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Original Research Article

Removal of methylene blue from aqueous solution using Egyptian date pits

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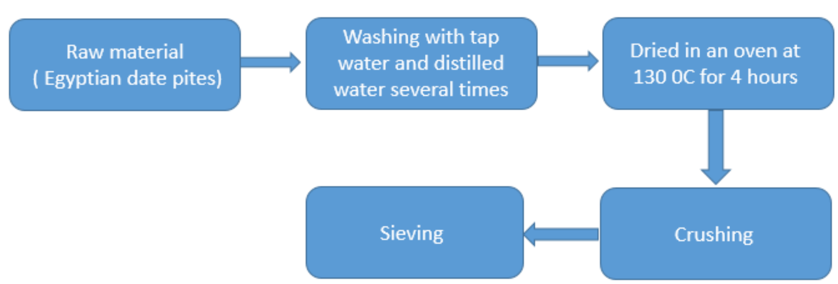
ABSTRACT

This study aimed to investigate Egyptian date pits' potential to remove a cationic dye, specifically methylene blue (MB), from aqueous solutions. Characteristics of methylene blue and interaction between methylene blue and Egyptian date pits were characterized using the Fourier transform infrared spectrometer, scanning electron microscope, and Brunauer–Emmett–Teller analysis. The effect of several parameters including, adsorbent dose, and contact time, temperature and pH solution were assessed. The adsorption was increased by decreasing dye concentration, temperature, increasing contact time and dosage up to equilibrium values which was 25 °C, 20 min, and 0.1 g adsorbent, respectively. At high pH, the adsorption was promising. The results demonstrated that the Egyptian date pits are an effective and good adsorbent for removing Methylene blue in wastewater.

Graphical Abstract



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Introduction

Water is the root of life on Earth, a fundamental part of this world, and assumes a significant job in the Earth's biological systems' best possible working. These days, the principal issue is water quality degradation and the high increment in water requirements for various purposes (agricultural and industrial). Over 700 natural and inorganic contaminations have been accounted for in water, which is risky because of their profoundly poisonous and carcinogenic nature [1].

Wastewater effluents contain manufactured dyes which may make a potential risk nature. Due to the health and environmental concerns related with the wastewater effluents, distinctive division methods have been utilized in the removal of dyes from aqueous solutions. Physical, Chemical and Biological methods are dye removal techniques [2]. Dyes are considered a type of pollutant as they are toxic, due to oral ingestion and inhalation, skin and eye irritation leading to problems skin sensitization also due to carcinogenicity [3]. Methylene blue (MB) is a basic dye and appears as a dark green solid powder that yields a blue solution when dissolved in water [4]. It is used for printing calico, dyeing leather and indicating oxidation- reduction in analytical chemistry. Methylene blue has been found to cause bluish discoloration of the urine and stool so Methylene blue must be removed from waste water [5].

Many researchers have studied to develop cheap adsorbents to eliminate Methylene blue dye from wastewater. Some biological materials for example, agricultural waste, algae, fungi and fruit peels were used as effective and cheap adsorbent [6].

Different treatment techniques can be used to remove from industrial wastewater dyes for instance membrane process, electrocoagulation, chemical oxidation using chlorine, Fenton's oxidation, coagulation using alum, chemical and physical degradation and ozonization. Huge numbers of these techniques don't work at low dye concentration along these lines, adsorption must be utilized [7].

Adsorption has been reported to be the most effective method for water decontamination [8]. Adsorption is a process of using solids to remove substances from either gaseous or liquid mixture. The special solids that gas or liquid particles attached are called adsorbent but the substances adsorbed are called adsorbate [9].

Adsorption has attracted a great deal of attention due to its ease of operation and low cost of application in the decolorization process [10]. Commercially activated carbon is a highly adsorbent material with great application in the groundwater and industrial wastes treatment such as colored effluent [11]. However, the activated carbon is an expensive adsorbent due to its high costs of manufacturing. For the purpose of removing unwanted hazardous compounds from contaminated water at a low cost, much attention has been given to various naturally occurring adsorbents for instance chitosan, fly ash, coal, zeolites, agricultural waste products and various clay minerals [12].

Because of high adsorption capacity of date pits, structure of surface porous, and high surface area, Date pits can be utilized as adsorbent to remove methylene blue from industrial wastewater [13].

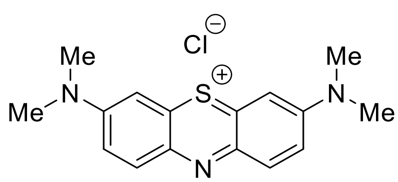
The aim of this work is to investigate the adsorption characteristics of Egyptian date pits used as an adsorbent for methylene blue in aqueous solution. The adsorption capacities were investigated using batch experiment. The influence of contact time, pH, and temperature, dosage and dye concentration were investigated.

