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Sorption of methylene blue onto the biomass of date palm seeds: kinetic study

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ABSTRACT

The removing of methylene blue dye (MB^+) from aqueous solution by using *biomass of Date palm seeds* (BDPS) has been studied in a batch sorption. The kinetics of sorption has been carried out by controlling different parameters such as initial concentration, dosage, temperature, and pH. The sorption equilibrium is achieved during the first 20 minutes. The maximum removal of MB^+ is 94 % upon the study conditions of C_i = 100 mg L^{-1}, T= 20 ºC, 80 rpm). The reaction kinetic models, such as pseudo-first-order and pseudo-second-order, and adsorption diffusion model, such as Weber-Morris intra-particle diffusion model, have been used to describe the sorption rate and mechanism of the MB^+ onto BDPS. The sorption process of MB^+ into BDPS has followed the pseudo-second-order model (R^2 = 1). The kinetic parameters, the rate constant, and sorption capacities have been calculated. The new information about this study suggests that *biomass of Date palm seeds* can be used as natural and safe materials for removing MB^+ from the water.

Keywords: *Biomass; Methylene Blue; Date Palm Seeds; Adsorption; Kinetic; Pseudo-second order*.

1. INTRODUCTION

Methylene blue is considered one of the heterocyclic chemical compounds, which has a chemical formula of $C_{16}H_{18}ClN_3S$. It has a dark green powder. Methylene blue is an organic and cationic dye that used in the field of chemistry, biology, as a drug and pharmaceutical product [1] (Lau *et al*. 2015). Methylene blue is used in analytical chemistry as an oxidation-reduction indicator [2]. Gene Link [3] reported that Methylene blue is used in the field of histology as a selective dye for tissue types, and in molecular biology for dying DNA and RNA in gels. Alan Hall (1995) mention that Methylene blue is used in medicine as an antidote to nitrite and aniline poisoning [4]. Wong et al. (2013) talk about that methylene blue can be used in the industry field, such as dying hair, cotton, wool, leather, and paper [5]. The dying effluent of the industrial processes contains large quantities of methylene blue. The presence of methylene blue in the water medium may lead to contamination of groundwater and food, which in turn leads to its arrival in the human body. The presence of methylene blue in water at high concentrations, in addition, to long-term exposure can cause human health impact. For example, it can cause vomiting, nausea, anemia, and hypertension [6]. Therefore, liquid wastes containing methylene blue must be treated before being thrown into the environment.

There are several important types of researches concern the removal of methylene blue from the water, especially those studies that take into account the idea of the selectivity and technical scientific approaches. However, poor communities may be interested in choosing cost-effective processing technology, which is the most important issue for researchers and chemists. Various physical, chemical and biological methods, including adsorption and biosorption, are used for this regards. For example, some research works use the technique of coagulation/flocculation [7], advanced oxidation [8], ozonation [9], membrane filtration [10-12], electrodialysis [13], and liquid-liquid extraction are used [14]. Furthermore, the adsorption kinetics and facilitated transport of two cationic dyes (Methylene Blue (MB) and Rhodamine B (RB)) were carried on polymer inclusion membrane (D2EHPA-PIM) [15]. Wherein, Hameed (2009) [16-17] and Salleh et al. [18] review the advantages and disadvantages of such processes and techniques for the removal of pollutants and toxic materials from water.

In this regards, it is found that the adsorption is the most effective choice for achieving low-cost, simple design, ease of operation and its high efficiency to the toxic substances. Rafatullah et al. [19] (Rafatullah et al. 2010) have reviewed the use of low-cost adsorbents for the removal of methylene blue (MB) from the water. For example, they use carbon [20], graphene [21], and carbon nanotubes [22], carbon produced from tea (Camellia Sinensis L.) seed shells [23], yellow passion fruit peel [24], agricultural residue walnut shell [25], $ZnCl_2$ activated cornhusk carbon [26], untreated parthenium hystrophorous weed [27], chitosan/zeolite composite from shrimp waste [28], coconut Husk [29], nano-zerovalent iron [30], Fe_3O_4 Nanoparticles [31], amorphous nanostructure [32], elaeagnusan gastifolial [33], sewage sludge-based granular activated carbon [34], TiO_2/UV-C photocatalytic process [35], nano $LaFeO_3$ particles [36], activated carbon/urea formaldehyde composite resin [37], eggshell powder [38], activated carbon web [39], agricultural waste of musa paradisiac [40], pink guava (Psidium Guajava) waste-based activated carbon [41], cylindrical graphene-carbon nanotube hybrid [42], solvothermal-synthesized graphene/magnetite composite [43], graphene oxide [44], and electrolytic chemical treatment [45], waste material activated carbon and activated rice husks [46], activated and Non-activated bentonites [47],

lignocellulosic materials [48], amorphous aluminosilicate gels and zeolite X [49], perlite [50], garlic peel, an agricultural waste biomass [51].

