Effective adsorption of basic dye onto different carbon kinds prepared from date stones based on Taguchi design method, kinetic and thermodynamic

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Abstract: Different kinds of carbon (Raw date stone, baked date stone and activated carbon) were prepared and characterized as inexpensive, high surface area, large micropore volume and Effective adsorbents. Material characterization was done using XRD, SEM-EDAX, FTIR and UV-Vis spectroscopy. The activated carbon (AC) possesses a surface area of 571 cm².g⁻¹. The micropore volume and total pore volume of AC were found to be 0.4785 cm³.g⁻¹ and 0.7267 cm³.g⁻¹ respectively. The effect of backing temperature and activation treatment on surface area and micropore volume were studied. Taguchi factorial design method was used to get the maximum MB dye adsorption onto the surface of AC sorbent. Contact time (60 min), initial dye concentration (10 mmol), adsorbent dosage (0.25g) and solution temperature (293 °K) were found to be the best conditions for the more effective absorption process.

Keywords: Date stone, Taguchi method, methylene blue, isotherms, kinetics

1. Introduction
Various kinds of precursors have been modified with different materials and methods to produce high surface activated carbon to remove undesirable dye stuffs from effluents and waste water in many countries worldwide for both environmental and water reuse concerns [1, 2]. Cationic Methylene blue (MB) dye (basic dye) is very carcinogenic and mutagenic, which is used in many industries like textile, paper, rubber, plastics, and cosmetics [3]. Various chemical methods were introduced to extract dyes from waste water, but many of them are expensive or require intensive energy [4, 5]. Agricultural wastes have recently been used as adsorbents in the dyes removal processes because they are cheap, sustainable and abundantly accessible [6, 7]. Various kinds of precursors have been modified with different materials and methods to produce high surface activated carbon (AC) such as coconut husk [8], rice husk [9], bamboo [10], fruit stone [11] and papaya leaves [12]. Among of these agricultural wastes, date stones (DS) considered as the best candidate because it is cheap and abundantly available [13]. Moreover, it has high surface area and it is easy be to treated and activated [14, 15]. Taguchi statistical method was used to find the ideal parameters for efficient and maximum adsorption capacity of MB dye with low experiments cost and less time consuming [16,17]. Dates
stone (DS) are typically disposed to fill the field with environmental issues, but it may be a good metric for preparing activated carbon (AC) as an adsorbent replacement of organic and inorganic matter [17]. In this study we will assess the performance of MB adsorption on raw treated date stone to remove MB from aqueous solutions to avoid pollution of the environment. The MB adsorption equilibrium and isotherms will be determined.

2. Materials And Methods

2.1 Materials

Adsorbate: MB (C_{16}H_{18}ClN_{3}S.3H_{2}O, MW=373.9 g/mol), in analytical grad, was used from Uni-Chem. It is recognized useful in characterizing adsorptive material for removing organic contaminants from aqueous solutions [18].

Adsorbent: Yemeni palm-date stones (DS) were washed several times with water, dried, crushed and sieved to 250 μm particle size. Baked date stones was prepared by filling powdered date stones into the 50- ceramic crucible with a lid and baked it at 150, 250,350 °C for 3 hours. The samples were labeled as (DS150, DS250 and DS350) respectively. Activated carbon was prepared by soaked DS powder in (30%) KOH at room temperature with 1:5 weight ratio (DS:KOH) for 24 hour, the solution was shaken from time to another. Potassium hydroxide was decanted and the impregnated sample was put in porcelain crucible which was tightly covered. The sample was carbonized at a temperature of to 375°C in a muffle furnace for 2 hour. Then the sample was cooled and washed firstly with H_{2}SO_{4} (0.01 M) and then with distilled water until pH reached 7. After that, sample was filtrated, dried and labeled as (AC). All samples were preserved in airtight bottle for use as adsorbents.