Experimental

Materials and methods

Egyptian date pits were collected from Assuit city in Egypt and washed using distilled water several times to remove surface adhered particles. Then it dried in (J.P.SELECTA, Spain) furnace at 130 °C for 4 h. At that time dried date pits were crushed to give a dark brown powder and then sieved using (Retch Sieve Shaker, German) to achieve mean diameter equal to 75 µm.

Methylene blue, its molecular formula is $C_{16}H_{18}ClN_3S$ as shown in Scheme 1, was obtained from Trust Chemical Industries (Egypt). Stock solution of MB was done by dissolving 1 g of MB in one liter of distilled water to provide 1000 ppm solution.



Scheme 1. Chemical structure of methylene blue

Batch adsorption studies

Adsorption studies were conducted using the batch technique and the samples kept in shaker water bath at constant speed of 240 rpm. A simulated wastewater contaminated by methylene blue was used for all experiments in this study. Different concentrations of methylene blue in range of (10:50 ppm) used to perform studies at different contact time, temperature, adsorbent dosage and pH to obtain rate and equilibrium isotherms. Egyptian date pits were gravity separated before measuring the final concentration C_f by spectrophotometer. Adsorption experiments were carried out by shaking Egyptian date pites samples with 50 mL of dye solution. In all adsorption experiments, pH was controlled using a solution of 0.1 mol/HCl and 0.1 mol/NaOH. The adsorption behaviors of the samples were studied by calculation of percent removal of dye using the equation [14].

$$\% \text{ Removal of MB} = \frac{Ci-Cf}{Ci} \, X \, 100 \qquad (1)$$

Where:

C_i ....Initial dye concentration (mg/L)

C_f ....final dye concentration (mg/L)

Effect of contact time

Effect of contact time on the rate of adsorption using Egyptian date pits were performed at natural pH, 25 °C temperature and adsorbent dose of 0.1 g/50 mL solution and automatically shaken for the selected period of time (5, 10, 15, 20, 30, 40, 50 min).

Effect of temperature

The optimum temperature for the adsorption of MB solution was investigated by taking the following values as constant: 20 min contact time, adsorbent dose of 0.1 g/50 mL solution, shaking speed of 240 rpm and four temperatures (30, 50, 70, 90 °C).

The effect of adsorbent dosage

The adsorption was investigated by taking the following values as constant: shaking speed of 240 rpm, 20 min contact time, 25 °C temperature and different adsorbent dosage (0.02, 0.04, 0.06, 0.08, 0.1, 0.2 g/50 mL solution).

Effect of pH

The effect of pH on the adsorption rate was investigated in conditions of 20 min contact time, 25 °C temperature, adsorbent dose of 0.1 g/50 mL solution and shaking speed of 240 rpm.

The pH adjusted using solution of NaOH and HCl (PH values 3, 5, 7, 9).

Equilibrium isotherms

The amount of adsorbed dye on Egyptian date pits was calculated using this equation:

$$q_e = \frac{(Ci - Ce)\ V}{W}\ X\ 0.001 \qquad (2)$$

Where:

C_i ………….Concentration of MB at initial (mg/L)
C_e … Concentration of MB at equilibrium (mg/L)
V… …………………………..Volume of solution (mL)
W…………………………… Mass of dry adsorbent (g)

q_e Concentration of MB in solid phase at equilibrium (mg/g).

The adsorption isotherm indicates how the adsorbed molecules are distributed between the solid and liquid phases at equilibrium [15]. Finding a suitable model to describe the adsorption process is an important step and it is done by analyzing of the equilibrium data where these data is fitted with different isotherm models**.** The study of adsorption isotherm was done on four isotherm models: the Langmuir, Freundlich, Temkin and Dubinin isotherm models. The applicability of the isotherm equation to describe the adsorption process was judged by the correlation coefficient (R^2) values [16].

Langmuir isotherm model

Langmuir isotherm was developed to represent chemisorption. The Langmuir equation relates the coverage of molecules on a solid surface to concentration of the gas or liquid medium [17]. The Langmuir equation is given as the following:

$$\frac{Ce}{qe} = \frac{Ce}{qm} + \frac{1}{qm\ kl} \qquad (3)$$

Where:

C_e Equilibrium Concentration of dye solution (mg/L).

q_e adsorption capacity at equilibrium (mg/g).
q_m maximum adsorption capacity (mg/g).
k_L Langmuir affinity constant (L/mg) related to q_m and rate of adsorption.

The nature of isotherm is indicated by dimensionless constant R_L. The adsorption is favorable if values of constant parameter R_L lay between zero and one. R_L is defined by:

$$Rl = \frac{1}{1 + Kl\ Co} \qquad (4)$$

Where: C_o is the initial dye concentration (mg/L).

