Hadhramout University Journal of Natural & Applied Sciences

Volume 16 | Issue 2 Article 4

2019

Thermodynamics and Kinetics Studies of Methylene Blue Adsorption Onto Yemeni Palm-Date Stones

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Abstract

A raw and baked date stones were used for the removal of methylene blue (MB) from aqueous solutions. The maximum adsorption capacity was 111 mg/g for raw and 41 mg/g for baked date stones with 10 mmol/l initial concentration of MB, 5 pH and 0.5 g/l adsorbent dose. The adsorption isotherm was found to follow the Langmuir model. Two simplified kinetic models including pseudo-first-order and pseudo-second-order equation were selected to follow the adsorption processes. Kinetic studies showed that the adsorption followed pseudo-second order model. Various thermodynamic parameters such as ΔH, ΔS and ΔG were evaluated. The results in this study indicated that the raw Yemeni palm-date stones could be employed as an effective adsorbent for the removal of MB from aqueous solutions.

Keywords: Date stones**,** Methylene blue, Adsorption, Isotherms, Kinetics.

Introduction:

Dyes are important hazardous substance found in textile, pharmaceutical, and plastic industries [19]. Waste water from food coloring rubber , plastics and cosmetics are polluted by dyes [6, 23]. The presence of very low concentration of dyes in these effluent (less than 1ppm for some dyes) is highly visible and undesirable [10, 24]. Some dyes are also carcinogenic and mutagenic [22]. Dyes are very stable to light, temperature and microbial attack, making them recalcitrant compounds [8].The largest class of dyes are azo compounds i.e. molecules with one or several azo (N=N) bridge slinking substituted aromatic structures [15].The azo dyes used widely both in textile and in research and teaching laboratories primarily and offer a greater resistance to photodegradation [13,17]. These dyes are hazardous as such and its degradation products like Naphtaquinone are still more carcinogenic [14].Various treatment methods for removing dyes from waste water were applied. The separation methods can be divided into physiochemical, chemical and biological methods [4, 26]. Adsorption process is one of the effective techniques that have been successfully employed for color removal from waste water. Physical characteristic of the adsorbent such as surface area, porosity, size distribution, density and surface charge have high influence in the adsorption processes [21]. Although commercial activated carbon (AC) is the most widely used adsorbent for dye removal, it is too expensive [7]. Recently agricultural waste biomass have been investigated intensively as adsorbent for removal of pollutant from aqueous solution. Because of these materials are cheaper, renewable and abundantly available [2]. Consequently, numerous low-cost alternative adsorbent have been proposed including chemically modified sugarcane bagasse lignin [11], coffee husk-based activated carbon [3], rice husk [25], synthetic calcium phosphate [1], natural untreated clay [16], fruit stone[20] and Cotton fiber [9].

Dates stone (DS) as one of the best candidate among the agricultural waste because it is cheap and quite abundant. Therefore, its recycling or reutilization is very useful [18]. Date stone are good metrical for preparing activated carbon (AC) as adsorbent removal of organic and inorganic matter [12].In our previous study[27] we use raw Yemeni palm-date stones as an effective adsorbent for the removal of Eriochrome black-T from aqueous solutions. We found that the adsorption equilibrium were best described by the Langmuir isotherm model, with maximum adsorption capacity 142 mg/g. The kinetics of the adsorption process was found to follow the pseudo first-order kinetic model, and the adsorption process is exothermic and spontaneous in nature at all temperature.

From the above, we find that it is very necessary to remove dye pollutants from waste water before discharge. The main objective of this work is to study and evaluate the adsorption performance of locally derived date stones for the removal of methylene blue (MB) from aqueous solutions to avoid environmental pollution. The methylene blue adsorption equilibrium and kinetics onto raw and treated date stones will be determined.