2.2. Adsorption Isotherms

A 0.25 g of each adsorbent was add to 50 ml of MB solutions with different concentrations (1, 2, 5, 10 mmol/l) and placed on a magnetic stirrer with a thermostat to control the temperature to reach equilibrium. The samples were filtered and the absorbance of filtrates were measured by a UV-Vis Spectrophotometer (Jasco V-730) at λmax = 665 nm. Two very popular isothermic models were applied namely Langmuir (2) and Freundlich (3). The equilibrium isotherms of MB adsorption on date stones is calculated by conducting adsorption tests in 100 ml Erlenmeyer flasks where 50 ml of different initial concentrations (1, 2, 5, 10 mmol/l) was placed in each flask. The solution's pH equalled five. A 0.25 g of date stones having particle size of 250 μm, was added to each flask.

Equation (1) was used to calculate the uptake, q_{e} (mg/g). Two very famous equilibrium isotherm models including Langmuir (2) and Freundlich (3) were applied

\[ q_{e} = \frac{(C_{0} - C_{e})V}{W} \]  

(1)

\[ q_{e} = \frac{q_{L}K_{L}C_{e}}{1 + K_{L}C_{e}} \]  

(2)

\[ q_{e} = K_{F}C_{e}^{1/n} \]  

(3)

Where C_{0} and C_{e} (mg/l) present the initial and equilibrium concentrations and (V) is the volume of solution. W (g) is the weight of date stones and the Langmuir constants are q_{L} (mg/g) and K_{L} (l/mg), while K_{F} [(mg/g).(l/mg)] and (n) are Freundlich constants. The higher coefficient of correlation R_{2}, the most fitting agreement between experimental and measured isotherm model results.

2.3. Surface area and pore structure calculation

Equations (4, 5, 6) were used to calculate surface area, micro pore volume (Vm) and total pore volume (Vt) of the samples [19]:
S\left( \text{cm}^2 \cdot \text{g}^{-1} \right) = 2.28 \times 10^2 - 1.01 \times 10^{-1} \text{MBN} + 3.00 \times 10^{-4} \text{IN} + 1.05 \times 10^{-4} \text{MBN}^2 + 2.00 \times 10^{-4} \text{IN}^2 + 9.38 \times 10^{-4} \text{MBN IN} \quad (4)

V_m\left( \text{cm}^3 \cdot \text{g}^{-1} \right) = 5.60 \times 10^{-2} - 1.00 \times 10^{-3} \text{MBN} + 1.55 \times 10^{-4} \text{IN} + 7.00 \times 10^{-6} \text{MBN}^2 + 1.00 \times 10^{-7} \text{IN}^2 - 1.18 \times 10^{-7} \text{MBN IN} \quad (5)

V_t\left( \text{cm}^3 \cdot \text{g}^{-1} \right) = 1.37 \times 10^{-1} + 1.9 \times 10^{-3} \text{MBN} + 1 \times 10^{-4} \text{IN} \quad (6)

Where: (IN) is iodine number and (MBN) is methylene blue number.

2.4 Taguchi statistical method

A standard L27 array was used to conduct a set of experiments and to determine the ideal conditions for MB adsorption process [15,16], four factors with three levels were selected in Table 1, and the higher S/N (signal to noise) ratio (7) was chosen as the better experiment conditions.

\[
\frac{S}{N} = 10 \log \left( \frac{1}{Y_1^2} + \frac{1}{Y_2^2} + \ldots + \frac{1}{Y_n^2} \right) \quad (7)
\]

Where: n the number of replicates and y is the experimental value.

| Factor                  | Level 1 | Level 2 | Level 3 |
|-------------------------|---------|---------|---------|
| Contact time (min)      | 15      | 30      | 60      |
| Initial conc. (mmol)    | 2       | 5       | 10      |
| Adsorbent dosage (g)    | 0.25    | 0.5     | 1       |
| Temperature (K)         | 293     | 313     | 333     |

2.5 Adsorption kinetics

Two simple models pseudo-first-order model (8) and pseudo-second-order model (9) were used. The aqueous samples were taken at present time intervals, and the concentrations of MB were similarly measured:

\[
\ln \left( q_t - q_e \right) = \ln \left( q_e \right) - K_1 t \quad (8)
\]

\[
\frac{t}{q_t} = \frac{t}{K_2 q_e} + \frac{t}{q_e} \quad (9)
\]

Where \( q_t \) and \( q_e \) (mg/g) are the uptakes at time t (min), \( K_1 \) (1/min) and \( K_2 \) (g/mg. min) are the first-order and second-order equation constants respectively.

