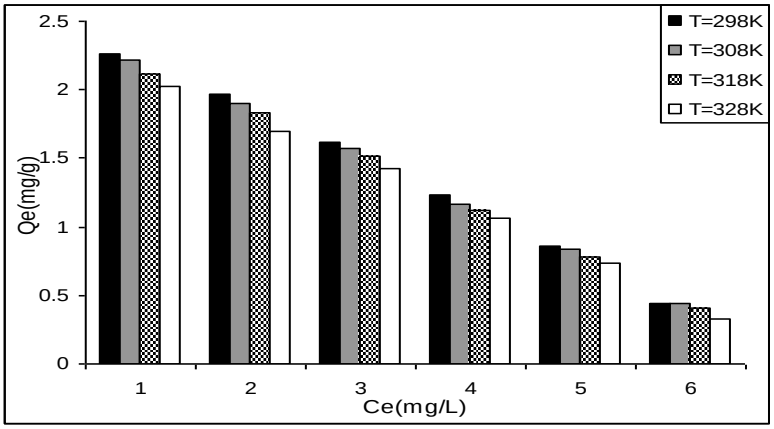

Figure 8: Adsorption isotherm of the MB on sawdust wood surface at different temperature

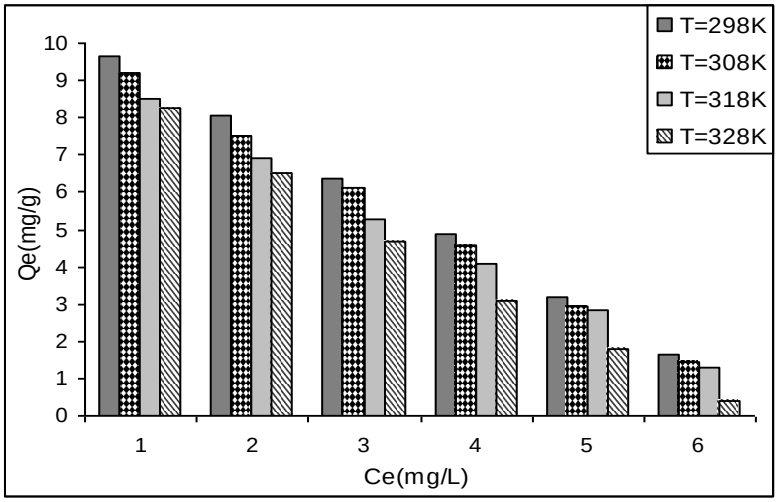

Figure 9: Adsorption isotherm of the MB on activated carbon from dates seeds surface at different temperature

The thermodynamic parameters for the adsorption nature of MB on two surfaces at various temperatures were calculated and listed in table 2. The values of free energy change ΔG^o, enthalpy change ΔH^o and entropy change ΔS^o were calculated to evaluate the thermodynamic feasibility of the process and to confirm the nature of the adsorption process, Based on the following literature available equations 4-6 .

$\Delta G^o = -$ RT Lin k ……..……(4)

log Xm = - ΔH^o\2.303 RT + constant ……(5)

$\Delta G^o = \Delta H^o - T \Delta S^o$ ……(6)

Where:

R: is the ideal gas constant 8.314 J/mol. k

T: is the absolute temperature

K: is the equilibrium constant for the adsorption process at each temperature[18].

Xm: is the maximum uptake of adsorption at a certain value of equilibrium concentration Ce that was fixed for all temperature of study[19].

Table2: Thermodynamic values of methylene blue using sawdust wood and activated carbon from dates seeds as an adsorbents.

Adsorbent	$-\Delta H$ kJ..mol^{-1}	$-\Delta G$ kJ..mol^{-1}	$-\Delta S$ kJ.mol^{-1}.k^{-1}
sawdust wood	3.217	0.744	0.008299
dates seeds	4.48	4.029	0.001513

The negative ΔH^o values indicates the exothermic nature of MB dye adsorption onto surfaces sawdust wood and activated carbon from dates seeds. The negative ΔG^o values confirm the spontaneous nature of adsorption process which indicates that better adsorption is obtained at low temperature. The negative ΔS^o values suggest the decrease in adsorbate concentration in solid – solution interface

indicating thereby the increase in sorbate concentration onto the solid phase. This is the normal consequence of the physical adsorption phenomenon, which takes phase through electrostatic interactions[20].

Conclusion

-The present investigation has shown that Sawdust wood can be effectively used as a raw material for the removal of MB dye from aqueous solution over a wide range of concentration.

- Activated carbon from dates seeds were obtained by chemical treatment, showing a high adsorption capacity for methylene blue dye from aqueous solution.

-The Freundlich adsorption isotherm was found to have the best fit to the experimental data.

-The activity of surfaces in adsorbing the dye was found to follow the order: activated

carbon from dates seeds > sawdust wood.

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