* Chemistry department, College of Science, Hadhramout University .Received on 22/1/2019 and Accepted for Publication on14/1/2020

Materials And Methods:

Materials:

I. Adsorbate: Methylene blue (MB) dye was chosen in this study because of its known strong adsorption onto solids, its recognized usefulness in characterizing adsorptive material, and is often serves as a model compound for removing organic contaminants and colored bodies from aqueous solutions. Methylene blue is a heterocyclic aromatic chemical compound with ($C_{16}H_{18}ClN_3S$, $3H_2O$) as molecular formula and a molecular weight of 373.9 g/mol. The structure of methylene blue is given in Fig.(1).

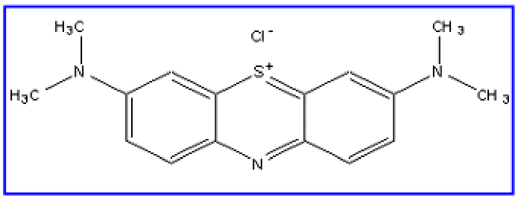


Fig.(1): Methylene Blue Structure

II. Adsorbent: Yemeni palm-date stones were used as adsorbent. Stones as received were first washed several times with distillated water to get rid of impurities, dried, crushed using disk mill, and sieved. Fraction of average particle size of 250 µm was selected for this study. Table (1) shows the properties of raw date stone. The content of moisture and ash were 8.8 % and 1.4% respectively. The bulk density was 0.76 g/ml. Baked date stones was prepared by filling powdered date stones into the 50- ceramic crucible with a lid and baked it in thermostatic oven at 250 °C for 3 hours.

Table (1): Properties of raw date stone

Properties	Value
Ash %	1.4
Moisture%	8.8
Bulk density (g/ml)	0.76
Particle size (µm)	250

Adsorption isotherms:

The equilibrium isotherms of MB adsorption on date stones were determined by performing adsorption tests in 100 ml Erlenmeyer flasks where 50 ml of MB solutions with different initial concentrations (0.1, 0.5, 1, 2, 5, 10, 20 mmol/l) was placed in each flask. The pH of the solutions was equal to five. A 0.5 g of date stones, with particle size of 250 µm, was added to each flask and placed on a magnetic stirrer with a thermostat to control the temperature to reach equilibrium. Then the samples were filtered and the residual concentrations of MB in the filtrate were analyzed by a UV-Visible Spectrophotometer (Jasco V-730) at maximum wave lengths of 665 nm. λ_{max} was determined by performing a scan on a MB solution sample by the spectrophotometer. A calibration curve of absorptivity versus MB concentrations form 0.001 to 0.01 mmol/l in deionized water was constructed as shown in Fig.(2). The relationship is represented by straight line equation (Absorptivity= 89.888 C + 0.0028). The correlation factor is R^2= 0.9992, over the studied range of concentrations.

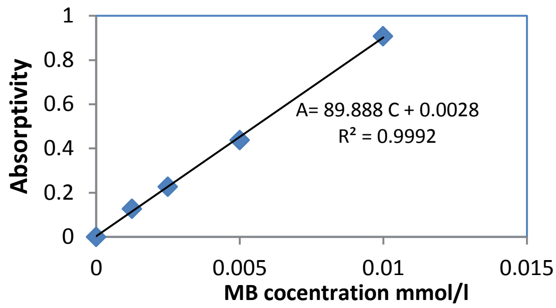


Fig.(2): Standard calibration curve

The uptake of MB at equilibrium, q_e (mg/g), was calculated by the following expression:

$$q_e = \frac{(C_o - C_e)\,V}{W} \qquad (1)$$

Where Co and Ce (mg/l) are the initial and equilibrium concentrations of MB solution, V (l) is the volume of solution, and W (g) is the weight of date stones. Two famous isotherm equations, namely the Langmuir equation (2) and Freundlich equation (3) were applied to fit the experimental isotherm data of MB adsorption on date stones. The equations can be written as:

$$q_e = \frac{q_L\, K_L C_e}{1 + K_L C_e} \qquad (2)$$

$$q_e = K_F\, C_e^{1/n} \qquad (3)$$

Where q_L (mg/g) is the Langmuir maximum uptake of MB per unit mass of date stones, K_L (l/mg) is the Langmuir constant related to rate of adsorption, K_F [(mg/g).(l/mg)] $^{1/n}$ and n are Freundlich constants which give a measure of adsorption capacity and adsorption intensity, respectively, Least-squares regression program based on Hooke-Jeeves and Gauss-Newton method was used to analyze experimental data. This program gave the parameters of each equation and the agreement between experimental and calculated data in terms of correlation coefficient R^2.

Adsorption kinetics

The procedure used for kinetic tests was identical to that used for equilibrium experiments. The aqueous samples were taken at present time intervals, and the concentrations of MB were similarly measured. The uptake of MB at time t, q_t (mg/g), was calculated by following expression:

$$q_t = \frac{(C_o - C_t)\,V}{W} \qquad (4)$$

Where, C_t (mg/l) is the liquid-phase concentration of MB solution at time t (min). Pseudo-first order model (5) and pseudo-second order model (6) were used to analyze the kinetic data. These models can be expressed as:

$$\ln(q_t - q_e) = \ln(q_e) - K_1 t \qquad (5)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{t}{q_e} \qquad (6)$$

Where q_e and q_t (mg/g) are the uptake of MB at equilibrium and at time t (min), respectively, K_1 (1/min) is the adsorption rate constant of first-order equation, K_2 (g/mg. min) is the rate constant of second-order equation.

Adsorption thermodynamics

Thermodynamic behavior of the adsorption of MB on date stones was evaluated by the thermodynamic parameters including the change in free energy (ΔG), enthalpy (ΔH), and entropy (ΔS). These parameters are calculated from the following equations:

$$\text{In}\,(K_d) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (7)$$

$$\Delta G = -RT\,\text{In}\,(K_d) \qquad (8)$$

$$K_d = \frac{q_e \cdot (W/V)}{C_e} \qquad (9)$$

Where, R is the universal gas constant (8.314 J/mole. K), T is temperature (K), and K_d is the distribution coefficient for the adsorption.

Results and discussion:

Effect of contact time on the adsorption:

The effect of contact time on adsorption of MB on date stones is shown in Fig. (3). The figure presented uptakes versus contact time with different initial concentration (0.1, 0.5, 1, 2, 5, 10, 20 mmol/l). The results show that the uptake of adsorbent increases rapidly with the increase of contact time at the first 15 min and remained constant after an equilibrium time was reached in about 30 minutes at lower concentrations from 0.1 to 2 mmol/l and 60 minutes at higher concentrations from 5 to 20 mmol/l. this is because at low concentrations the ratio of surface active sites to the total dye molecules in the solution is high and hence all dye molecules may interact with the activated carbon. The fast adsorption at the initial stage may be due to the higher driving force making fast transfer of MB ions to the surface of date stone particles and the availability of the uncovered surface area and the remaining active sites on the adsorbent [5]. The maximum uptake was 157 mg/g with 20 mmol/l initial concentration of MB.