$0 < R_L < 1$ …………………………..favorable isotherm
$R_L > 1$ …………………………...unfavorable isotherm
$R_L = 1$ …………………………………..Linear isotherm
$R_L = 0$ …………………………………………irreversible

Freundlich isotherm

Freundlich isotherm can describe the adsorption of organic and inorganic compounds on a wide variety of adsorbents [18]. The nature of isotherm is indicated by the slope (1/n). If n=1 then the partition between the two phases are independent of the concentration.

If the value
(1/n) < 1 ………..it indicates a normal adsorption
1 < (1/n) < 1 ……it confirms favorable adsorption
(1/n) =1 …………….it indicate a linear adsorption

The linear form of Freundlich is given as:

$$\text{Ln } q_e = (1/n) \ln C_e + \ln K_f \qquad (5)$$

Where,

C_e Equilibrium Concentration in liquid phase (mg/L).
q_e adsorption capacity in solid phase (mg/g).
K_f Freundlich constant represent adsorption capacity (L/mg).
N Freundlich constant represent adsorption intensity or surface heterogeneity.

Temkin isotherm

Temkin isotherm assumes the adsorption heat of all molecules in the layer decreases linearly with coverage as a result of adsorbate/adsorbate interaction in addition to adsorption characterized by a uniform distribution of binding energy [19]. The linear form of Timken can be exposed as:

$$q_e = q_m \left(\ln K_T + \ln C_e \right) \quad (6)$$

Where,
C_e ... Equilibrium Concentration in liquid phase (mg/L).
q_e adsorption capacity in solid phase (mg/g).
K_T Temkin constant which is related to adsorption capacity and maximum binding energy (L/g).
q_m constant represent heat of adsorption (J/mole).

Dubinin-Radushkevich isotherm

The Dubinin isotherm assume that the adsorption occurs on heterogeneous surface with Gaussian energy distribution. This isotherm fitted at high solute activities and intermediate range of concentrations [20]. Dubinin isotherm can be expressed in linear form as

$$\text{Ln } q_e = \ln q_m - D\,\varepsilon^2 \quad (7)$$

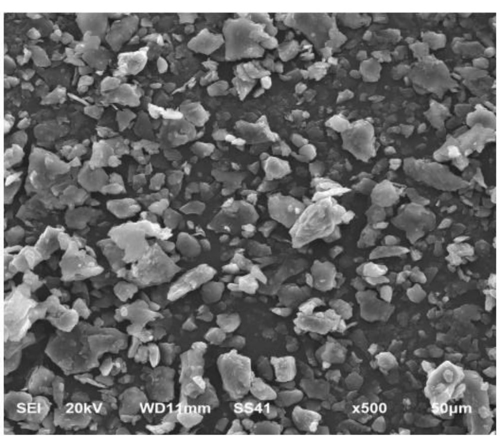
$$\varepsilon = RT \ln \left(\frac{Ce+1}{Ce}\right) \quad (8)$$

Where,
C_e ...Equilibrium Concentration in liquid phase (mg/L).
q_e......adsorption capacity in solid phase (mg/g).
D........constant represent the energy of transfer
q_m................................Dubinin constant (mg/g).
ε..Polanyi potential.
R.................................. gas constant (KJ/mol.k).
T ....absolute temperature (K).

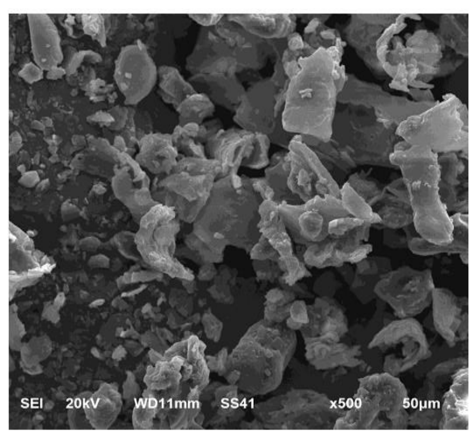
Result and Discussion

Characterization of adsorbent (Egyptian Date Pits)

Scanning electron microscopy (SEM) is a primary instrument for characterizing the surface morphology and fundamental physical properties of the adsorbent surface and is used to determine porosity, the particle shape and appropriate size distribution of the adsorbent [21, 22]. The surface of Egyptian date pits prior and after the adsorption experiments was studied using SEM. As shown in Figure 1**a** and **b**; Egyptian date pits exhibits a heterogeneous morphology or rough and porous surface structure which was promising for adsorption of MB dye.



