



Investigation of the treatment of colored water using efficient locally available adsorbent

Hossam Altaher, Emad ElQada

Chemical Engineering Technology Department, Yanbu Industrial College P.O. Box 30436, Saudi Arabia.

Abstract

In this study, the effectiveness of local agricultural waste in removing methylene blue dye from aqueous solution (date stones) was investigated. Both batch kinetics and isotherm experiments were conducted in order to determine the sorption behavior of the examined dye. The effects of initial dye concentration, initial pH, adsorbent particle size, and adsorbent dose were studied. The results indicate that the adsorption process follows pseudo second order kinetic models. The particle sizes of the adsorbent and pH had a significant effect on the adsorption process. In addition, a clear correlation was found between augmentation of the initial dye concentration and a subsequent increase of adsorption capacity. The results obtained are consistent with the Freundlich model.

Copyright © 2011 International Energy and Environment Foundation - All rights reserved.

Keywords: Adsorption; Basic dyes; Date stones; Isotherm; Kinetic studies.

1. Introduction

A large number of manufacturing industries such as textile [1-3], cosmetics [4], metal plating [5], leather [3], pulp and paper [6], and plastics [7] produce waste-water which contains dyes. Methylene blue is a dark green powder or crystalline solid. It is widely used as a stain and has a number of biological uses. It dissociates in aqueous solution in the same way that electrolytes dissociate into methylene blue cation and the chloride ion. The removal of methylene blue from any wastewater is of utmost importance due to the serious environmental damage that can occur as a result of contact with it, particularly in the case of people.

Methylene blue is utilized in coloring paper, temporary hair coloring, dyeing cotton and wools, and coloring of paper stocks [8]. One of the most challenging problems that the manufacturing industries face today is effectively treating wastewater that contains dyes. Discharge of industrial wastewater containing dyes into bodies of water is highly undesirable because of the objectionable side effects. Most of the dyes used for industrial purposes are highly toxic to aquatic life [9]. The color blocks the penetration of sunlight into water [10], which retards photosynthesis, inhibiting the growth of biota. Dyes also impede the solubility of gases in water as well as producing trihalomethanes during chlorination. Many methods, examples being biological treatment, chemical oxidation [11], coagulation [12], ozonolysis [10], electrochemical degradation [13], and reverse osmosis, have been investigated for treatment of wastewater containing dyes. These established technologies are often unable to adequately reduce concentration of the dyes to desired levels. Moreover, the economic impact of these processes remains

prohibitive. Therefore, the search for more effective and economically viable treatment techniques is of utmost importance.

Adsorption is the technique that is most widely used in the removal of dyes from aqueous solutions, being both highly effective and non-destructive. However, the cost of active carbon used in this technique is excessively high [8]. In an attempt to make the treatment process more economically feasible, many researchers have investigated cheap natural adsorbents as an alternative to active carbon [14]. Khan [6] cited 15 different classes of cheap substances that can be used as adsorbent, among them diatomaceous earth, industrial waste products, bagasses fly ash, clay minerals, biodegradable waste, coffee grounds, dusts, kudzu waste metal hydroxide sludge, agriculture wastes, dolomite sorbents, charcoal, extracted residue of coffee beans, bentonite and polymer aluminum hydroxide.

At the end of 2003, Saudi Arabia accounted 19.3% of the world date production, the country having fifty date processing plants. The number of the registered date palms in the Kingdom of Saudi Arabia stands at 20 million trees. There are also 3.7 million unregistered date palms. These trees annually produce 800,000 metric tons of dates. A huge amount of agriculture waste is produced as a byproduct of date processing. Many researchers have investigated the use of date stones in the production of active carbon. However, the use of the date stones themselves in treating wastewater hasn't received adequate attention from researchers.

The present study was undertaken in order to evaluate the effectiveness of using date stones in the removal of methylene blue from aqueous solution by using batch adsorption experiments. The effects of pH, contact time, adsorbent particle size, initial dye concentration and adsorbent dosage on adsorption capacity were studied. In addition, equilibrium and kinetic models were used to fit experimental data.

2. Materials and methods

2.1 Adsorbate

Methylene blue obtained from Mallinckrodt, USA, was used as an adsorbate without further purification. A stock solution of dye (1000 mg/l) was prepared by dissolving the solid powder in distilled water suitably diluted to the required initial concentrations (27.5-108.5 mg/l). Concentration of methylene blue was measured using UV-Visible Spectrophotometer (Varian Cary 50, Australia). A calibration curve was prepared at 665 nm. Figure 1 represents the dye before and after adsorption by different masses of date stones.



Figure 1. 50 ml aliquot of methylene blue after addition of different masses of adsorbent. The first flask on the left contains the original solution without addition of adsorbent

2.2 Preparation of adsorbent

The date stones (DS) were washed several times with distilled water, soaked in distilled water overnight, filtered and dried overnight at a temperature of 110°C. The dried DS were then ground using a kitchen grinder, sieved to be sorted according to size and then dried at 110°C for 24 hours. Figure 2 depicts the shape of different particle sizes of states stones.



Figure 2. Different particle sizes of the dried dates stones. The three particles on the right are whole stones while on the left are powdered particles

2.3 Adsorption isotherm experiment

Batch mode studies were conducted using 0.05 to 1.2 g of DS having a particle size 250-355 μm . Each adsorbent was added to 75 ml aqueous solution of MB of a concentration of 108 mg/l and stirred at a velocity of 300 rpm at room temperature for 4 hours. At the end of the stirring, the adsorbent was removed by simple centrifugation. The supernatants were analyzed for the residual (unadsorbed) MB, spectrophotometrically.

