



Experimental study and modeling of basic dye sorption by diatomaceous clay

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Abstract

This paper presents a study on the adsorption of basic dye, methylene blue, from an aqueous solution onto diatomaceous earth (diatomite). The effect of initial dye concentrations, adsorbent particle size and concentration, and agitation speed on adsorption was investigated. Adsorption isotherms obtained at different solutions temperatures revealed an irreversible adsorption with a capacity of 42 mmol dye/100 g diatomite reached within 10 min. This value slightly increases with increasing the solution temperature. A proposed correlation to describe the irreversible adsorption isotherm was introduced, which resulted in a better fit to the experimental data than that of Langmuir's and Freundlich's. Two simplified kinetics models, *pseudo-first order* and *pseudo-second order*, were tested to investigate the adsorption mechanisms. It was found that the kinetics of adsorption of methylene blue onto the surface of diatomite at different operating condition are best described by the pseudo-first-order model.

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1. Introduction

Water contamination resulted from dyeing and finishing in textile industry is a major concern. Discharging large amount of dyes in water resources accompanied with organics, bleaches, and salts can affect the physical and chemical properties of freshwater. In addition to their unwanted colors, some of these dyes may degrade to produce carcinogens and toxic products. Consequently, their treatment do not

depend on biological degradation alone (Kannan and Sundaram, 2001). One of the powerful treatment processes for the removal of dyes from water with a low cost is adsorption. Several adsorbents are eligible for such a purpose. Activated carbon is the most popular adsorbent and has been used with great success (Yang and Al-Duri, 2001). However, the activated carbon is considered an expensive adsorbent, which makes the wastewater treatment a cost-challenging step especially in developing countries. Several studies have tried to replace the activated carbon with naturally and less expensive synthetic materials. Meshko et al. (2001) compared the uptake of basic dyes using natural zeolite with that of

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activated carbon. Ghosh and Bhattacharyya (2002) used kaolinite for methylene blue removal from basic solution.

Several equilibrium and kinetic models were used to predict the adsorption behavior of solutes in solution. Examples are Freundlich's (1906), Langmuir's (1918), external film resistance model (Hougen and Marshal, 1947), pore diffusion models for batch reactors (Edeskuty and Amundson, 1952a,b), lumped external and internal diffusion models (King, 1965), and dual particle-diffusion model (Liang, 1984).

The main object of this work is to utilize diatomaceous clay for adsorption of a basic dye, specifically methylene blue from water, and to study the isotherm and kinetic models that fits the experimental findings.

2. Experimental

2.1. Materials and methods

Diatomite was recently discovered in Jordan with large quantity. It is a pale-colored, soft, lightweight sedimentary rock principally composed of silica microfossils of aquatic unicellular algae (Lemonas, 1997). These rocks were supplied by the Natural Resource Authority from Al-Azraq basin-Jordan. Sample of 200 g was washed with 6 N nitric acid followed by washing with 6 N hydrochloric acid, then washed thoroughly with deionized water until achieving neutralization of the decantant. Then, the sample was washed with 1.8 l of 0.05 M tetrasodium pyrophosphate to dipper the components of the diatomite and 0.05 M sodium hydroxide to remove impurities and organics. Finally, the sample was washed several times by deionized water, filtered, dried at 100 °C, sieved, and stored in closed containers for further tests. X-ray diffraction analysis was performed by grinding a dried sample using an agar mortar and pestle and tested at 40 kV and 40 mA. Fourier Transform Infrared Spectroscopy was performed by mixing a sample of diatomite with a fine dried powder of KBr and then hydraulically pressed at 10 ton/m² to obtain a thin transparent disk. All the chemicals were analytical grades obtained from Sigma and the glassware was Pyrex washed with diluted nitric acid, soap, and deionized water to minimize surface adsorption of methylene blue.