The wastewater resulting from the use of waters in Jordan whether in manufacturing, cleaning, cooling and others contain methylene blue dyes. The industrial wastewater initially treated by a plant before disposal to the sewage network, which complies with the sanitation instructions issued by the Jordan Industrial Estate Corporation. The industrial wastewater shall be disposed to the sewage network, providing that the quality of wastewater is matching with the characteristics included Methylene blue active substances with less than 26 mg L^{-1}. Because of this problem and due to the availability, advantages and the accessibility of *the biomass of date palm seeds* (BDPS) in Middle East countries, it is possible to use BDPS for removing pollutants, metal ions [52] and organic dyes such as methylene MB^+ from aqueous solutions. To the best of my knowledge, up to date, we do not find any study related to use the *biomass of date palm seeds* (BDPS) as a natural material for removing methylene blue dye from an aqueous solution. Herein, the kinetics of sorption is carried out by using several models such as pseudo-first-order and pseudo-second-order. Sorption diffusion model, such as Weber-Morris intra-particle diffusion model, have been also used to describe the adsorption rate of the MB^+ onto solid particles of the biomass of date palm seeds. The equilibrium interface between the MB^+ solution and the BDPS solid particles of the sorbent can be determined in the condition of the greatest sorbet capacity.

2. EXPERIMENTAL SECTION

2.1 Material and methods.

2.1.1 Biomass of Date Palm Seeds (BDPS). The *biomass* of the *Date Palm Seeds* (BDPS) was obtained locally from the market (Jordan). We have used one type of date seeds (Barhy-type) in our batch sorption experiments. These seeds were washed with distilled water and then were dried at room condition. They were washed three times by *n*-hexane and then were dried at room temperature. After drying, the BDPS were dried in the oven (120 ºC) overnight producing a model of the *biomass* of the *Date Palm Seeds*. They were crushed and ground into powder form. The powder was screened (75- 125 μm mesh size) by using standard Tyler screen series.

2.1.2 Reagents. All chemicals were used as received as an analytical grade. Methylene Blue was purchased from Fluka AG (Buchs, Switzerland). NaOH (0.1 mol L^{-1}) and HCl (0.1 mol L^{-1}) were purchased from Merck (Darmstadt, Germany). A stock solution of methylene blue was prepared by dissolving a stoichiometric amount of MB^+ powders in 1 L of distilled water. Standard solutions of MB^+ (30, 50, 100, 150, and 200 mg L^{-1}) were prepared by appropriate dilution. An "initial" pH and its subsequent adjustment for all experimental runs were conducted less than 7.4 at the maximum value.

2.2 Apparatus and instruments.

Methylene blue absorbs light in the field between about 530 to 700 nm so that the peak is at about 660 nm. Therefore, the MB^+ concentration in the solution was measured by using the UV-Vis spectrophotometer (Shimadzu UV-1800 UV-Vis Spectrophotometer). All the reported results were the average of at least triplicate measurements at 660 nm. The mixtures were mixed by a thermostatic mechanical shaker at constant temperature (20, 30, and 40 °C, Isothermal Gefellschaft Fur 978). To ensure accuracy in preparation, analytical balance is used (Sartorius, CP324-S/ management system certified according to ISO 9001).

2.3 Equilibrium studies.

The batch removal of the Methylene blue (MB^+) was calculated from the mass balance, which was stated as the amount of MB^+ molecules adsorbed onto the solid particles of the BDPS sorbent. It equals the amount of MB^+ molecules that removed from the water and adsorbed into BDPS. Mathematically can be expressed in Eqs. (1)-(2):

$$q_e = \frac{(C_i - C_e)}{S} \quad (1)$$

$$q_t = \frac{(C_i - C_t)}{S} \quad (2)$$

Where q_e is the adsorbed amount of MB^+ into BDPS solid surface at equilibrium (mg g^{-1}).; q_t is the adsorbed amount of MB^+ into BDPS solid surface at a specific time (mg g^{-1}); C_i is the initial concentration of MB^+ in the aqueous solution (mg L^{-1}); C_e is the equilibrium concentration or final concentration of MB^+ in the aqueous solution (mg L^{-1}); and C_t is the final concentration of MB^+ in the aqueous solution (mg L^{-1}) at a specific time.