(a) before adsorption



(b) After adsorption

Figure 1. Scanning electron microscopy of a) Egyptian date pits before adsorption process and b) Egyptian date pits adsorbed with MB

Brunauer-Emmett-Teller (BET) has been studied using N_2 adsorption/desorption measurement at 77K and 760 mmHg. As shown in Figure 2 the slope and intercept are calculated and from them surface area was found. The BET surface area of Egyptian date pits is equal to 0.5827 m^2 /g at time 30 min and degassing temperature 400 °C (Figure 2).

Fourier transform infrared spectrometer (FT-IR) was used to characterize the surface functional groups of Egyptian date pits before and after adsorption process [23]. Figure 3 and Figure 4 represents the Fourier transform infrared spectrum of Egyptian date pits before and after adsorption. The changes detected in the FT-IR spectrum as shown in Table 1 reflects the sign for the interaction between the functional groups present on the surface of Egyptian date pits and MB molecules that might be concerned in the adsorption process of the dye. Moreover, the appearance and absence of bands is a strong indication for the absorption process.

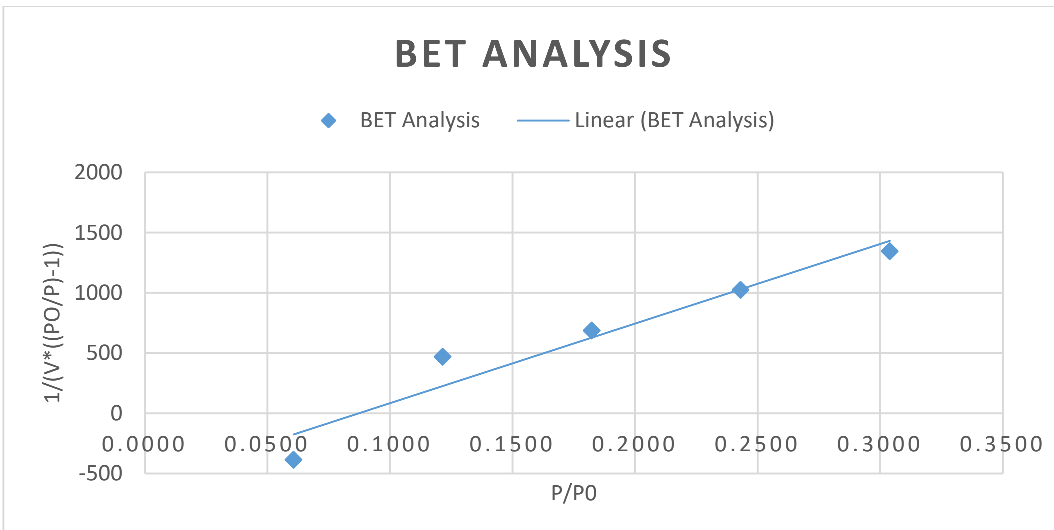


Figure 2. Brunauer-Emmett-Teller (BET) analysis of Egyptian date pits

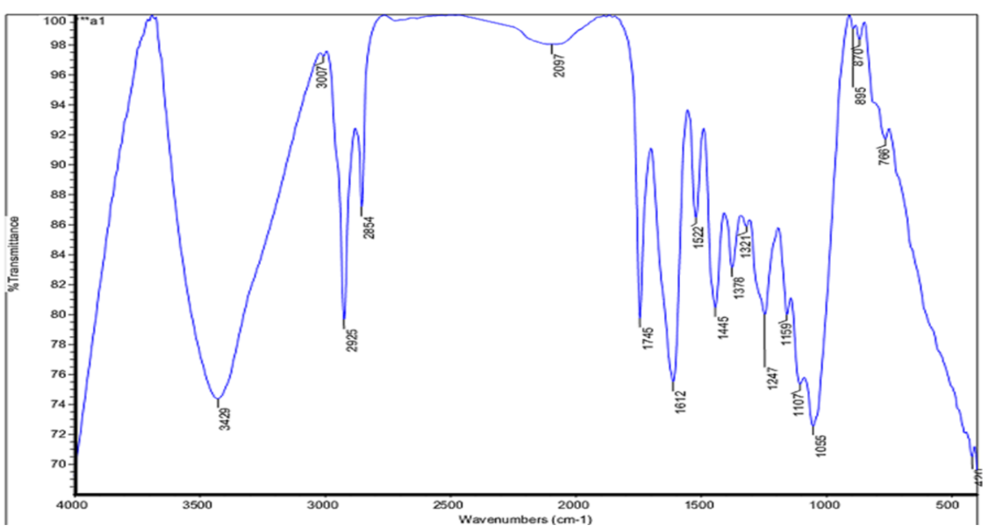


Figure 3. represents the Fourier transform infrared spectrum of Egyptian date pits before adsorption