2.2. Adsorption isotherm

Adsorption isotherms were performed in a set of 43 Erlenmeyer flasks (250 ml) where solutions of methylene blue (100 ml) with different initial concentrations (0.13–1.87 mmol/l) were placed in these flasks. Equal mass of 0.2 g of particle size (45–63 μm) diatomite was added to methylene blue solutions and kept in an isothermal shaker (25 ± 1 °C) for 3 days to reach an equilibrium of the solid solution mixture. Similar procedure was followed for another set of Erlenmeyer flask containing the same methylene blue concentration without diatomite to be used as a blank. The pH was adjusted to 7 by adding either few drops of dilute hydrochloric acid or sodium hydroxide. The flasks were then removed from the shaker and the final concentration of methylene blue in the solution was measured using 21 Baush and Lomb spectrophotometer. Similar procedures were performed at solution temperatures of 15 and 40 °C. The amount of methylene blue uptake by the surface of diatomite, q_e (mmol/g), was obtained as follows:

$$q_e = \frac{C_0 - C_e}{m_s} \quad (1)$$

where C_0 and C_e (mmol/l) are the initial and final concentrations of methylene blue, respectively, and m_s is the concentration of diatomite in solution (g/l).

2.3. Adsorption kinetics

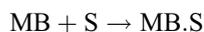
Kinetic studies were carried out in 2-l beaker where a fixed mass of diatomite of 1.27 g (unless otherwise stated) was introduced into 1.7 l of methylene blue solution with different concentrations. The beaker was equipped with four Plexiglas baffles to prevent vortex formation. Moreover, a two-flat-blade impeller was adjusted on top of the beaker driven by fixed speed motor to keep good contact between the solution and the solid particles. The kinetics parameters of initial concentration and temperature of methylene blue solution, mass and particle size of diatomite, and agitation speed of the mixer were varied during the experiments. Samples of 2 ml were drawn from the solution each minute for the first 5 min, and then each 5 min until the end of the experiment. The samples were drawn using fritted

glass tube to prevent any contact of the drawn solution with the adsorbent particles outside the adsorption beaker. Then, these samples were analyzed and tabulated for further discussion.

3. Theoretical

3.1. Adsorption isotherm

Adsorption coverage over the surface of diatomite was studied using the two well-known isotherm models; Langmuir's and Freundlich's. These models are considered the best to describe the reversible adsorption isotherm. When the experimental data show chemisorption with an irreversible behavior, the above-mentioned models could not fit the data precisely. An alternative correlation is presented in this study to follow the trend of experimental data. The adsorption process is assumed here to be non-elementary chemical reaction as



where MB is the methylene blue, S is the active surface of diatomite, and MB.S is the chemisorbed species of methylene blue at the surface of diatomite. The rate of disappearance of MB from solution is related to the rate equation:

$$-\frac{\Delta C_e}{\Delta t} = kC_e^\beta \quad (2)$$

where k is the reaction constant and β is the order of reaction. The rate of change of MB concentration with time is related to that adsorbed at the surface of diatomite by the differential form of Eq. (1):

$$\Delta q_e = -\frac{1}{m_s} \Delta C_e \quad (3)$$

where Δq_e is the difference between the concentration of MB on the surface of diatomite and that of saturation value, q_s , at any time.

Substituting the above equation with Eq. (2) and dividing by q_s yields

$$\frac{q_s - q_e}{q_s} = \frac{k\Delta t}{m_s q_s} C_e^\beta \quad (4)$$

Recalling that $\alpha = k\Delta t/m_s q_s$ and rearranging the above equation yields

$$q_e = q_s(1 - \alpha C_e^\beta) \quad (5)$$

The linear form of the above equation is

$$\ln\left(1 - \frac{q_e}{q_s}\right) = \ln\alpha + \beta \ln C_e \quad (6)$$

The equilibrium data were also fitted with Langmuir's model according to

$$q_e = \frac{QbC_e}{1 + bC_e} \quad (7)$$

where Q (mmol/g) is the maximum amount of methylene blue that can be adsorbed per unit mass of diatomite to form a complete monolayer, and b (l/mmol) is the Langmuir constant related to the affinity of binding sites. Langmuir model is usually linearized as

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{Qb} \frac{1}{C_e} \quad (8)$$