The dosage (slurry), S, the concentration of CDPS is expressed by equation 3:

$$S = \frac{m}{v} \quad (3)$$

Where ν is the initial volume, of MB^+, solution used (L) and m is the mass of BDPS adsorbent.

The percent adsorption (%) was also calculated using Eq. (4):

$$\% \text{ Adsorption} = \frac{C_i - C_e}{C_i} \times 100\% \quad (4)$$

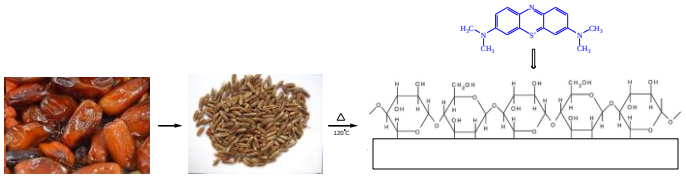
2.4 Effect of contact time.

The sorption experiments were carried out by shaking 0.5 g of the BDPS with 50 mL of 100 mg L^{-1} of MB^+ solution (pH_i = 7.4, dosage = 2 g L^{-1}). The solutions were shaken vigorously using thermostatic mechanical shaker at constant temperature (20, 30, 40 and 50 °C). The agitation speed was fixed at 80 rpm for a known period in the interval of 0.5 to 180 minutes with increment of 10 minutes from 10 to 60 minutes, and then 30 minutes from 60 to 180 minutes. At the end of the predetermined time, the filtrate samples were analyzed. All the reported results were the average of at least triplicate measurements.

3. RESULTS SECTION

3.1. The sorption of MB^+ onto the BDPS sorbent.

The sorption of MB^+ onto the solid particles of the BDPS sorbent could be performed through the suggested chemisorptions mechanistic through the binding of MB^+ ion with the –OH functional group on the sorbent surface. The MB^+–BDPS sorption achieve Lagergren pseudo-second-order model (R^2 = 0.999). This can support the suggestion of chemisorptions mechanistic between MB+ and BDPS as reported in the study of Ho [53]. We could say that two possible mechanisms of adsorption of MB^+ onto BDPS adsorbent may be considered include: (a) electrostatic interaction between the adsorbent and the MB^+ molecule, (b) a chemical reaction between the MB^+ and the adsorbent as shown in Scheme 1. Based on this suggestion, the kinetic sorption of methylene blue onto the biomass of date palm seeds is considered in our explanations



Scheme 1. The possible mechanism of adsorption of MB^+ on the BDPS adsorbent.

3.2. Effect of MB^+ Concentration.

The effect of the initial MB^+ concentration on the sorption efficiency is investigated in the concentration range of 1 - 100 mg L^{-1} at 20 ºC. Figure (1) shows that the percentage of removal increases with increasing the initial concentration of MB^+. The higher uptake is due to the nature of the interaction between methylene blue and functional groups available in the surface area of Cellulose. The basic dye of MB^+ can react with the weak acidic functional group in cellulose. Wherein, the increase in the initial concentration of MB^+ can activate the acidic functional group in *cellulose* to react. We could say that the basic medium of methylene blue solution can improve the negative surface charge of adsorbent and its sorption capacity. Another suggestion depends on the idea of that; initial MB^+ dye concentration provides an important driving force to overcome the mass transfer resistance of the dye between the aqueous and solid phases. For example, the removal percentage was 91 % using high-level concentration (100 mg L^{-1}); while it was 25 % using low-level (1.0 mg L^{-1}). This result compatible with the recent studies, for example; Simarouba glauca seed shell powder [54] and as what found by using biomass of the *Eucalyptus sheathiana* bark [55].