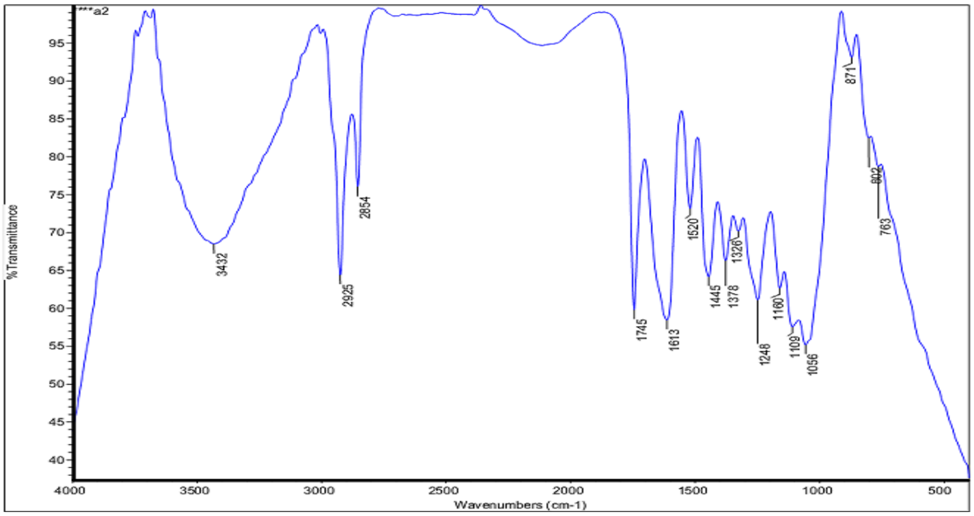


Figure 4. represents the Fourier transform infrared spectrum of Egyptian date pits after adsorption

Table 1. wave numbers and ascription of the principle bands in the FT-IR spectra of the Egyptian date pits before and after adsorption

Frequency Before adsorption	bond	Functional group	Frequency after adsorption	bond	Functional group
3429	O–H stretch, H–bonded	alcohols, phenols	3432	O–H stretch, H–bonded	alcohols, phenols
3007	=C–H stretch	Alkenes, aromatics		disappear	
2097	C–H stretch	aldehyde		disappear	
1745	C=O stretch	esters, anhydride		As it is	
1612	N–H bend	1. amines	1613	N–H bend	1. amines
1522	N–O asymmetric stretch	nitro compounds	1520	N–O asymmetric stretch	nitro compounds
1454	C–C stretch (in–ring)	aromatics	1445	C–C stretch (in–ring)	aromatics
1321	N–O symmetric stretch	nitro compounds	1326	N–O symmetric stretch	nitro compounds
1247	C–N stretch	aliphatic amines	1248	C–N stretch	aliphatic amines
1159	C–H wag (–CH2X)	alkyl halides	1160	C–H wag (–CH2X)	alkyl halides
1107	C=S stretch	thiocarbonile	1109	C=S stretch	thiocarbonile
870	C–H bend	alkanes	871	C–H bend	alkanes
895	C–H bend	aromatics		disappear	
	Does not exist		802	C–Cl stretch	Chloro compound
420	S-CN bend	thiocyanates		disappear	

Adsorption study

Contact time

The contact time on the adsorption of MB on Egyptian date pites. Figure 5 shows the effect as shown, the rate of adsorption was rapidly at the start and high amount of MB removed in the first 10 min due to low resistance to mass transfer and higher driving force. Rate of adsorption became lower from 10 to 20 min to reach the equilibrium at 20 min. it is shown, adsorption of MB decrease with the increase of MB concentration.

Temperature

As seen in Figure 6, increasing of the temperature reduced the rate of adsorption of MB as the solubility of MB increased. It was also found that the adsorption was exothermic.