2.6 Adsorption thermodynamics

The free energy (\( \Delta G \)), enthalpy (\( \Delta H \)), and entropy (\( \Delta S \)) parameters were estimated by (10, 11, 12) to evaluate the adsorption thermodynamic:

\[
\ln(K_d) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (10)
\]

\[
\Delta G = -RT \ln(K_d) \quad (11)
\]
\[ K_d = \frac{q_e \cdot (W/V)}{C_e} \]  

Where, \( R \) equal to 8.314 (J/mole. K), \( T \) (K) temperature, \( K_d \) distribution coefficient.

3. Results and discussion

3.1 Characterizations of the Adsorbents

The metals present in the raw date stone, including potassium, calcium, magnesium, phosphor and nitrogen as major constituents and copper, ferrous, sodium, zinc and manganese as minor constituents, were put in Table 2. The concentration of these metals are very low, thus the DS samples used in this study can be used in removing these toxic metals from waste waters [7] and the present of these metals depends mainly on the material sources.

Table 2: Metal content of the raw date stone

| Elements | mg/Kg | % |
|----------|-------|---|
|          |       |   |
| Cu       | 14    | 0.04 |
| Fe       | 121.4 | 0.05 |
| Mn       | 8.0   | 0.13 |
| Zn       | 17.4  | 0.39 |
| Na       | 162   | 0.57 |
| Ca       |       |     |
| Mg       |       |     |
| P        |       |     |
| K        |       |     |
| N        |       |     |

Table 2 summarized some of physical properties of different carbon kinds prepared from date stone. It shows the ash values of the raw date stone is 1.4 %, which reflects the low amount of inorganic substituent present in date stone under studied comparing with the ash content of most the agricultural products which is within 0.2-13.4 % [20]. The moisture content tended to be low for DS samples used in this study indicating that these DS samples were properly prepared and handled well. The Bulk density is dependent on an organic matter, texture and packing arrangement. Generally, well rich in organic matter have lower bulk density. The bulk density was 0.76 g.ml\(^{-1}\) for DS. The bulk density of the baked date stone samples increases with increasing the treated temperature but it decreases with chemical activation, because chemical activation process makes more microporosity and less metal content in the produced activated carbon. The surface areas and pores volumes for all samples were calculated from equations (4,5,6) and put in the table 3. The results show that the surface areas and pores volumes were decreased by thermal treatment, the higher the treated temperature the lower the surface area and pore volume that’s because micropore widening followed by collapsing occurred during thermal treatment and the micropores turned into meso or macropores. But the surface areas and pore volumes increase by chemical activation because it is led to development of micropores in the resulting activated carbon, so increasing number of pores in the surface unite and increases activated sites.

Table 3: Properties of treated date stone samples

| Properties                  | DS          | DS150       | DS250       | DS350       | AC          |
|-----------------------------|-------------|-------------|-------------|-------------|-------------|
| Ash %                       | 1.4         | 1.6         | 1.7         | 1.9         | 0.9         |
| Moisture %                  | 8.8         | 7.8         | 7.9         | 8.1         | 1.3         |
| Bulk density (g/ml)         | 0.76        | 0.78        | 0.79        | 0.81        | 0.2         |
| Iodine number (mg/g)        | 552.01      | 475.88      | 285.52      | 209.38      | 610.54      |
| Surface area (m\(^2\)/g)   | 563.27      | 450.91      | 336.97      | 299.78      | 704.65      |
| Micropore volume (cm\(^3\)/g) | 0.1545   | 0.1161      | 0.0778      | 0.0691      | 0.9965      |
| Total pore volume (cm\(^3\)/g) | 0.4031  | 0.3708      | 0.2435      | 0.2086      | 1.0055      |

The FT-IR spectrum (Figure 1-a) of the raw material displays a number of adsorption peaks. The broad band around 3400 cm\(^{-1}\) can be O-H stretching of hydroxyl groups, while the double peaks at 2924 cm\(^{-1}\) and 2854 cm\(^{-1}\) may be due to C-H stretching. The strong band at 1745cm\(^{-1}\) is related to stretching C=O carbonyl group. The band 1634 cm\(^{-1}\) due to C=C aromatic stretching. While the spectra(Figure 1-b) of date stone after activation by KOH 30 % reveals development of the surface texture, band
appearance at 2350 cm\(^{-1}\) may be for N≡N or C≡C. Two bands were appeared at 1745 and 1434 like a highly formation of oxygen functional groups they related to C≡O conjugated with C≡C stretching or with another C≡O stretching in carboxylic groups [20]. A new broad band at 1000–1300 cm\(^{-1}\) for C–O stretching in acids, alcohols, phenols, ethers and esters groups [17]. This indicates an increasing in the oxygen content on the surface after activation process.