Freundlich model, which is a special case for heterogeneous surface energies, is used as

$$q_e = QC_e^{1/n} \quad (9)$$

where Q , roughly, represents the adsorption capacity and can be related to the surface energy as

$$Q \propto RTnbe^{\Delta H/RT} \quad (10)$$

and $1/n$ is the adsorption intensity. The value of n is usually greater than 1 and must reach some limit when the surface is fully covered. The linear form of Freundlich model is

$$\ln q_e = \ln Q + \frac{1}{n} \ln C_e \quad (11)$$

3.2. Adsorption kinetics

In order to study the rate-determining step for the adsorption of methylene blue onto the surface of diatomite, two kinetic models of Ho and McKay (1999) (Wu et al., 2001) were employed: pseudo-

first-order and second-order model. The simple pseudo-first-order model assumes that the rate of change of solute uptake with time is directly proportional to the difference in saturation concentration and the amount of solid uptake with time.

$$\frac{dq(t)}{dt} = k_1(q_e - q(t)) \quad (12)$$

where $q(t)$ is the amount of solute adsorption at any time (mmol/l), and k (1/min) is the rate constant of pseudo-first-order model. When substituting Eq (1) in Eq. (9) and integrating over concentration and time, the following equation is obtained

$$\frac{C(t)}{C_0} = 1 - \frac{m_s q_e}{C_0} (1 - e^{-k_1 t/m_s}) \quad (13)$$

The *pseudo-second-order* equation based on adsorption equilibrium capacity is expressed in the form (Ho and McKay, 2000; Wu et al., 2001)

$$\frac{dq(t)}{dt} = k_2(q_e - q(t))^2 \quad (14)$$

where k_2 is the rate constant of pseudo-second-order adsorption. With a similar manner performed for the previous model, the concentration of solute can vary with time according to

$$\frac{C(t)}{C_0} = 1 - \frac{m_s t}{q_e^2/k_2 + t/q_e} \quad (15)$$

3.3. Thermodynamics consideration

The thermodynamic parameters such as enthalpy and entropy of adsorption process can be related to the distribution coefficient of solute between the solid and liquid phases as (Khan et al., 1995; Ghosh and Bhattacharyya, 2002)

$$\log \frac{q(t)}{C(t)} = \frac{\Delta S^\circ}{2.203R} - \frac{\Delta H^\circ}{2.303RT} \quad (16)$$

where ΔH° and ΔS° is the standard enthalpy and entropy for adsorption process, R is ideal gas constant and T is the temperature.

4. Results and discussion

The chemical composition of Jordanian diatomite determined by X-ray diffraction (XRD) is shown in Table 1. This table shows that the main constituent of diatomite samples is SiO₂ (72.5%). The high content of silica in diatomite gives its structure credibility as a good adsorbent. Results of infrared technique (IR) (Fig. 1) show that the main absorption bands of diatomite were at 3695, 3620, 1101, 1031, and 912/cm, where the bands at 3695 and 3620 are due to the chemical interaction between the oxides and the surface silanol groups. The weak and narrow bands occur due to free surface silanol group (Si–OH). The bands at 1101 and 1031 are strong and broad because of siloxane (Si–O–Si) stretching, while 912 is weak and broad which is due to (Si–O) stretching of silanol group (Colthup et al., 1990). The surface area of diatomite was estimated using the method proposed by Sears (1956) for silica materials and further calibrated to Brunauer, Emmett, and Teller (BET) method to be 33 m²/g. The isoelectric point was measured using Hunter procedure (1981) and found at pH_{ZPC}=4.

4.1. Adsorption isotherm

Equilibrium data of methylene blue onto diatomite at different solution temperatures is shown in Fig. 2. It is clear that diatomite has an adsorption capacity ranging from 40 to 45 mmol/100 g when the solution temperature is between 15 and 40 °C. This capacity is increased, to some extent, with increasing temperature. This was clear at lower

Table 1
Typical spectrographic analysis of Jordanian diatomite

Oxide	Composition (%)
SiO ₂	72.50
TiO ₂	–
Al ₂ O ₃	11.42
Fe ₂ O ₃	5.81
MnO	–
MgO	0.25
CaO	1.48
Na ₂ O	7.21
K ₂ O	0.69
P ₂ O ₅	–

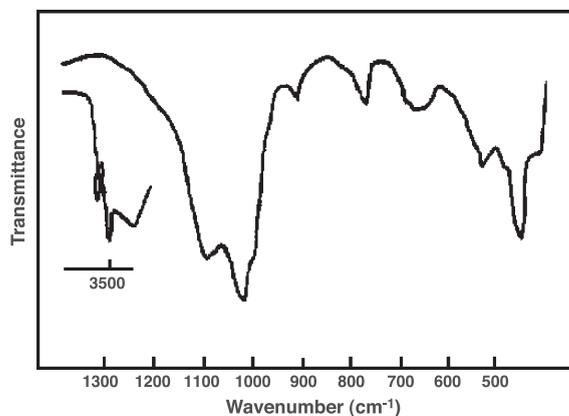


Fig. 1. IR spectra of diatomite.