A similar procedure was followed to determine the effect of initial dye concentration on adsorption capacity.

2.4 Kinetics study

Kinetic experiments were performed in a set of 150 ml beakers into which solutions of dye (75 ml) with initial concentration of 167mg/l were placed. Equal mass of 0.6 g (measured to the fourth decimal point) of particle size 250-355 μm was added to dye solution and stirred using mechanical stirrer at a speed 300 rpm at room temperature (25 ± 2 °C) for varying intervals of time. At the end of each interval, a sample was taken, and the adsorbent was separated from adsorbate by centrifuge for 10 minutes. The supernatant was analyzed for methylene blue. The adsorption capacity amount of adsorption at time t, q_t (mg/g), was calculated by:

$$q_t = \frac{(C_o - C_t)V}{W} \quad (1)$$

C_o is the initial liquid-phase concentration of dye (mg/l), C_t is the liquid-phase concentration of dye at any time (mg/l) (t), V is the volume of the solution (l), and W is the mass of dry adsorbent used (g). Percentages of dye removal were calculated according to the following equation:

$$\text{Dye removal (\%)} = \frac{C_o - C_e}{C_o} * 100 \quad (2)$$

where C_o and C_e are the initial and equilibrium dye concentration (mg/l), respectively.

2.5 Effect of initial pH

An identical procedure to that outlined above was carried out to determine the effect of pH on adsorption process. The initial solutions' pHs were adjusted using NaOH (0.01N) and H₂SO₄ (0.01N) to the required

values. The adsorbent was added and the solutions were stirred for 4 hours, followed by separation of the adsorbent from adsorbate.

2.6 Effect of particle size

Previously measured amounts of DS having different particle sizes (<250 µm, 250-355µm, 355-500 µm, 500-700 µm, 700-1000 µm and 1000-2000 µm) were added to 75 ml aliquot of methylene blue having initial concentration of 100 mg/l. The solutions were stirred for 4 hours at room temperature. After equilibrium was attained the solution was centrifuged and the supernatants were analyzed for methylene blue.

2.7 Mathematical modeling

2.7.1 Equilibrium study

An adsorption isotherm is critically important because it illustrates exactly how adsorbate interacts with adsorbents. Thus, the correlation of the equilibrium data by either theoretical or empirical equations is essential to practical operation [15]. According to Thomas and Crittenden [16], equilibrium adsorption isotherms are important for the design of the adsorption system. The most widely used isotherms equation for the design of adsorption systems are the Langmuir and Freundlich equations.

Langmuir (1918) developed a model for characterizing the equilibrium adsorption of gases onto solid. Langmuir assumed that the adsorption occurs in a layer one molecule deep (monolayer coverage of adsorbate) and on localized sites with no interaction between adsorbate molecules and constant energy of adsorption [17].

The well-known Langmuir model is expressed in the following equation:

$$q_e = \frac{Q \cdot K_L \cdot C_e}{1 + (a_L \cdot C_e)} \quad (3)$$

where: q_e is the solid phase equilibrium concentration (mg/g); C_e is the liquid phase equilibrium concentration (mg/l); Q is an energy term and is in most cases equal to unity and K_L (l/g) and a_L (l/mg) are Langmuir constants.

The linearization form of Langmuir equation is:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad (4)$$

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, R_L :

$$R_L = \frac{1}{1 + K_L C_o} \quad (5)$$

where C_o is the initial concentration of dye solution (mg/l) and K_L is the Langmuir constant (l/g). The parameter R_L indicates the shape of the isotherm accordingly.

Value of R_L Type of isotherm

$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$R_L = 0$	Irreversible
$0 < R_L < 1$	Favourable

A large amount of research has shown that the concentration on the adsorbent is usually proportional exponentially to the concentration that remains unadsorbed. Freundlich formulated this relationship in a model that endorsed the heterogeneity of the surface and assumed that the adsorption occurs at sites with different energy of adsorption [18, 19].

$$q_e = K_F C_e^n \quad (6)$$

where: K_F is Freundlich constant (mg/g.(mg/l)^n) and n is the heterogeneity factor. The K_F value is related to the adsorption capacity; while $1/n$ value is related to the adsorption intensity. The Freundlich model is represented by the linear form as follows:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7)$$

2.7.2 Kinetics study

In order to quantify the extent of uptake in adsorption kinetics and investigate the mechanism of the adsorption of MB onto the date stones, the kinetic data was analyzed by the following pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_t} \quad (8)$$

and

$$h = K_2 q_e^2 \quad (9)$$

where k_2 is the rate constant of second-order adsorption (mg/g.min), q_t (mg/g) and q_e (mg/g) are the amount of dye adsorbed at time t and equilibrium, respectively.

3. Results and discussion

3.1 Effect of initial dye concentration

Initial dye concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases. Hence, a higher initial concentration of dye will enhance the adsorption process [20-22].

Figure 3 shows the effect of initial dye concentration on the adsorption capacity of MB onto date stones. It is obvious from the figure that the equilibrium dye uptake was significantly enhanced (3.5-12.8 mg/g) as the initial concentration of the dye was increased from 27.5-108.5 mg/l. This is can be attributed to the increase in the driving force of the concentration gradient as the dye concentration increases.

Hameed [23] reported a similar tendency with regard to the adsorption of MB onto papaya seeds. The author found that as the initial dye concentration increases, the dye uptake increases. Özeret *et al.* [24] illustrated that the initial MB concentration provides an important driving force to overcome all mass transfer resistance and attributed the increase of the adsorption of MB onto peanut hull to the higher interaction between MB and adsorbent.