![Figure 1](image1.png)

**Figure 1.** FT-IR spectrums (a) for DS and (b) for AC.

The SEM image of AC (Figure 2) shows that the average particle size was about 100 \(\mu\)m with average micropore size 10 nm and the relatively height of oxygen peak in the EDX spectrum of AC (Figure 3) indicate high content of oxygen on the surface of the activated carbon. The XRD data for AC particle (Figure 4) shows that all the peaks are related to octetcarbon C\(_8\) cubic crystallite which were confirmed with the standard JCPDS data (P63/mmc).

![Figure 2](image2.png)

**Figure 2.** The SEM image of the AC.

![Figure 3](image3.png)

**Figure 3.** The EDX spectrum of the AC.
3.2 Effect of Contact Time and Initial Concentration on the Adsorption Capacity

To study the effect of contact time and initial concentration on adsorption, the uptakes were presented versus different time intervals (15, 30, 60, 90 and 120 min) with different concentrations (1, 2, 5 and 10 mmol/L) in Figure 5 for DS and Figure 6 for AC adsorbents. The results show that the adsorbent uptake increases rapidly with the increasing of contact time at first 30 min. and remained constant after 60 min. That is because at the beginning the ratio of surface active sites to dye molecules is high and present large binding sites for adsorption at the initial stage. Maximum uptake was 120 mg/g, 72 mg/g, 32 mg/g and 16 mg/g for DS adsorbent and 596 mg/g, 310 mg/g, 154 mg/g and 62 mg/g for AC adsorbent with 10 mmol/l, 5 mmol/l, 2 mmol/l and 1 mmol/l initial MB concentration respectively, so it’s clear that the adsorption capacity dependent on initial dye concentration which provides necessary driving force making fast transfer of dye ions between the aqueous and solid phase[11].

Figure 5. Uptakes for MB adsorption onto DS
3.3 Effects of Parameters on the Adsorption Process

Taguchi factorial modeling approach was used to test the effects of parameters on the adsorption of MB dye on the absorbent AC. The results (table 4) show that the uptake of MB varied from 71 mg/g to 525 mg/g, and S/N ratios varied from 37.02 to 54.40. From table 5 and Figure 7, level 3 was found to be the best for each contact time and initial dye concentration factors. Level 1 was found to be the best for absorbent dosage and temperature factors. On the other hand, the order of importance of factors for the MB adsorption into AC is initial dye concentration, contact time, absorbent dosage and temperature respectively, and the best uptake amount of MB dye 525 mg/g with ideal conditions is very close to this experimentally achieved 596 mg/g. From Figure 7, it is clear that the contact time and MB initial concentration are important parameters and the highest MB uptake reached at contact time 60 min and 5 mmol initial concentration, both of them at the third level. This may be due to a lot of pores and active sites on the AC adsorbent surface are available. On the other hand, by increasing adsorbent dosage and temperature, the MB dye uptake decreases and the lowest value was achieved at level 3 of absorbent dosage (0.25g) and temperature (333°K).

3.4 Adsorption Isotherms

Two different two-parameter isotherm equations were represented in the form of 1/qe versus 1/Ce for in Figure 8 Langmuir isotherms (2) and in the form of Log qe versus Log Ce in Figure 9 for Freundlich isotherms (3). A comparison of correlation coefficients (R^2) of equations shows that the Langmuir model have higher R^2 values than the Freundlich model, and it has a better fit for MB adsorption onto both DS and AC adsorbents. Table 6 presents the maximum adsorption capacity and other constants of the isothermic adsorption.