3.3. Effect of Temperature.

The influence of temperature on the removal of MB^+ from the aqueous solution has been studied through a variety of temperatures 20, 30 and 40 °C. It is observed in Figure 2 that the removal percentage decreased with increasing temperature; wherein it is highly affected through raise the temperatures. The maximum removal percentage of 20 ºC is 82 %, while the lowest percentage is 27 % at a temperature of 40 ºC. This indicates that low temperature could enhance the chemical interaction of MB^+ with BDPS surface (chemisorptions) [56]. This type of interaction is typical to the adsorption of the aqueous MB^+ on the sulfuric acid–treated orange peel [57].

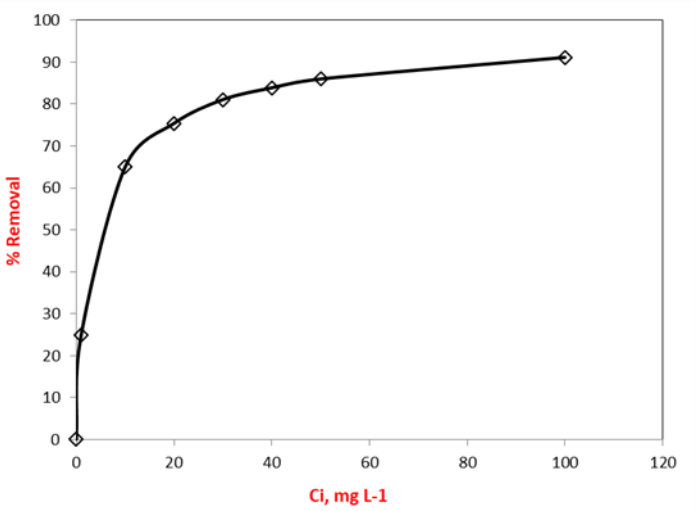


Figure 1. Effect of initial concentration of MB^+ (t = 40 min, 20 ºC, 50 ml, 0.1 g carbon date seeds, 80 rpm).

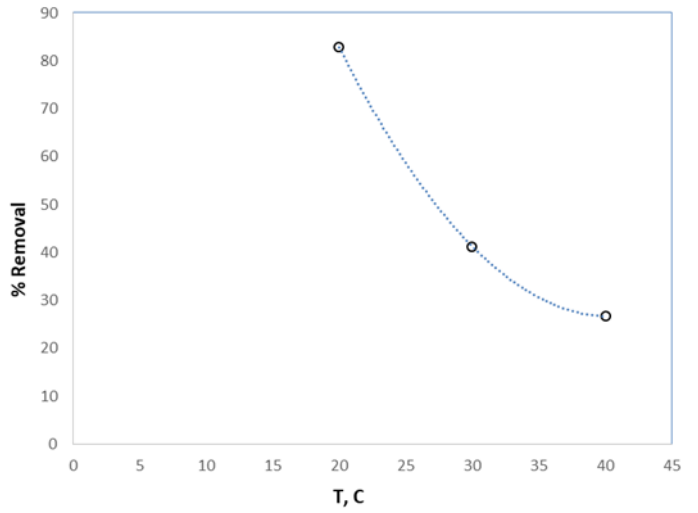


Figure 2 Effect of temperature (t = 40 min, 50 ml, C_i = 100 mg L^{-1}, 0.1 g carbon date seeds, 80 rpm).

3.4. Dosage effects of BDPS adsorbent.

The removal percentage of MB^+ from 100 mg L^{-1} solution using different dosages of BDPS (2, 4, 10, 20, 30 and 40 g L^{-1}) has been described in Figure 3. The removal percentage increases sharply as the adsorbent dose increases. This is due to the reason for increasing the number of the functional group and adsorption active site in the BDPS surface area [52]. The maximum removal (95 %) has been observed using the dosage of 40 g L^{-1}. These results are in line with the study, which related to the utilization of the Jatropha Curcas fruit Pericarp and seed coat as raw material for the removal of methylene blue from water [58].