solution concentrations when the equilibrium condition is not yet reached. A typical plot of $\log q(t)/C(t)$ versus $1/T$ for the average of three equilibrium data, as shown in Fig. 3, revealed a straight line with slope of -335.66 and intercept of 1.3175 . Using Eq. (13), the values of enthalpy and entropy were calculated to be 6.42 kJ/mol and 25.2 J/mol K, respectively. These results show that the adsorption process of methylene blue is an endothermic in nature (Mall and Upadhyay, 1995; De and Basu, 1999; Singh and Srivastava, 1999).

The adsorption behavior of methylene blue onto diatomite follows an irreversible process where the solid uptake increased sharply with increasing the solution concentration from 0 to 0.02 mmol/l to reach an adsorption capacity of 40 mmol MB/100 g diatomite. This is followed by a gradual increase in the adsorption capacity in the regions 0.03 – 0.67 mmol/l until it reaches 42 mmol/l, then a slight decrease in the range 0.67 – 0.94 mmol/l. This occurrence in equilibrium behavior may depict a chemisorption process that is taking place at the surface of diatomite in the first region followed by a second layer of adsorption in the second region, while the adsorption capacity decreases in the third region, which could be explained as a result of undergoing dimerization of methylene blue at high concentration (Spencer and Sutter, 1978). The molecular structure of methylene blue has an ionic quality besides its organic one, with decentralized positive charge on the organic structure. This ionic nature could play a large role in retaining the species on the surface of the diatomite, leading to a chemical reaction besides the adsorption phenomena. It is worth noting that dilute hydrochloric acid is produced from this reaction, which supports the slight increase of solution acidity with time during the sorption process for some non-buffered experiments. The solution in the isotherm experiments was buffered

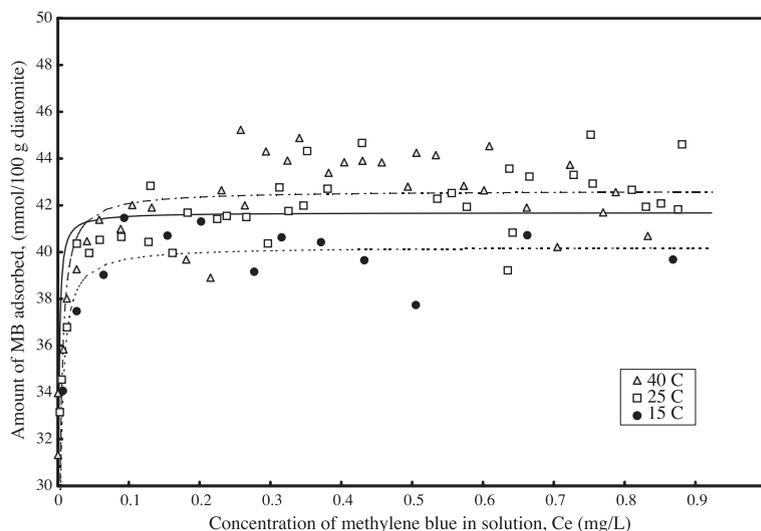


Fig. 2. Equilibrium adsorption of methylene blue on diatomite at different solution temperatures.