Table 4: L27 orthogonal arrays

| Expt. No. | Contact time (min) | Initial conc. (mmol) | adsorbent dosage (g) | Temperature (K) | Uptake (mg/g) | S/N ratio |
|-----------|--------------------|----------------------|----------------------|-----------------|---------------|-----------|
| 1         | 15                 | 2                    | 0.25                 | 293             | 80            | 38.06     |
| 2         | 15                 | 2                    | 0.25                 | 313             | 76            | 37.61     |
| 3         | 15                 | 2                    | 0.25                 | 333             | 72            | 37.14     |
| 4         | 15                 | 5                    | 0.5                  | 293             | 79            | 37.95     |
| 5         | 15                 | 5                    | 0.5                  | 313             | 76            | 37.61     |
| 6         | 15                 | 5                    | 0.5                  | 333             | 71            | 37.02     |
| 7         | 15                 | 10                   | 1                    | 293             | 145           | 43.22     |
Table 5: S/N value and rank of each factor

| Level | Contact time (min) | Initial conc. (mmol) | Adsorbent dosage (g) | T (K) |
|-------|--------------------|----------------------|---------------------|-------|
| 1     | 39.38              | 38.10                | 46.85               | 43.93 |
| 2     | 44.71              | 42.54                | 43.69               | 43.69 |
| 3     | 46.90              | 50.35                | 40.45               | 43.37 |
| Delta | 7.52               | 12.25                | 6.40                | 0.56  |
| Rank  | 2                  | 1                    | 3                   | 4     |

Figure 7. The variation of S/N ratio of different factors
Figure 8. Langmuir adsorption isotherms onto DS and AC.

Figure 9. Freundlich adsorption isotherms onto DS and AC.

Table 6: Isotherm model parameter for MB adsorption onto DS and AC

| adsorbent | Langmuir Parameter | Freundlich Parameters |
|-----------|--------------------|------------------------|
|           | $Q_m$  | $K_L$  | $R_L$  | $R^2$  | $K_f$  | $n$    | $R^2$  |
| DS        | 111    | 0.0123 | 0.9271 | 0.9909 | 2.4592 | 1.871  | 0.9721 |
| AC        | 526    | 0.131  | 0.5439 | 0.9825 | 120.78 | 4.5434 | 0.7512 |

Over all, we found that the activation process increases the maximum adsorption capacity from 111 to 526 mg/g due to an increase in the micropores and the surface area. The $R_L$<1 value indicates that the adsorption process was suitable and the Yemeni date stones are an excellent adsorbent for removing MB from waste solution. The Freundlich constants $K_f$ and $n$ values suggest that the adsorption of MB on all adsorbents is physical adsorption [20].

3.5 Adsorption kinetics

Two kinetic adsorption models onto date stones were studied, pseudo-first order (8) presented in Figure 9 and pseudo-second order (9) presented in Figure 10 with 10 mmol/l initial adsorbate concentration and 303 K. It is clear that the $R^2$ value for pseudo-second order equation is higher than $R^2$ value for pseudo-first order equation, and the calculated $q_e$ value for pseudo-first order equation equal to 131.58 mg/g agree well with the experimental $q_e$ value equal to 120 mg/g. This suggests that the adsorption onto date stones is better represented by second-order kinetics.
Figure 10. First-order Pseudo kinetics at 303K for MB adsorption.

Figure 11. Second-order Pseudo kinetics at 303 k for MB adsorption.

3.6 Adsorption thermodynamics

Figure 12 gives the plot of ln (Kd) versus 1/T by which the adsorption parameters ΔH and ΔS (10) of MB onto date stones were calculated. We found that enthalpy's negative value (ΔH = -37031 J/mole) indicates the exothermic existence of the adsorption, and entropy's negative value (ΔS = -116 J/mole) implies a decrease in the randomness during the adsorption process. The Gibbs free energy change (ΔG) values calculated using equation (11) and found to be: -1470, -430, 742 and 2791 J/mole 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.
4. Conclusion

Based on the result of this study, Raw Yemeni palm-date stones have a high surface area and can be used as an adsorbent to extract methylene blue from aqueous solutions without pretreatment, and it may be a good metrical for preparing activated carbon (AC) to increase its surface area for successful adsorption process.

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