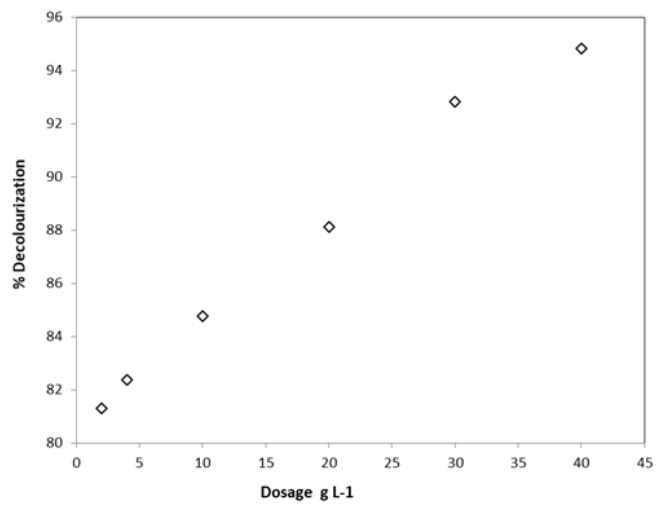
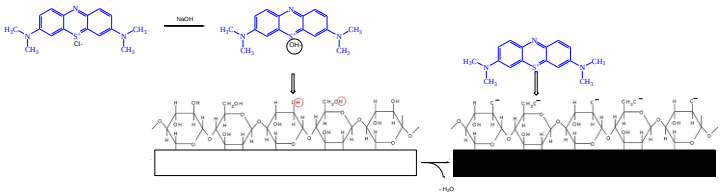


Figure 3. Effect of BDPS dosage (t = 40 min, 50 ml, T = 20 ºC, C_i = 100 mg L^{-1}, 80 rpm).

3.5 Effect of pH.

Figure 4 represents the removal percentage of MB^+ from 100 mg L^{-1} aqueous solution using different pH values (2, 3, 5, 7, 9 and 12). The maximum removal percentage 87 % is achieved with pH =12, while it is 0 % by using pH = 2. This indicates that the acidic medium of solution leads to decrease the percentage of removal, which is in opposite by using the basic medium. When pH of the solution increases, OH^- can replace of Cl^- producing NaCl, wherein the OH^- binds with MB^+ weakly as shown in Scheme 2. This causes the surface of the BDPS to become deprotonated easily and, as a result, the negative charge of the used BDPS surface will be amplified. Therefore, the electrostatic attractive force between the MB^+ dye, which has a positive charge, and the adsorbent surface increases, and consequently, the rate of dye adsorption increases. Therefore, we could say that the BDPS adsorbent surface is acidic and needs to be activated by the basic medium. Acidic medium lead to decrease the negatively charged on the surface area of adsorbent then shows low sorption capacity. Some compatible results are reported that match our findings, such as utilization of the Jatropha Curcas fruit Pericarp and seed coat as raw material for the removal of methylene blue from water [58].



Scheme 2. The basic medium can activate and deprotonate of the BDPS surface.

The effect of contact time is shown in Figure 5. At the initial stage, the removal rate of MB+ is high during the first 5 minutes. The initial faster rate may be due to the availability of the uncovered surface area of the BDPS. The final equilibrium of sorption starts after 90 minutes yielded a maximum removal of 93 % (approx.). At the later stages, there is slightly increasing removal efficiency by increasing the contact time. This is due to the decreased or lesser number of active sites. Similar results have been reported in the literature for the removal of dyes, organic acids and metal ions by various adsorbents [59].

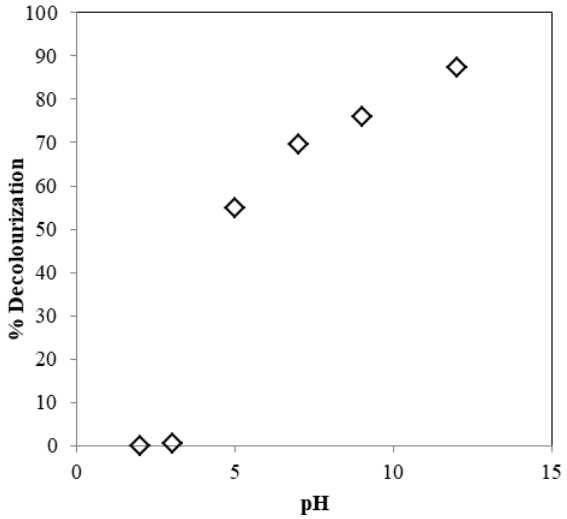


Figure 4. Effect of pH (C_i= 100 ppm, 20 ºC, 0.1 g carbon date palm seeds, 50 ml, 80 rpm).