Results show that as the initial dye concentration increases, the percentage dye removal decreases. This is due to the saturation of the adsorption sites on the adsorbent as the concentration of the dye is increased [20]. Dye removal percentage decreased from 88 to 79.7 as the concentration increased from 27.5 to 108.5 (mg/l). At lower concentrations, all MB present in the adsorption medium could interact with the binding sites so higher percentage removal was obtained. At higher concentrations, the adsorption sites were saturated and this led to lower percentage removals [24].

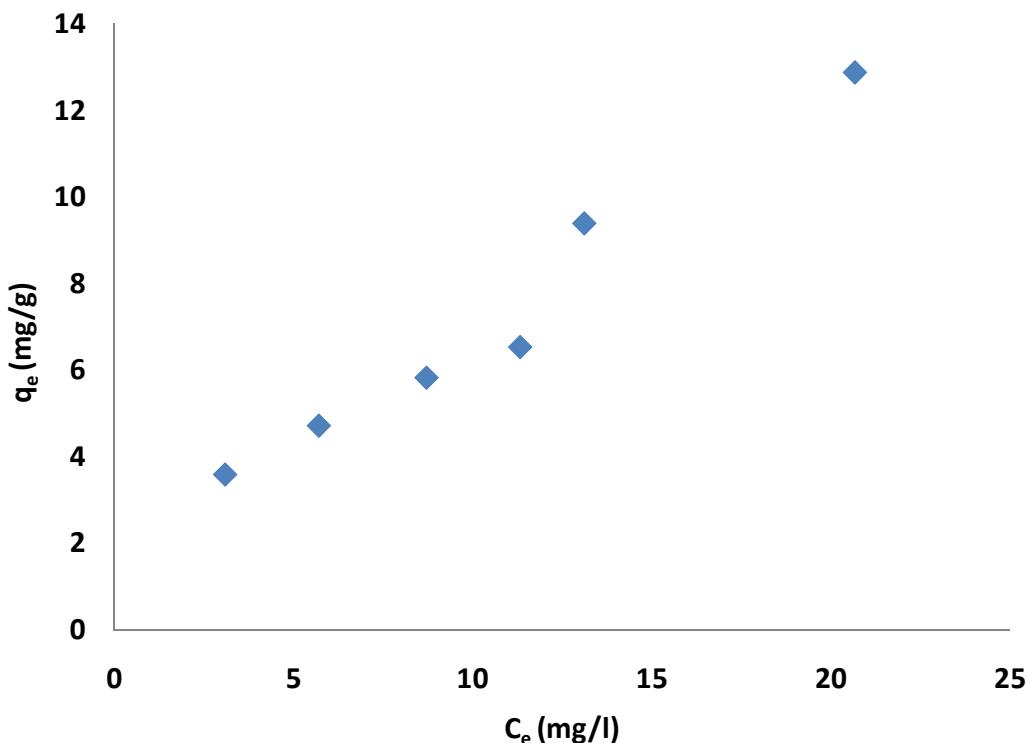


Figure 3. The effect of initial dye concentration on the MB adsorption onto dates stones. Temperature = 25 °C, volume= 75 ml, mass of adsorbent = 0.51 g, particle size = 250-355µm and initial pH = 5.94

3.2 Effect of adsorbent dose

Figure 4 indicates the effect of adsorbent dose on the removal of MB. It is obvious from the figure that the increase in the adsorbent mass resulted in a decrease in the solid phase equilibrium concentration, q_e , although the percentage removal was increased. The increase in percentage removal can be ascribed to the increase of the available sorption surface and availability of more adsorption sites. As the mass increases from 0.19-1.18 g, the percentage of dye removal increases from 26.7 – 89%.

Özeret *et al.*, [24] explained the increase in the uptake of MB with the adsorbent dose and related this to the increase of surface area and the sorption sites. Since the particle size range is constant, the surface area will be directly proportional to the mass of adsorbent in the solution.

3.3 Effect of the particle size

Figure 5 depicts a plot of solid phase concentration versus particle sizes. As the particle size decreased the adsorption capacity of the date stones increased. The adsorption capacity increased from 6.8 (mg/g) to 19.1 (mg/g) as the particle size decreases from 1000-2000 µm to <250µm. That is equivalent to increase in percentage removal from 33.9 to 95.1% as the particle size decreases from 1000-2000 µm to < 250 µm.

An increase in capacity with decreasing particle size strongly suggests that dye do not completely penetrate the particle pores or that the dye partly preferentially adsorb near the outer surface of the particle [15]. Walker [19] attributed this to the crushing process, the breaking up large particles resulting in the opening of tiny sealed channels in the adsorbent that then might become susceptible to adsorption. Another explanation was given by Doğan *et al.* [22]. The authors attributed the increase in adsorption capacity to a corresponding decrease in particle size when treating MB with hazelnut shell to the larger surface area that was associated with smaller particles. For larger particles, the diffusion resistance to mass transport is higher and it may be possible that most of the internal surface of the particle not be utilized for adsorption and consequently the amount of dye adsorbed is small.

The surface area of a non-porous adsorbent considerably increases with a decrease in particle size. Consequently, the adsorptive capacity should increase with a reduction in particle diameter. However, for highly porous adsorbents, the case is different since most of the surface area resides in the internal pore structure. Therefore, the adsorptive capacity is expected to be independent of the particle size [25]. So, the results may indicate the non-porous structure of the date stones.