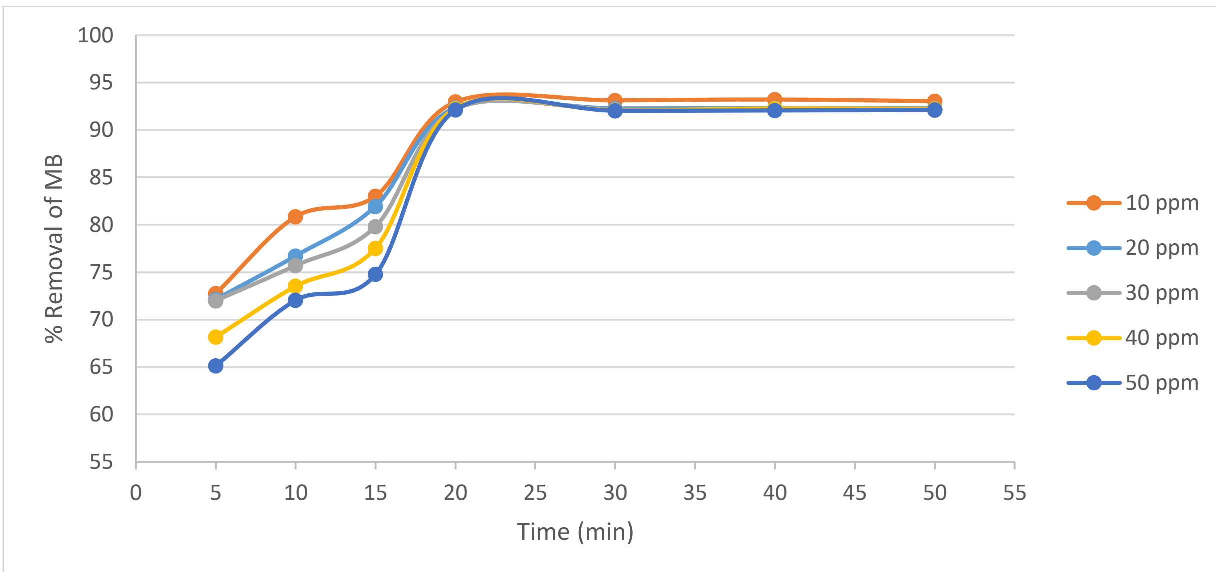


Figure 5. effect of contact time on the adsorption of MB on Egyptian date pites

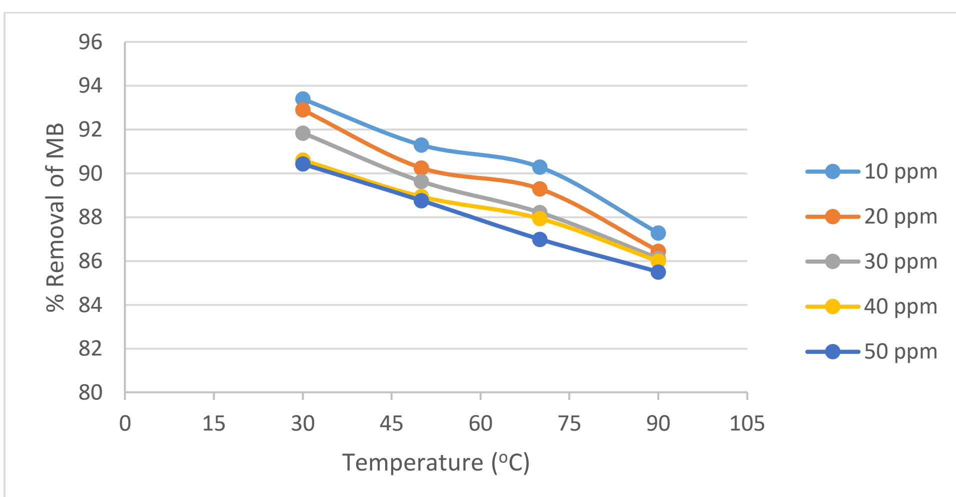


Figure 6. Effect of temperature on the adsorption of MB on Egyptian date pites

Adsorbent Dose

As can be seen in Figure 7, rate of adsorption increase with the increase of dosage of Egyptian date pites due to increased active sites and surface area. The rate of adsorption became constant after 0.1 g dosage of Egyptian date pits.

pH of dye solution

As seen in Figure 8 at low pH (pH<5), the surface of Egyptian date pites is positively charged. Therefore, there is a decrease in the adsorption of MB due to electro static repulsion between MB and the surface of Egyptian date pites.

At high pH (pH>5), the surface of Egyptian date pites is negatively charged therefore, there is an increase in the adsorption of MB as the electrostatic attraction between MB and the surface of Egyptian date pites. In addition to at pH=3, rate of adsorption is in very high value.