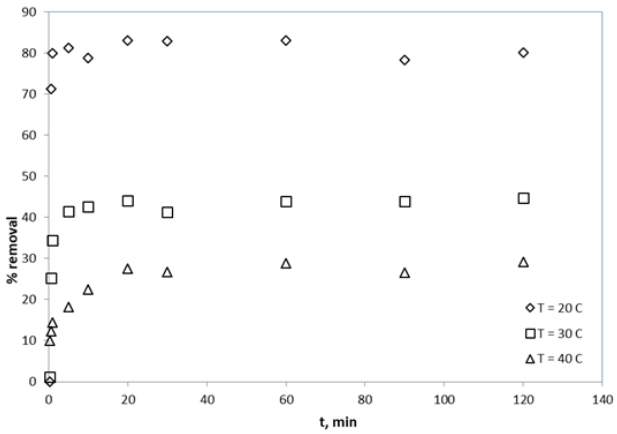


Figure 5. Effect of contact time on MB^+ sorption, C_i = 100 mg L^{-1}.

The kinetics sorption describes the removal rate of MB^+ from the 100 mg L^{-1} of an aqueous solution. The kinetic sorption was analyzed using two kinetic models including the pseudo-first-order and pseudo-second-order. The role of contact time was studied under the shaking conditions, for instance, the pH of the solution was 7.4, 80 rpm, 2 g L^{-1} dosage of BDPS and by applying 20, 30, or 40 ºC. Samples were collected at regular intervals and then analyzed after filtration.

The pseudo-first-order kinetic model and its integral can be expressed by Eq. (10) [60]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (10)$$

Where q_e and q_t (mg g^{-1}) are the amounts of adsorbed MB^+ at equilibrium and at the time (t), respectively, k_1 (min^{-1}) is pseudo-first-order rate constant, and t (minutes) is contact time. The coefficient of determination value (R^2) is less than 0.2411. Therefore, the fitting of the experimental data to the pseudo-first order was not so good. Thus, this conclusion leads us to use a pseudo-second-order kinetic model and its integral form. This model is expressed by Eq. (11), which was reported in ref. [61-62]:

$$\frac{t}{q_t} = \frac{1}{k_2 q^2_e} + \frac{1}{q_e} t \qquad (11)$$

where k_2 is the equilibrium rate constant of the pseudo-second-order kinetic model (g mg^{-1} min^{-1}). The value of k_2 can be

determined by plotting t/q_t versus t to obtain a straight line of slope $1/q_e$ and intercept of $1/(k_2)$ as shown in Figure 6 and Table 1. From the determination coefficient value R^2 = 1 (approx.), the adsorption model of MB^+ onto BDPS surfaces is well described by pseudo-second-order. Furthermore, the compression of q_e values from the experimental work of this study and calculated one of the pseudo-second-order kinetic model (difference smaller) also show the applicability of this model.

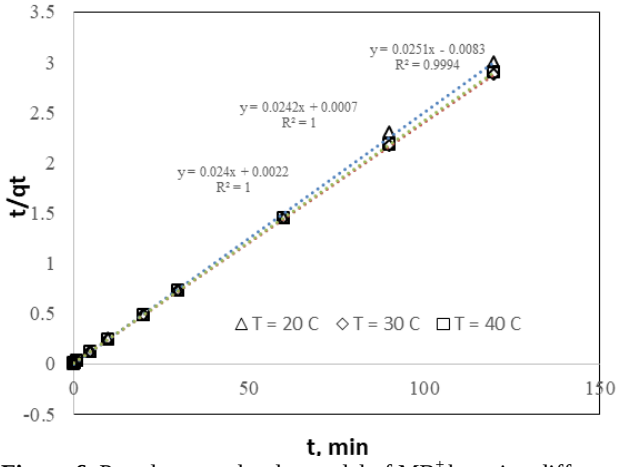


Figure 6. Pseudo-second order model of MB^+ by using different Temperature (20, 30, and 40 °C), dosage = 2 g L^{-1}, t = 40 min., 80 rpm, and Ci = 100 mg L^{-1}.