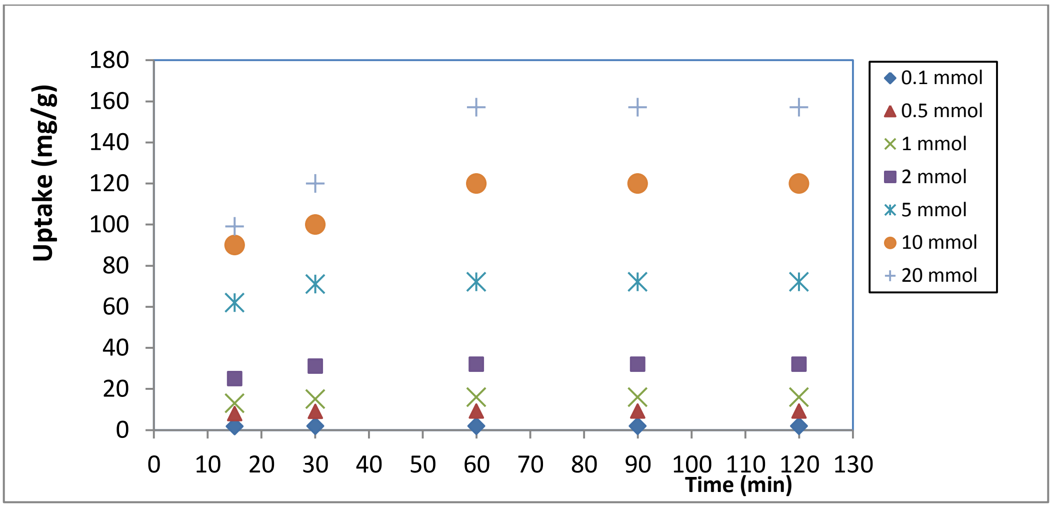


Fig.(3): Uptakes of MB versus time

Adsorption isotherms:

The experimental equilibrium data for MB adsorption on date stones calculated from Eq. (1), are fitted with Langmuir Eq. (2) and Freundlich isotherms Eq. (3). The results are presented in fig. (4) in the form of $1/q_e$ versus 1/Ce and in fig (5) in the form of Lnq_e versus Ln Ce. The comparison of correlation coefficients (R^2) of the linearized form of both equations indicates that the Langmuir model shows higher R^2 values and yields a better fit for the experimental equilibrium adsorption data than the Freundlich model of MB adsorption on both raw and baked date stones [5,13]. The maximum adsorption capacity was 111 mg/g for raw and 41 mg/g for baked date stones with 10 mmol/l initial concentration of MB. Since at baked temperature the pores get wider followed by collapsing and the micropores turn into mesoporses or macropores. So, the surface area and total pore volume of the baked date stones get smaller and the uptake decreases.

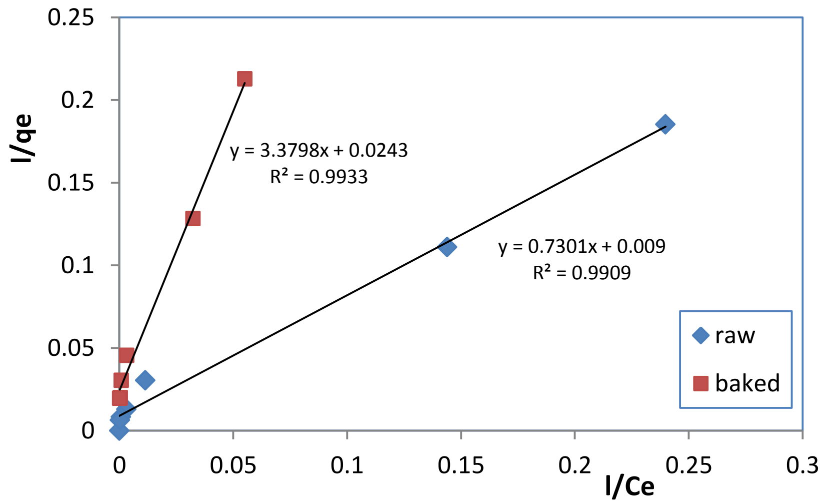
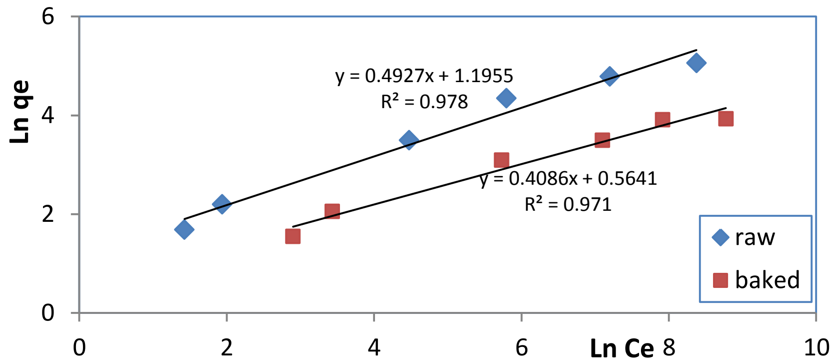