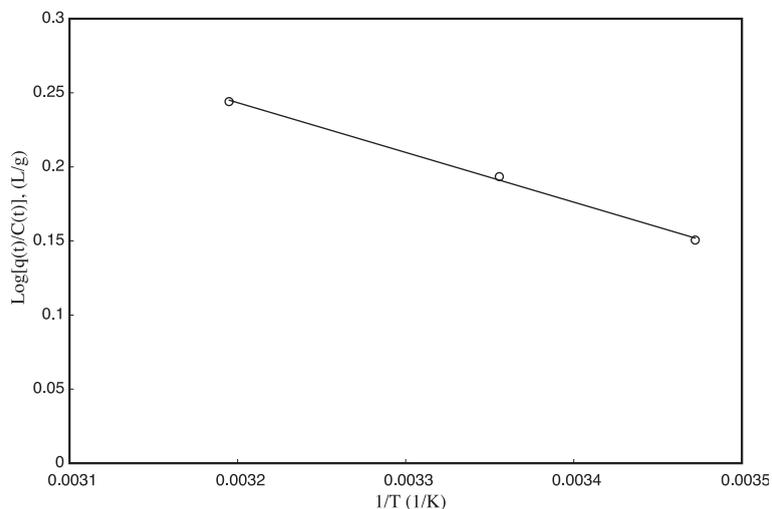


Fig. 3. Log $q(t)/C(t)$ versus $1/T$ for the average of five different equilibrium data.

at pH 7 to study the actual uptake of diatomite towards methylene blue in domestic water. When the solution pH is increased, the methylene blue uptake is expected to increase. This phenomenon could not be attributed to adsorption behavior but to two different themes: either the methylene blue undergoes dimerization at higher concentration or reacts with sodium hydroxide. To prove that, a sample of 50 ml of 2.7 mmol/l methylene blue was mixed with

equal volume of 2 M sodium hydroxide without adding diatomite. The color of the solution was monitored with time and showed a change in its intensity with time until it became clear after 5 days.

The equilibrium isotherm at 25 °C was fitted using Langmuir and Freundlich models and compared with the proposed correlation. Fig. 4 shows the deviation of these models from the experimental data. It appears that Langmuir and Freundlich models were poorly

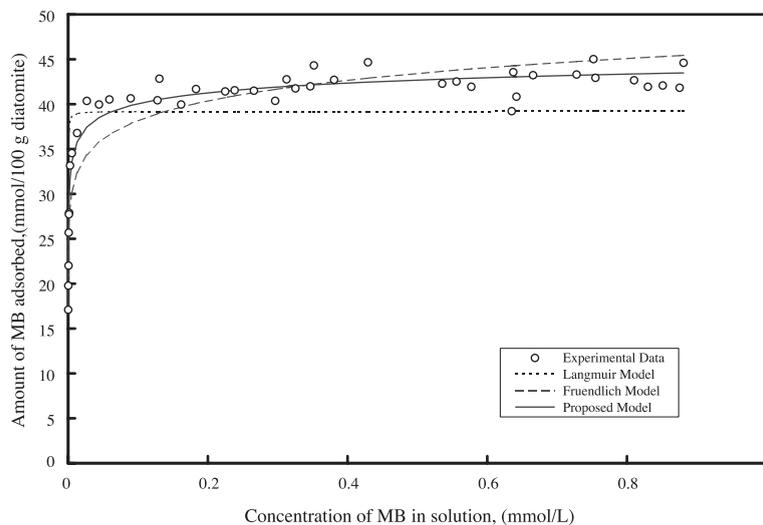


Fig. 4. Fitting adsorption isotherm data for methylene blue by different models.

Table 2

Parameters in the adsorption isotherms for the system of MB-diatomite

Model	Equation	R^2	$\Sigma(q_{\text{experimental}} - q_{\text{calculated}})^2$
Langmuir model	$q_e = 4.9915 \times 10^5 C_e / 1 + 12,733.5 C_e$	0.690	1.2361
Freundlich model	$q_e = 45.9 C_e^{0.0799}$	0.879	0.0257
Proposed model	$q_e = 53.8(1 - 0.1886 C_e^{-0.1316})$	0.910	0.0107

fitted with these data at low solute concentration. The parameters for these models with their sum of square errors and regression coefficient were displayed in Table 2. The proposed correlation depicted higher regression coefficient ($R=0.91$) and lower error discrepancy, $\Sigma(q_{\text{experimental}} - q_{\text{calculated}})^2 = 0.0107$.