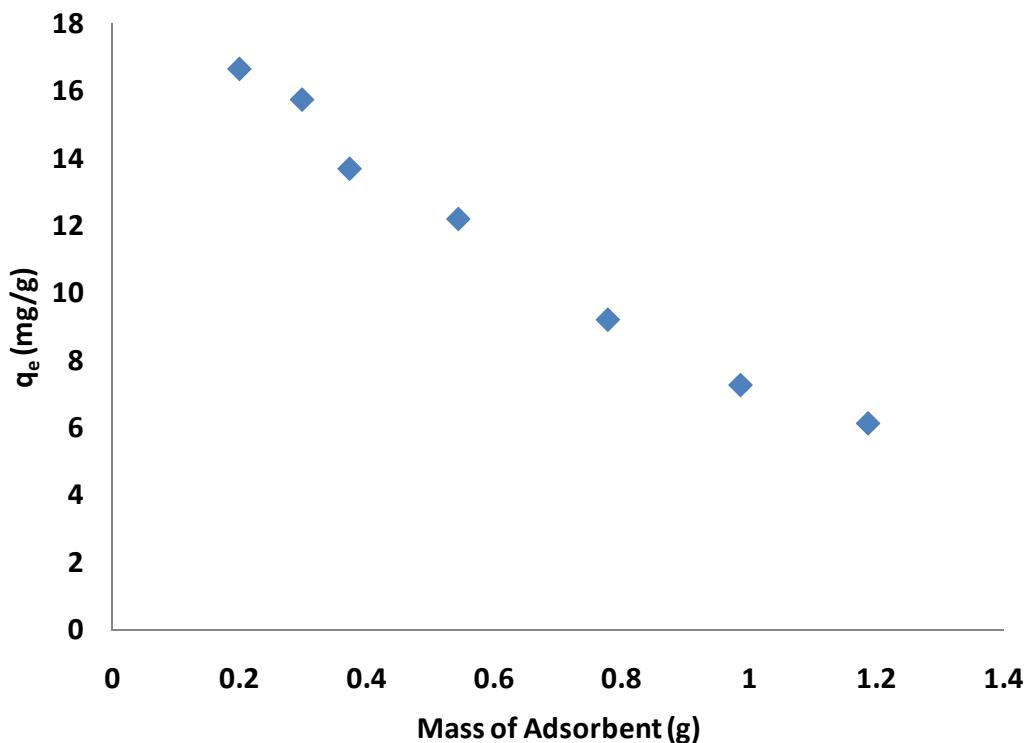


Figure 4. The effect of adsorbent mass on the MB adsorption onto dates stones. Initial dye concentration = 108.5 ppm. Temperature = 25 °C, volume = 75 ml, particle size = 250-355 µm and initial pH = 5.94

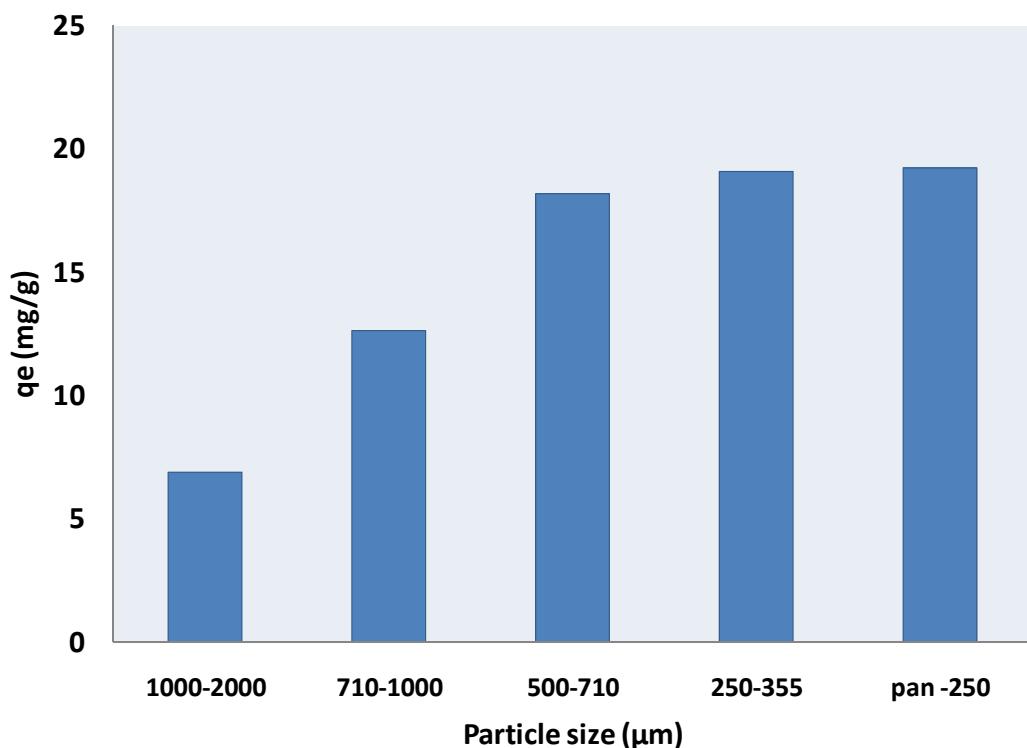


Figure 5. The effect of adsorbent particle size on the adsorption of MB onto dates stones. Initial dye concentration = 167 ppm. Temperature = 25 °C, volume = 75 ml, adsorbent mass = 0.62 g and initial pH = 5.94

3.4 Effect of pH

Figure 6 illustrates the effect of initial solution pH on the percentage of MB removal from the aqueous solution. The percentage removal was more than 88% in the pH range 4.2–10.4. Lower percentage removal at pH = 4.2 (although still high (more than 88%) may be ascribed to the presence of excess of H⁺ ions competing with the dye cations for adsorption sites [26].