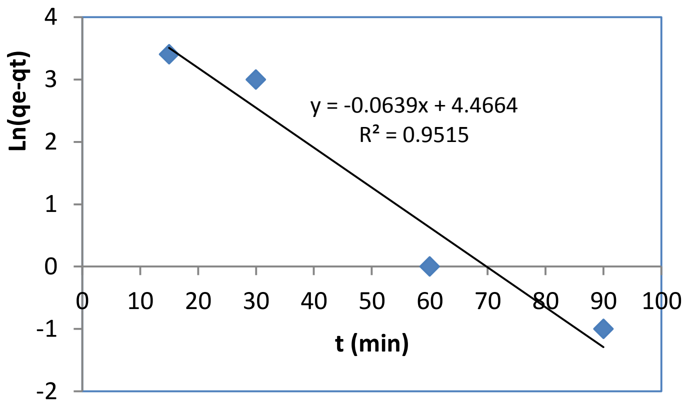
Fig.(4): Langmuir isotherm for raw and baked date stones



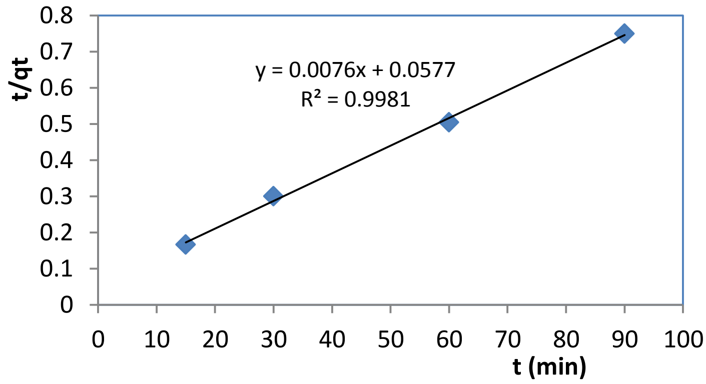
Fig(5): Freundlich isotherm for raw and baked date stones

Adsorption kinetics:

The experimental kinetic data for MB adsorption on date stones are fitted with pseudo-first order and pseudo-second order models Eqs. (5,6), and presented in Figs. (6,7) respectively with 10 mmol/l initial adsorbate concentration and 303 K. The linear plot of ln(qe-q_t) versus time for pseudo-first order equation is of low R^2 values as shown in Fig. (6) indicating a poor pseudo-first order fit to the experimental data. High R^2 values are obtained for the linear plot of t/q_t versus time for pseudo-second order equation as shown in Fig. (7). It can be seen that the pseudo-second order kinetic model better represented the adsorption kinetics and the calculated q_e values equal to 131.58 mg/g agree well with the experimental q_e values equal to 120 mg/g. This suggests that the adsorption of MB on date stones follows second-order kinetics [5,13].