Table 1. The parameters of the pseudo-second order kinetic model.

	k_2 (g mg^{-1} min^{-1})	$q_{e,\,Exp}$ (mg g^{-1})	$q_{e,\,Calc}$ (mg g^{-1})	R^2
20 ºC	0.075903	41.521	39.841	**0.9994**
30 ºC	0.26181	41.521	41.667	**1**
40 ºC	0.83664	41.521	41.322	**1**

To determine the diffusibility of the MB^+ into the adsorbent, Weber-Moris intraparticle diffusion model [63] were used in the form of the Eq. (12):

$$q_t = k_{int}\sqrt{t} + C \qquad (12)$$

Where C is constant, q_t the amount of MB^+ adsorbed at the time (mg g^{-1}) and k_{int} is the intraparticle diffusion rate constant (mg g^{-1} $min^{-1/2}$). A plot of q_t *vs.* $\sqrt{t}$ giving straight line confirms intraparticle diffusion sorption as shown in Figure 7. Due to the plot is not linear, and *moreso* do not pass through the origin, then intraparticle diffusion could not be the only mechanism involved. Therefore, it, such plot, presents multi-linearity, which indicates that two or more steps occur. The first, sharper portion (ca. $\sqrt{t}$ range from 0 to 1 $min^{1/2}$; *i.e* from 0 up to 5 minutes of adsorption period) is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage (ca. $t^{1/2}$ range from 1 to 4.47 $min^{1/2}$; *i.e* from 5 up to 20 minutes of adsorption period), where the intraparticle diffusion is rate- controlled (k_{int} = 0.176 mg g^{-1} $min^{-1/2}$ and R^2 = 0.999, see Fig. 7). The third portion is final equilibrium stage where the intraparticle diffusion starts to slow down due to extremely low solute concentrations in the solution and chemisorptions stage is taken part on the BDPS surface and pores (which already has been successfully explained by pseudo-second-order kinetic model from 20 to 120 minutes of adsorption period. This result agree with the recent results that published by using Chitin [64].

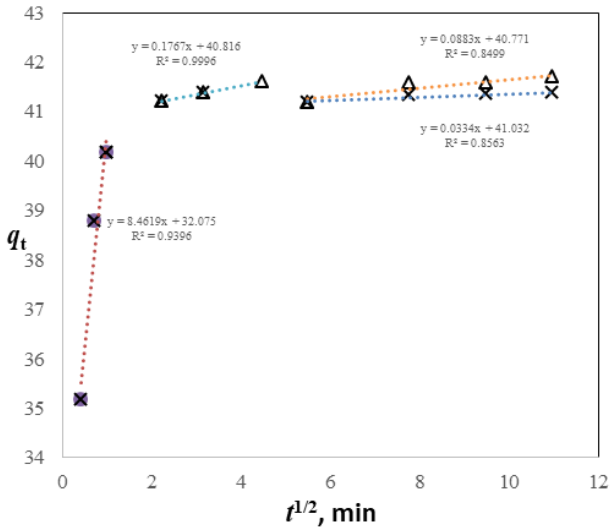


Figure 7. Weber-Moris intra-particular diffusion kinetic model.

4. CONCLUSIONS

In this work, the sorption process has followed the pseudo-second-order model. The equilibrium time achieved within 20 minutes of the adsorption process. The maximum removal of MB^+ is 94 % upon the study conditions of C_i = 100 mg L-1, T= 20 °C, 80 rpm) in the basic medium. The kinetic rate constant k_2 of sorption is increased by increasing the temperature.

Depending on the kinetic information that has been collected from this study, we can determine the mechanistic aspects as follows: (i) the external surface adsorption or instantaneous adsorption stage within 0 to 5 minutes of adsorption period. (ii) The intraparticle diffusion stage within 5 up to 20 minutes of the adsorption period (it is a physisorption process). (iii) The MB^+ binds to the O-H functional group within the framework of the BDPS particles. This adsorption reaction is done by forming an electrostatic interaction.

The new information in this study suggests that BDPS particles can adsorb MB^+ from the water at normal conditions. The new finding is to exploit the large quantities of *Date Palm Seeds* (BDPS) waste in treating polluted water in the Middle East countries. Thus, we recommend designing a suitable membrane containing BDPS for removing the MB^+ from the water. Furthermore, this kind of BDPS biomass can be added to other types of recent and low cost adsorbents (e.g. Aluminium-modified activated carbon [65], lignocellulosic plant materials [66], Coffee Waste [67], Graphene-like carbon (GLC) material [68], sodium alginate and clinoptilolite [69], humic acid [70], carbon nanotubes [71], Activated lignin-chitosan extruded blends [72], Solanum xanthocarpum Plant [73], and banana agricultural waste [74]) as their immense potentials in toxic water remediation.

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