In the pH range 7.2-10.4, the percentage removal was almost constant. Hameed and Ahmad [26] reported similar results for the adsorption of MB onto garlic peel. The authors attributed this behavior to the availability of large number of active sites on the adsorbent surface, and related the solute (dye) uptake to the active sites and also to the chemistry of the solute in the solution. At higher pH, the surface of GP particles might become negatively charged, which enhanced the positively charged MB cations through electrostatic forces of attraction.

Bestaniet al., [27] studied the effect of pH on the adsorption of MB onto Salsolavermiculata (desert plant). The authors noticed that at low pH values, the dye uptake decreased whereas in the range 6–8, the uptake efficiency was only slightly affected by pH. The authors explained the decrease in the dye uptake at lower pH values in terms of protons competing with dye molecules for the available adsorption sites.

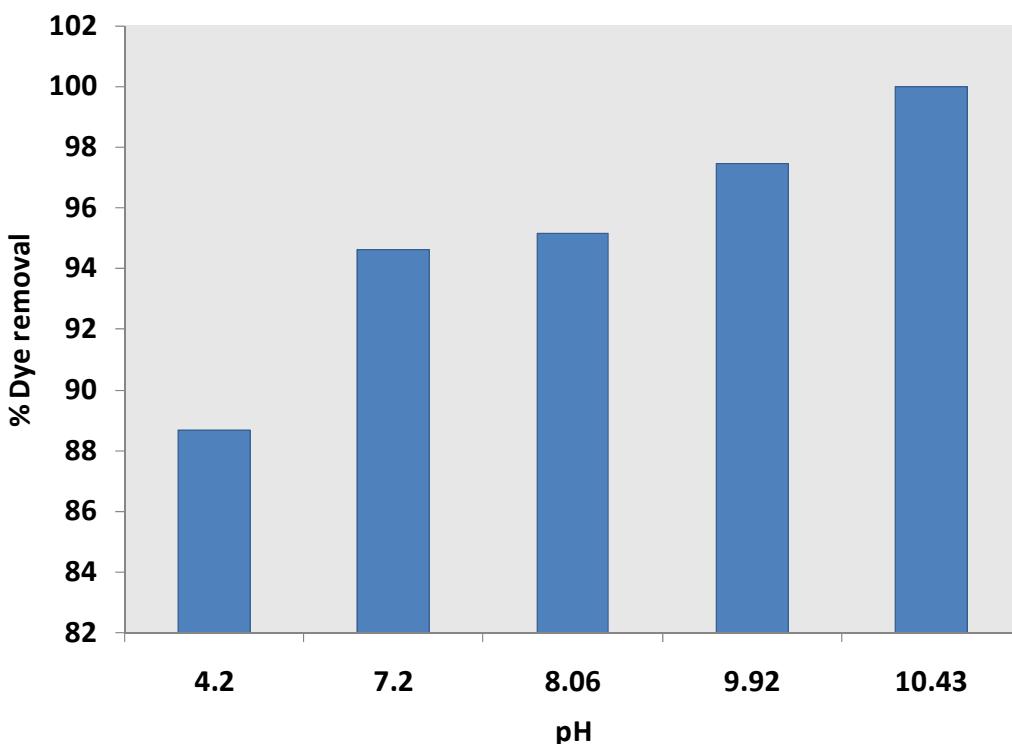


Figure 6. The effect solution pH on the adsorption of MB onto dates stones. Initial dye concentration = 167 ppm. Temperature = 25 °C, volume = 75 ml, adsorbent mass = 0.61 g and particle size = 250-355 µm

3.5 Adsorption isotherms

Adsorption isotherms were analysed following the linear form of the Langmuir and Freundlich models. The parameters, k_L, a_L k_f, and n of Langmuir and Freundlich were determined for methylene blue dye. Table 1 displays these results.

Table 1. Langmuir and Freundlich isotherm constants for dates stones and MB dye system

Parameter	Langmuir			Freundlich			
	k _L (l/g)	a _L (l/mg)	r ²	R _L	k _f (mg/g)/(l/g) ⁿ	n	r ²
Effect of Conc.	0.9980	0.0359	0.5330	0.9022	1.513	1.49	0.932
Effect of Mass	0.7600	0.0235	0.8730	0.9230	1.900	1.81	0.91

The Freundlich isotherm model satisfactorily describes the experimental data. The coefficient of correlation was high ($r^2 = 0.932$) showing a good linearity. A good representation of the Freundlich equation probably indicates multilayer adsorption.

The results show that the value of n is greater than unity indicating that the dye is favorably adsorbed on to the date stones. This conforms to the findings regarding to R_L value. The values of the heterogeneity factor (n) in Table 1 indicate that all the adsorbent particles have a heterogeneous structure.

In order to assess the different isotherms and their ability to correlate the experimental results, the theoretical plots for each isotherm have been shown with the experimental data for the adsorption of MB onto date stones. Figure 7 shows the fit of the isotherm models to the experimental data for the adsorption of MB onto date stones at varying levels of initial dye concentration.