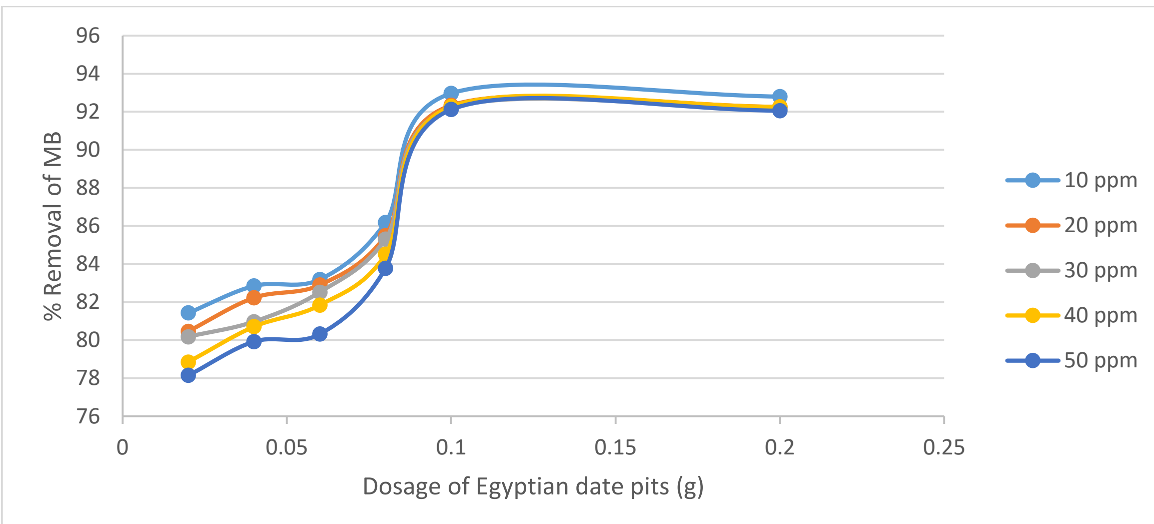


Figure 7. Effect of adsorbent dose on the adsorption of MB on Egyptian date pites

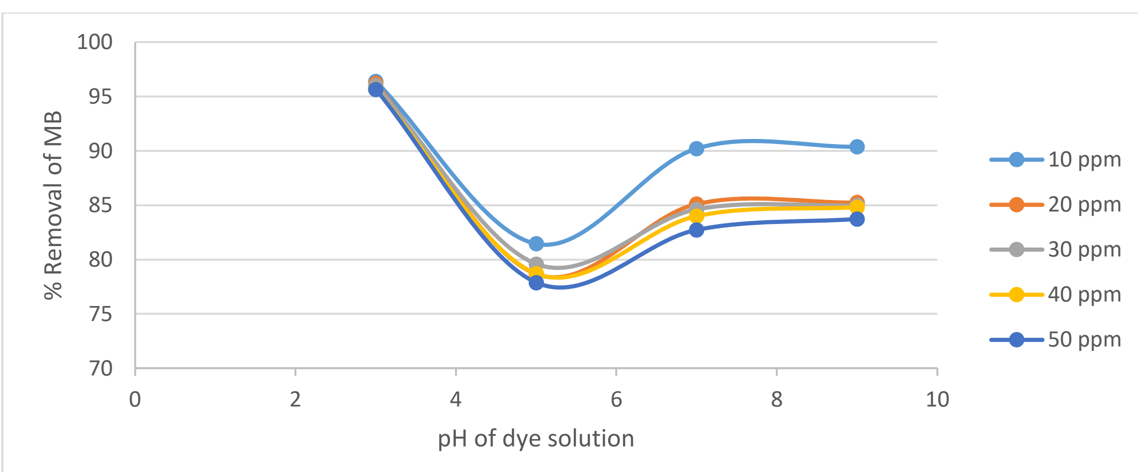


Figure 8. Effect of pH of dye solution on the adsorption of MB on Egyptian date pites

Adsorption isotherm

The study of adsorption isotherm was carried out on four isotherm models (Langmuir, Freundlich, Temkin, and Dubinin). The applicability of the isotherm models equations to describe the process of adsorption was judged by the correlation coefficients (R2) values [24].

Table 2 displays the values of Constant and correlation parameter for the four isotherms at different temperature. The correlation coefficient from the four isotherm models equation shows that Freundlich model produces a better fit for experimental data than other models. This indicated that adsorption of MB onto Egyptian date pits is multilayer and happens on heterogeneous surfaces. The highest value of n at equilibrium is 1.331, which indicates that the adsorption is physical, which is referred to the adsorption bond which becomes weak and conducted with Van der Waals forces. Comparison of adsorption capacities of MB by different adsorbents is shown in Table 3.

Table 2. Constants and correlation parameter for the four isotherms at different temperature

Isotherm	Temperature (°C)			
	30	50	70	90
		Langmuir		
q_m (mg/g)	59.056	54.324	109.541	145.01
K_l (L/mg)	0.111	0.109	0.052	0.041
R^2	0.968	0.817	0.619	0.924
		freundlich		
n (g/L)	1.278	1.331	1.117	1.062
K_f (mg/g)	5.966	5.201	4.323	3.310
R^2	0.996	0.995	0.995	0.999
		Temkin		
q_m (J/mol)	8.859	8.135	9.457	9.545
K_t (L/g)	1.955	1.841	1.394	1.002
R^2	0.963	0.918	0.921	0.948
		Dubinin		
D (mol/J)	26.1	25.786	25.912	26.268
q_m (mg/g)	18.331	18.001	17.786	17.254
R^2	0.876	0.867	0.869	0.872