4.2. Kinetics of adsorption

Kinetics data of methylene blue onto diatomite are shown in Figs. 5–8. The initial concentration of methylene blue, concentration of diatomite in solution, particle size of diatomite, and agitation speed were kept constant at 0.26 mmol/l, 0.95 g/l, < 63 μm , and 200 rpm, respectively, unless otherwise stated. The time required to obtain 90% removal was less

Table 3

Parameters in the adsorption kinetics for the system of methylene blue-diatomite

Effect	Value	q_e (mmol/100 g)	k_1 (l/g s)
Initial concentration (mmol/l)	40.1 53.5 80.2	40.1 40.1 40.1	0.15 0.16 0.18
Mass of diatomite (g)	0.85 1.27 2.55	38.8 34.2 17.7	0.05 0.12 0.4
Agitation speed (rpm)	100 200 300	28.1 28.1 28.1	0.15 0.5 0.5
Particle size (μm)	45–63 250–500 >500	27.8 17.4 13.4	0.015 0.015 0.015

than 10 min. Fig. 5 displays the effect of changing initial concentration of methylene blue from 0.4 to 0.8 mmol/l on the rate of adsorption. Increasing the initial concentration increases the competition of methylene blue molecules at the active site of the adsorbent, and as a result, more methylene blue adsorbed per gram of diatomite. Table 3 shows the saturation values obtained from the pseudo-first-order model, which are in good agreement with the experimental value ($q_e = 42$ mmol/g) at 25 °C. The values of q_e were kept constant with the increasing initial concentration. This

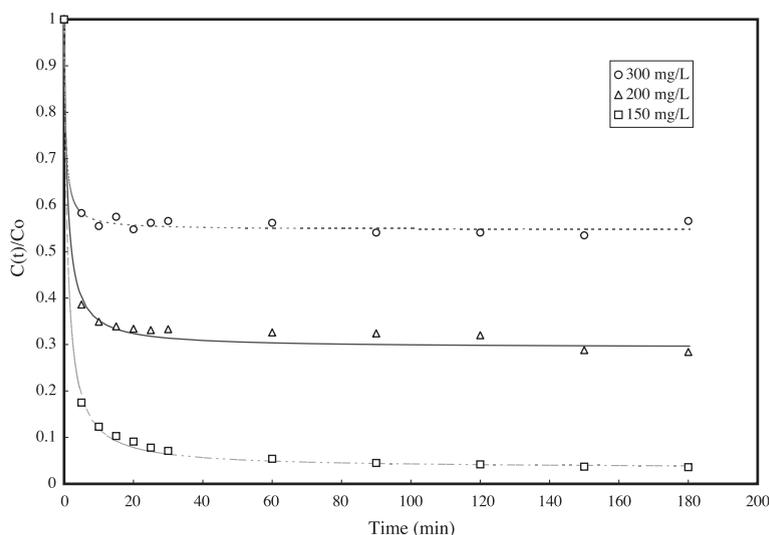


Fig. 5. Effect of initial concentration on the adsorption of methylene blue.

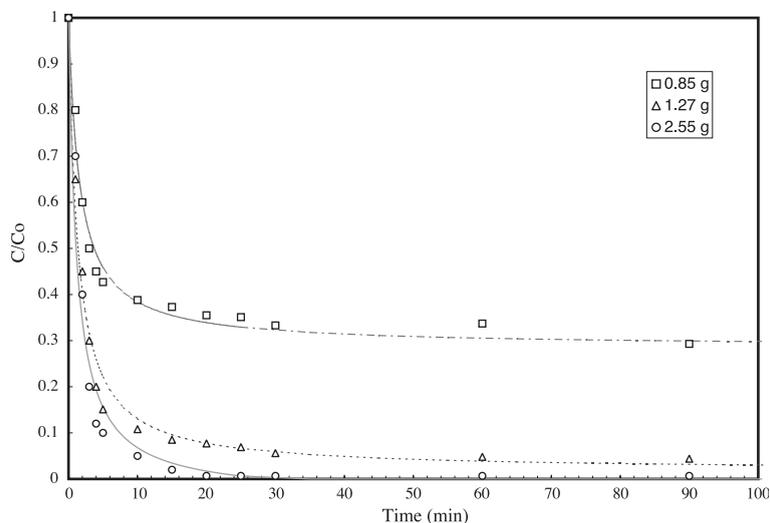


Fig. 6. Effect of mass of diatomite on the adsorption of methylene blue.

