Batch kinetic study of sorption of methylene blue by perlite

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Abstract

Batch sorption kinetics of methylene blue by perlite have been studied in terms of pseudo-first-order, pseudo-second-order and intra-particle diffusion models. The results showed that sorption process was best described by the pseudo-second-order model. The correlation coefficients, r^2, obtained from pseudo-second-order model were higher than 0.98 under all the experiment conditions. The effects of agitation speed, initial dye concentration and solution temperature on kinetic parameters (sorption rate constant, initial sorption rate, equilibrium sorption capacity, etc.) are discussed. While the values of sorption rate constants (k_2) and initial sorption rates (h) increased with increasing agitation speeds and solution temperatures, it was seen that the values of k_2 decreased and the values of h increased with increased initial dye concentration. The values of equilibrium sorption capacity from pseudo-second order (q_2) were in the best agreement with experimental data (q_e) in each experimental condition. Moreover, the activation energy (E_a) of sorption calculated using the pseudo-second-order rate constants was found to be 10.31 kJ/mol from an Arrhenius plot. The value of E_a indicated that sorption was controlled by an intra-particle diffusion mechanism as well as by pseudo-second-order kinetics.
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Keywords: Kinetics; Perlite; Methylene blue; Sorption; Activation energy

1. Introduction

Pollution caused by industrial wastewaters has become a common problem for many countries. Especially, organic, inorganic and dye pollutions from industrial effluents disturb human health and ecological equilibrium. Therefore, it should be required that undesirable pollution is removed. For this purpose, many methods such as activated carbon sorption, chemical coagulation, ion exchange, electrolysis, biological treatments, etc. have been developed [1–3]. Of those methods, activated carbon sorption is highly effective for the removal of different pollutants from wastewater and industrial effluents. However, the use of activated carbon is not suitable for developing countries because of its high cost. Thus, it is more suitable to use adsorbents such as clay minerals [4–6], fly ash [7–9], peat [10–13], wood powder [14,15], sawdust [16], bark [17,18], lignin [19] etc. because of their lower cost.

In this work, cost-effective expanded perlite samples were selected as a sorbent for the investigation of sorption kinetics of methylene blue from aqueous solution. Perlite is a glass volcanic rock varying in color from gray to black. When it is heated to elevated temperatures (850–1100 °C), it expands to 35 times its internal volume, and it is named 'expanded perlite'(20). This product has a low density, high surface area, and a low thermal conductivity [21]. Also, since most perlite samples have a high silica content (greater than 70%), they have adsorptive characteristics [22–24]. The adsorptive character of perlite is due to the silanol groups which are formed by silicon atoms on the surface of perlite. The types of silanol groups are shown as follows [22–24]:
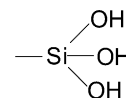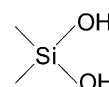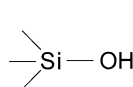
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The hydrous oxide surface groups in alumina are given as follows [22–24]:

$$\equiv Al - OH \quad \text{or} \quad = Al \begin{array}{c} OH \\ \\ OH \end{array}$$
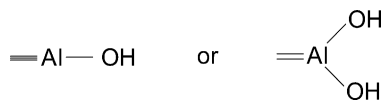
The silicon atoms at the surface tend to maintain their tetrahedral coordination with oxygen. They complete their coordination at room temperature by attachment to monovalent hydroxyl groups, forming silanol groups. The surface of perlite becomes more negatively or positively charged according to the pH of the solution medium. This situation affects sorption capacity.

Also, expanded perlite is used as an excellent filter aid and as a filler in various processes and materials [20,22–24] since they are chemically inert. Moreover, the use of expanded perlite is common and it is used in the processing of vegetable fat, juice, beer, wine in food industry; cleaning of dams and ponds in aquatic environment; obtaining of a clear liquid in filter produce (as filter aid); growing of seeds and regularizing of the soil in agriculture; building due to thermal in-solution characteristics; cast iron-steel production in cast metal industry; brick production due to heat adiabatic property, etc. [20].

The leading producers of perlite (crude, processed), among Asian–European countries, are Greece, Japan, Turkey, and Hungary [21]. About 70% of the world's known perlite reserves are present along Aegean Cost in Turkey [22–24]. However, there are only a limited number of published papers on the use of perlite in the literature. For example, earlier studies done with perlite as a sorbent are with regard to the sorption of some organic materials [25,26]. Recently, Dogan et al. have investigated the electrokinetic properties of perlite [22], as well as the dye [23,27] and metal sorption [24]. In another work, Dogan et al. have studied the sorption of methylene blue on activated perlite examples [23]. Kinetic studies on sorption of methylene blue by perlite have not been undertaken so far. The goal of this study is to investigate the sorption kinetics of methylene blue from aqueous solution onto perlite by batch sorption technique and to interpret the results in terms of the kinetic theory summarized below, and to determine how agitation speed, concentration and temperature affect on kinetics.