Table 3. Adsorption capacities q_m (mg/g) of MB by different adsorbents

Adsorbent	Maximum adsorption capacity (mg/g)
Wheat	8.32
Oat	17.54
Activated carbon (coconut shell)	19.59
Zeolite	53.1
Egyptian date pites	145.01
Guava (Psidium guajava) leaf	185.2
Activated carbon (Durian shell)	289.26
Activated carbon (olive stones)	303
Activated carbon (tea seed shell)	324.7
Pomelo (Citrus grandis peel)	344.83

Conclusions

Egyptian date pits were found to be an effective and a promising low cost adsorbent for the removal of Methylene blue in waste water. The adsorption of MB was increased with reducing the dye concentration and temperature; and increasing the contact time and dosage up to equilibrium values which was 25 °C, 20 min, and 0.1 g adsorbent, respectively. At pH>5, adsorption was promising. The BET surface area of Egyptian date pits was 0.5827 m^2 /g.

Disclosure Statement

No potential conflict of interest was reported by the authors.

Orcid

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References

[1]. Jodeh S., Amarah J., Radi S., Hamed O., Warad I., Salghi R., Alkowni R. *Moroccan Journal of Chemistry*, 2016, **4**:4
[2]. Comte I., Colin F., Whalen J.K., Grünberger O., Caliman J.P. *Advances in Agronomy*, 2012, **116**:71
[3]. Crini G., Badot P.M. Sorption processes and pollution: conventional and non-conventional sorbents for pollutant removal from wastewaters. Presses Univ. Franche-Comté, 2010
[4]. Dada A.O., Olalekan A.P., Olatunya A.M., Dada A. IOSR Journal of Applied Chemistry, 2012, **3**:38
[5]. Hao O.J., Kim H., Chiang P.C. *Critical Reviews in Environmental Science and Technology*, 2000, **30**:449
[6]. Patiha, Heraldy E., Hidayat Y., Firdaus M. *In IOP Conference Series: Materials Science and Engineering*, 2016, **107**:012067
[7]. Hijab M., Saleem J., ParthasarathyP., Mackey H.R., McKay G. *Biomass Conversion and Biorefinery*, 2020 https://doi.org/10.1007/s13399-020-00813-y
[8]. Jain S., Kumar P. In Impact of Textile Dyes on Public Health and the Environment, 2020; p 20-49
[9]. Jeppu T.P.C. *Journal of Contaminant Hydrology*, 2012, **129**:46
[10]. Koyuncu H., Kul A.R. *Applied Water Science,* 2020, **10**:1
[11]. Li Y., Li M., Xiao K., Huang X. *Journal of Cleaner Production*, 2020, **246**:118964
[12]. Mahmoodi N.M., Khorramfar S., Najafi F. *Desalination*, 2011, **279**:61
[13]. Maity J.P., Hsu C.M., Lin T.J., Lee W.C., Bhattacharya P., Bundschuh J., Chen C.Y. *Environmental Nanotechnology, Monitoring & Management*, 2018, **9**:18
[14]. Mbadcam J.K., Ngomo, H.M., Tcheka, C., Rahman A.N., Djoyo H.S., Kouotou D. *Journal of Enviromental Protection*, 2009, **3**:53
[15]. Menazea A.A., Eid M.M., Ahmed M.K. *International Journal of Biological Macromolecules*, 2020, **147**:194
[16]. Panigrahi T., Santhoskumar A.U. *Progress in Chemical and Biochemical Research*, 2020, **3**:135
[17]. Rafatullah M., Sulaiman O., Hashim R., Ahmad A. *Journal of Hazardous Materials*, 2010, **177**:70
[18]. Rahimian R., Zarinabadi S. *Progress in Chemical and Biochemical Research*, 2020, **3**:251
[19]. Ricci A., Olejar K.J., Parpinello G.P., Kilmartin P.A., Versari A. *Applied Spectroscopy Reviews*, 2015, **50**:407
[20]. Shahrokhi-Shahraki R., Benally C., El-Din M.G., Park J. *Chemosphere*, 2011, **264**:128455
[21]. Tan I.A.W., Ahmad A L., Hameed B.H. *Desalination*, 2008, **225**:13
[22]. Yang S.T., Chen S., Chang Y., Cao A., Liu Y., Wang H. *Journal of Colloid and Interface Science,* 2011, **359**:24
[23]. Yazdi M.K., Zarrintaj P., Hosseiniamoli H., Mashhadzadeh A.H., Saeb M.R., Ramsey J.D., Mozafari M. *Journal of Materials Chemistry B*, 2020, **8**:5992
[24]. Zulfikar M.A., Maulina D., Nasir M., Handayani N., Handajani M. *Environmental*

Nanotechnology, Monitoring & Management, 2020, **14**:100381

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