is because of the surface of diatomite that gets saturated at solution concentration of 42 mmol/l and no more adsorption can take place at the surface by increasing the concentration of methylene blue. The values of k_1 were slightly changed from 0.15 to 0.18. Fig. 6 displays the effect of changing of diatomite mass on methylene blue uptake. Increasing diatomite mass from 0.85 to 2.55 g increases the available surface area per unit volume of solution, and hence

more methylene blue is adsorbed from the solution within a specific time. However, the more increase in diatomite mass above 1.27 g, the less effect on methylene blue uptake as a result of availability more adsorption sites for a specific solution concentration. The model proves this trend where the values of q_e dropped from 38.7 to 17.8 mmol/100 g. Fig. 7 shows the effect of particle size for a fixed mass of the diatomite particles. It is clear that decreasing the

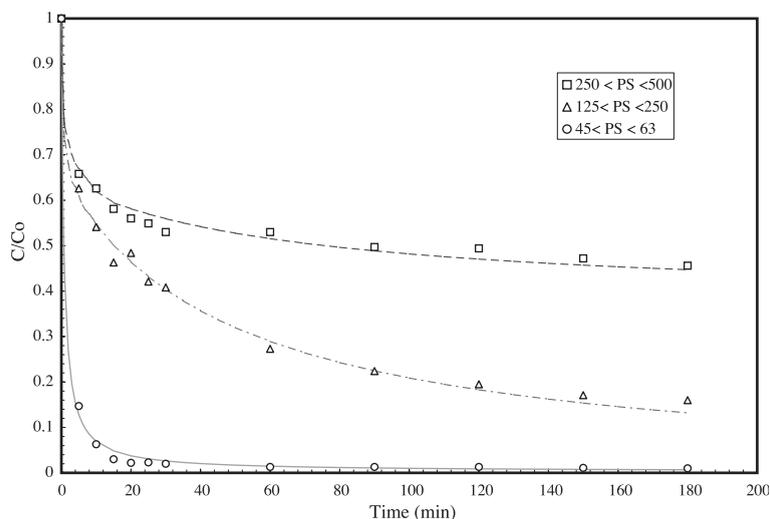


Fig. 7. Effect of particle size of diatomite on the adsorption of methylene blue.

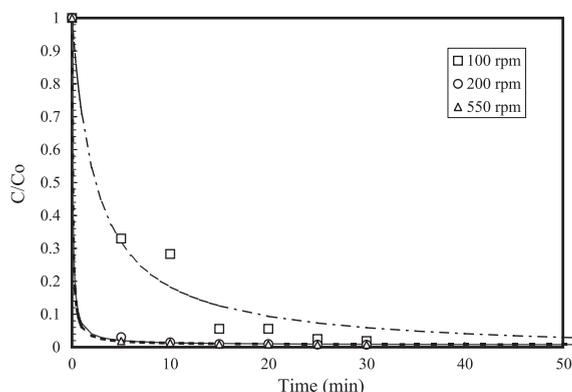


Fig. 8. Effect of agitation speed on the adsorption of methylene blue.

particle size of diatomite from 500 to 45 μm has increased the adsorption rate of methylene blue, and hence increased the values of q_e from 13.3 to 27.8 $\text{mmol}/100\text{ g}$. This is because of increasing the external surface area of diatomite particle, and as a result, more active sites are exposed to methylene blue molecules. However, the saturation value of 42 $\text{mmol}/100\text{ g}$ was not obtained at this range of particle size. Effect of agitation rate on the kinetic of adsorption was less important in the studied range (Fig. 8). It can be noticed that the adsorption rate has a slight increase with increasing the speed of agitation. Increasing the speed of agitation causes the thickness of the adsorbent boundary layer to decrease, which decreases the resistant for transfer of methylene blue to the surface of diatomite.

The pseudo-second-order model was also applied to fit the kinetic data. However, none of the experimental data could be described by this model.

5. Conclusion

Diatomite was used as an adsorbent for the removal of methylene blue dye from water. The adsorption equilibrium revealed that diatomite can uptake 42 $\text{mmol dye}/100\text{ g}$ in relatively low concentration in aqueous medium. This naturally occurring material could substitute the use of activated carbon as adsorbent due to its availability and its low cost. For the efficient use of such a material, its particle size, mass concentration, mixing speed, initial concentration, and temperature of methylene blue solution must be effi-

ciently designed to obtain the highest possible removal for methylene blue. A pseudo-first-order kinetic model can be efficiently used to predict the kinetic of adsorption of methylene blue by the diatomite.

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