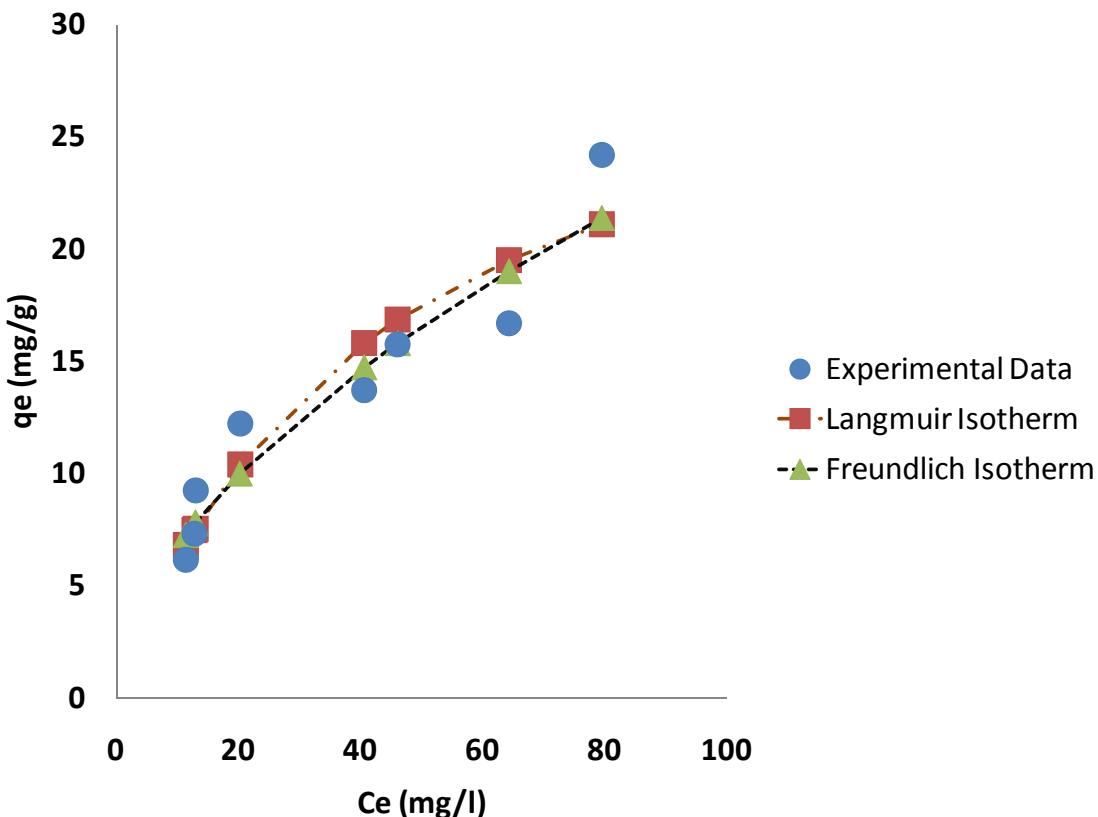


Figure 7. Model fit of adsorption isotherm of MB adsorption onto dates stones at different masses of adsorbent. Initial concentration = 108.5 ppm, temperature = 25 °C, volume = 75 ml, particle size = 250-355 µm and initial pH = 5.94

3.6 Kinetic study

Figure 8 shows the result for the effects of contact time on the adsorption of MB onto date stones. It was observed that dye uptake was rapid for the first 30 min and thereafter it proceeded at a slower rate and finally reached saturation. The initial rapid phase may be due to an increase in the number of vacant sites available at the initial stage.

Figure 9 shows the linear plots of t/q_e versus t . A good agreement between the pseudo-second order function and the experimental data was achieved ($r^2 = 0.9990$). This indicates the applicability of this kinetics equation and the second-order nature of the adsorption process of MB onto the date stones. The calculated values of the equilibrium adsorption capacity q_e also agree satisfactorily with the experimental value. The calculated rate constant, k_2 , of the date stones was 0.0203 (g/mg.min).

Thus, the pseudo second-order adsorption mechanism is predominant and the rate-limiting step may be chemisorptions [28].