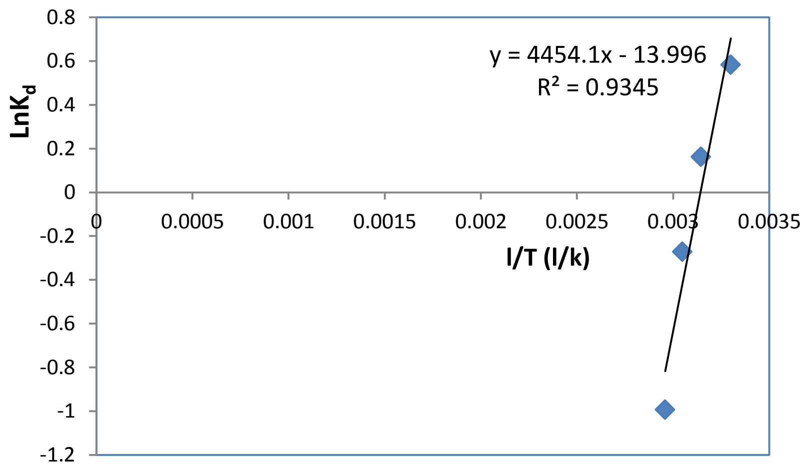


Fig(6): pseudo first-order kinetics for adsorption of MB at 303 K



Fig(7): pseudo second-order kinetics for adsorption of MB at 303 K

Adsorption thermodynamics:
According to Eqs. (7) the ΔH and ΔS parameters for adsorption of MB can be calculated from the slope and intercepts of the plot of In(K_d) versus 1/T Fig. (8). The values for Gibbs free energy change (ΔG) calculated from Eqs. (8) were -1470, -430, 742 and 2791 J/mole for MB adsorption on date stones at 303, 318, 328 and 338 K respectively. The adsorption process is thermodynamically spontaneous nature only at lower temperature due to negative ΔG values obtained and show an increase in feasibility of adsorption at lower temperature. The ΔH parameter was -37031 J/mole, the negative ΔH value is an indicator of exothermic nature of the adsorption. The ΔS values of adsorption was -116 J/mole, the negative ΔS value suggests an decrease in the randomness at sorbate-solution interface during the adsorption process. Thermodynamic parameters of MB adsorption on date stones were put in the table (2).



Fig(8): The plot of In(K_d) versus 1/T

Table (2): Thermodynamic parameters for adsorption process

T (K)	298	318	328	338
ΔG (J/mole)	-1470	-430	742	2791
ΔH (J/mole)	-37031	____	____	____
ΔS (J/mole.K)	-116	____	____	____

Conclusions:
The adsorption of MB from aqueous solution on date stones was studied. The uptake of adsorbent increases with the increase of contact time and reached equilibrium in about 30 minutes. The equilibrium data were best described by the Langmuir isotherm model, with maximum adsorption capacity 111 mg/g for raw and 41 mg/g for baked date stones. The kinetics of the adsorption process was found to follow the pseudo second- order kinetic model. On the other hand, the thermodynamic parameters indicate that the adsorption process is exothermic and spontaneous in nature only at lower temperature. As a result of this study, Raw Yemeni palm-date stones can be used without pretreatment as an effective adsorbent for the removal of methylene blue from aqueous solutions.

Acknowledgement:
we gratefully acknowledge Hadhramout university for assist and support of this work.

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دراسة ترموديناميكية وحركية امتزاز أزرق الميتلين على نوى التمر اليمني

عبدالرحمن يوسف وحود   سوسن عوض المقدي

ملخص

استخدم في هذه الدراسة نوى التمر الخام والمحمص في إزالة أزرق الميتلين من المحاليل المائية. وجد أن أيزوثيرم الامتزاز يتبع معادلة لانجمير. ووجد أن السعة العظمى كانت للخام 111 ملغ/غ والمحمص 41 ملغ/غ. أنجزت حركية الامتزاز على معادلتي الرتبة الأولى والثانية ووجد أن الحركية تتبع الرتبة الثانية. حسبت العوامل الثيرموديناميكية الأنتالبي والأنتروبي والطاقة الحرة للامتزاز. تدل نتائج الدراسة على أنه يمكن توظيف نوى التمر اليمني الخام بشكل فعال لإزالة أزرق الميتلين من محاليلها المائية.

الكلمات المفتاحية: نوى التمر، أزرق الميتلين، الامتزاز، أيزوثيرم، حركية.