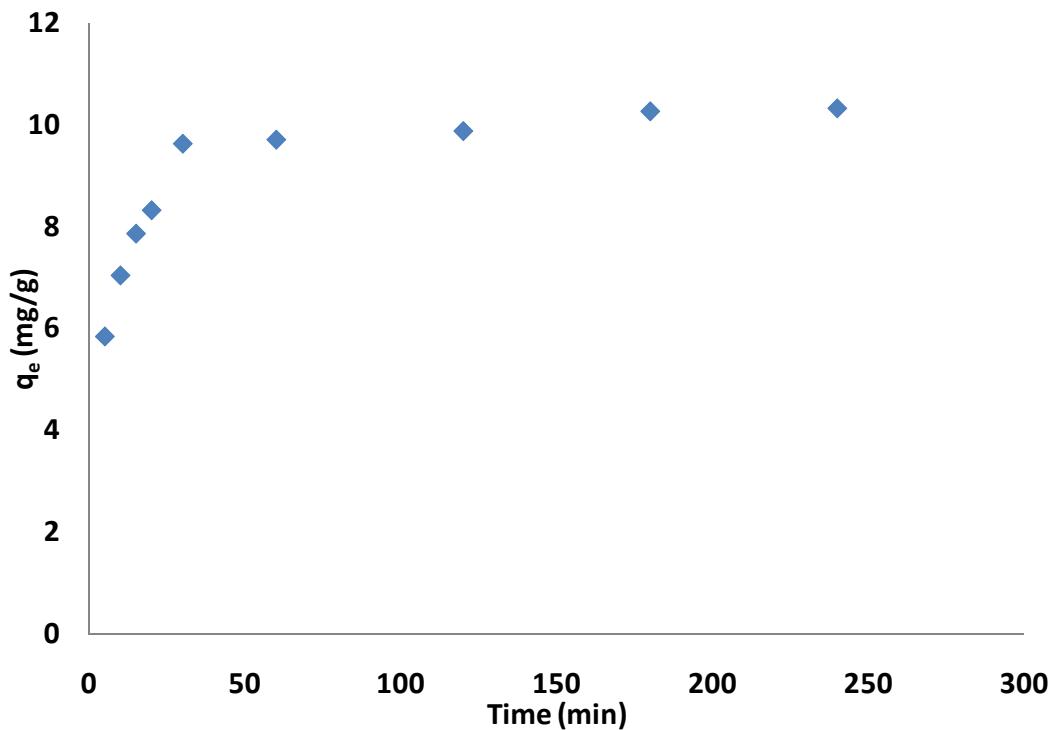


Figure 8. Effect of contact time of the adsorption of MB onto dates stones. Initial dye concentration =86 ppm, temperature = 25 °C, mass of adsorbent = 0.61 g, pH =7.59 and particle size =250-355 µm

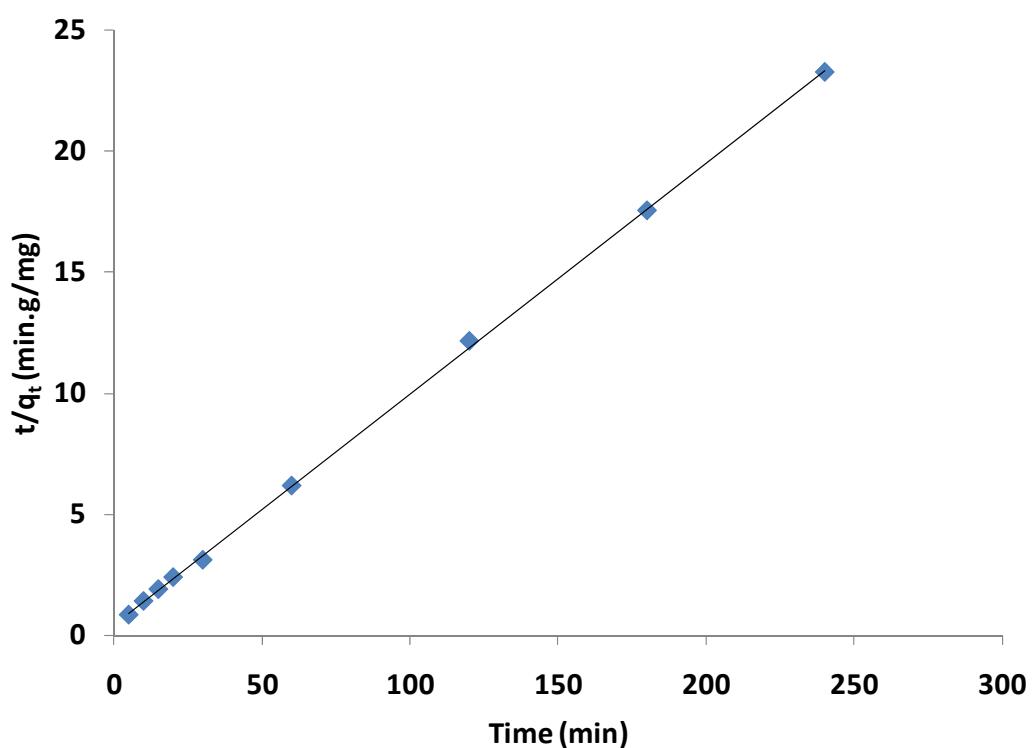


Figure 9. Second-order kinetic equation for adsorption of MB onto dates stones

4. Conclusion

The focus of this study was to investigate the potential use of raw date stones for the removal of MB from aqueous solution. Liquid-phase adsorption processes were employed and adsorption isotherms were constructed. The effects of experimental conditions on the performance of the adsorbents in the equilibrium study were investigated.

The main conclusions of this study are summarised thus:

- The results showed the role played by the adsorbent particle size on the adsorptive properties of date stones. As the particle size decreases, the adsorption capacity of the adsorbent increased. The increase in capacity with decreasing particle size strongly suggests that the dyes do not completely penetrate the particle or that the dyes preferentially adsorb near the outer surface of the particle to some extent. Therefore, it can be concluded that smaller date stone particles are recommended for such adsorption processes.
- As the initial MB concentration increases (27.5-108.5 mg/l), the adsorption capacity onto date stones increased (3.5-12.8 mg/g).
- Freundlich isotherm was found to best fit the experimental data over the whole concentration range. The adsorption system studied showed favourable adsorption of the MB as indicated from the low value of R_L ($0 < R_L < 1$).
- The rate of dye uptake was rapid in the initial stages and, then, slowed down gradually suggesting that the dye uptake occurred by surface binding. The fast rate region is characterised by rapid attachment of dye on the surface of the adsorbent. In the slower region, the surface was saturated by dye molecules and the dye molecules started to diffuse through the pores (intraparticle diffusion).
- In order to quantify the extent of uptake in adsorption kinetics, a pseudo second-order kinetic model was used to correlate the experimental data. The high values of the correlation coefficient ($r^2 > 0.99$) and the consistency of the experimental and theoretical values of q_e would indicate that the chemical adsorption might be the rate-limiting step.

References

- [1] S. E. Abechi, C. E. Gimba, A. Uziaru, I.G. Ndukwe. Comparative studies of adsorption of methylene blue (MB) by sawdust and walnut shells carbon coated with ZnO, Science world journal 1 (1) (2006) 33
- [2] C. E. Kaewprasit, N. Hequet, N. Abidi, J. P. Gourlot. Application of methylene blue adsorption to cotton fiber specific surface area measurement: Part I Methodology, The journal of cotton science 2 (1998) 164.
- [3] A. R. Khan, T. Hajira, F. Uddin, U. Hameed. Adsorption of methylene blue from aqueous solution on the surface of wool fiber and cotton fiber, J. Appl. Environ. Mgt. 9 (2) (2005) 29.
- [4] M. Sarioglu, U. A. Atay. Removal of methylene blue by using biosolids. Global NEST journal 8(2) (2006) 113.
- [5] N. A. Oladoja, C. O. Aboluwoye, Y. B. Oladimeji. Kinetics and isotherm studies on methylene blue adsorption onto Ground pal Kernel coat, Turkish j. Eng. Env. Sci. 32 (2008) 303.
- [6] T. A. Khan I. Ali, V. V. Singh, S. Sharma. Utilization of fly ash as low-cost adsorbent for the removal of methylene blue, malachite green and Rhodamine B dyes from textile wastewater, Journal of environmental protection science 3 (2009) 11.
- [7] M. M. Abde El-Latif, A. M. Ibrahim, M. F. El-Kady. Adsorption equilibrium, kinetics and thermodynamics of methylene blue from aqueous solution using biopolymer oak sawdust composite, Journal of American science 6(6) (2010) 267.
- [8] R. Han, Y. Wang, W. Yu, J. Shi H. Liu. Biosorption of methylene blue from aqueous solution by rice husk in a fixed-bed column, Journal of hazardous material 141(3) (2007) 713
- [9] A. E. Vasu. Studies on the removal of Rhodamine B and malachite green from aqueous solutions by activated carbon, E-journal of Chemistry 5 (4) (2008) 844.
- [10] Y. Yasin, M. Z. Hussein, F. H. Ahmed. Adsorption of methylene blue onto treated activated carbon, The Malaysian journal of analytical sciences 11 (11) (2007) 400.
- [11] H. S. Silva1, N. D. Martínez, A. C. Deiana, J. E. González. Catalytic oxidation of methylene blue In aqueous solutions, 2nd Mercosur Congress on Chemical Engineering 2005.

- [12] K. Tak-Hyun, C. Park, J. Yang, S. Kim. Comparison of disperse and reactive dye removal by chemical agulation and Fenton oxidation, *Journal of hazardous materials* 112 (2004) 95.
- [13] L. Fan, Y. Zhou, W. Yang, G. Chen F. Yang. Electrochemical degradation of aqueous solution of Amaranth azo dye on ACF under potentiostatic model, *Dyes Pigments* 76 (2008) 440.
- [14] R. Ansari, Z. Mosayebzadeh. Removal of basic dye methylene blue from aqueous solutions using sawdust and sawdust coated with polypyrrole, *J. Iran Chem. Soc.* 7 (2) (2010) 330.
- [15] R. S. Juang, R. L. Tseng, F. C. Wu, S. H. Lee. Adsorption behaviour of reactive dyes from aqueous solution on chitosan, *J. Chem. Technol. Biotechnol.* 70 (1997) 391.
- [16] W. J. Thomas, B. Crittenden. *Adsorption Technology and Design*, 1st ed., Butterworth-Heinemann, Oxford, 1998.
- [17] S. J. Allen, G. McKay, K. Y. H. Khader. Multi-component sorption isotherms of basic dyes onto peat, *Environmental Pollution* 52 (1988) 39.
- [18] W. Weber, F. DiGiano. *Process dynamics in environmental systems*, 1st ed., John Wiley and Sons, Inc. New York, 1996.
- [19] G. Walker. Industrial wastewater treatment using biological activated carbon, PhD Thesis, Queen's University Belfast, Belfast, UK, 1995.
- [20] Z. Aksu, G. Dönmez. A comparative Study on the biosorption characteristics of some yeast for remazol Blue Reactive Dye, *Chemosphere* 50 (2003) 1075.
- [21] M. Zhao, Z. Tang, P. Liu. Removal of methylene blue from aqueous solution with silica nano-sheets derived from vermiculite, *Journal of Hazardous Materials* 158 (2008) 43.
- [22] M. Do˘gan, H. Abak, M. Alkan. Adsorption of methylene blue onto hazelnut shell: Kinetics, mechanism and activation parameters, *Journal of Hazardous Materials* 164 (2009) 172.
- [23] B. H. Hameed. Evaluation of papaya seeds as a novel non-conventional low-cost adsorbent for removal of methylene blue, *Journal of Hazardous Materials* 162 (2009) 939.
- [24] D. Özer, G. Dursun, A. Özer. Methylene blue adsorption from aqueous solution by dehydrated peanut hull, *Journal of Hazardous Materials* 144 (2007) 171.
- [25] S. D. Faust, O. M. Aly. *Chemistry of water treatment*, 2nd ed., Ann Arbor Press, INC. Michigan, 1998.
- [26] B. H. Hameed, A. A. Ahmad. Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass, *Journal of Hazardous Materials* 164 (2009) 870.
- [27] B. Bestani, N. Benderdouche, B. Benstaali, M. Belhakem, A. Addou. Methylene blue and iodine adsorption onto an activated desert plant, *Bioresource Technology* 99 (2008) 8441.
- [28] M. S. Chiou, H. Y. Li. Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads, *Chemosphere* 50 (2003) 1095.