Several kinetic models have been proposed to clarify the mechanism of a solute sorption from aqueous solution onto a adsorbent: (a) a pseudo-first-order kinetic model of Lagergren [10,28,29] based on solid capacity, (b) a pseudo-second-order kinetic model of Ho [10,29] based on solid phase sorption, and (c) intra-particle diffusion model of Weber and Morris [10,29,30].

A pseudo-first-order kinetic model of Lagergren for the sorption of liquid/solid system based on solid capacity can be expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_1 - q_t) \tag{1}$$

Integrating this equation for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$.

Eq. (2) can be obtained as follow:

$$\log\left(\frac{q_1}{q_1 - q_t}\right) = \frac{k_1}{2.303}t \tag{2}$$

where q_1 is the amount of solute sorbed at equilibrium (mg/g), q_t the amount of solute sorbed on the surface of the sorbent at any time (mg/g) and k_1 is the rate constant of pseudo-first-order sorption (min^{-1}).

Eq. (2) can be rearranged to obtain a linear form of

$$\log(q_1 - q_t) = \log(q_1) - \frac{k_1}{2.303}t \tag{3}$$

The intercept of the straight line plots of $\log(q_1 - q_t)$ versus t should be equal $\log(q_1)$. If the intercept value does not equal $\log(q_1)$, the reaction is not likely to obey a first-order kinetics model, even this plot has a high correlation coefficient with experimental.

A pseudo-second-order kinetic model of Ho et al. is as the following:

$$\frac{dq_t}{dt} = k_2(q_2 - q_t)^2 \tag{4}$$

where k^2 is the rate constant for pseudo-second-order reaction (g/mg min), q^2 and q_t are the amounts solute sorbed at equilibrium and any time (in mg/g), respectively.

The equation can be rearranged as

$$\frac{dq_t}{(q_2 - q_t)^2} = k_2\, dt \tag{5}$$

Integrating this for boundary conditions $t = 0$ to $t = t$ and $q_t = q_t$ gives

$$\frac{1}{q_2 - q_t} = \frac{1}{q_2} + k_2 t \tag{6}$$

Eq. (6) can be rearranged to obtained a linear form of

$$\frac{t}{q_t} = \frac{1}{k_2\, q_2^2} + \frac{1}{q_2}t \tag{7}$$

The straight line plots of t/q_t versus t are used to obtain the constants for pseudo-second reaction. Herein, the initial sorption rate is $h = k_2 q_2^2$.

Intra-particle diffusion model can be expressed as follows [31]:

$$q_t = k_i t^{1/2} + C \tag{8}$$

where k_i is the intra-particle diffusion rate constant (mg/g min$^{1/2}$), and C is the intercept. In this model, due to the porous nature of adsorbent, pore diffusion is expanded to be surface sorption. Therefore, the rate constant of intra-particle transport (k_i) is estimated from slopes of linear portion of the plots of amount sorbed against square root of time.

Table 1
Chemical components of perlite

Constituent	Percentage (in weight)
SiO_2	71–75
Al_2O_3	12–16
Na_2O	2.9–4.0
K_2O	4–5
CaO	0.5–2.0
Fe_2O_3	0.5–1.45
MgO	0.03–0.5
TiO_2	0.03–0.2
MnO_2	0.0–0.1
SO_3	0.0–0.1
FeO	0.0–0.1
Ba	0.0–0.1
PbO	0.0–0.5
Cr	0.0–0.1

2. Materials and methods

The expanded perlite samples used as an adsorbent were supplied from a perlite Processing Plant of Etibank in Menderes near İzmir in Turkey. Its chemical composition and some physical properties are given in Tables 1 and 2 [20,22–24]. The samples were treated before use in the experiments as described elsewhere [22–24,27], and then it was utilized for the experiments. Methylene blue, a cationic dye (C.I. 52015), was purchased from Merck, and it was used as received without further purification. The structure of the dye containing a secondary amine group is presented in Fig. 1. The stock solutions at the desired concentrations were prepared with pure distilled water. To prevent the dimer or aggregation of the dye, the initial dye concentrations were kept below ≤ 20 mg/L ($\sim 5 \times 10^{-5}$ M) [32]. The pH value of the solutions was adjusted to 11 by dropping NaOH solution using a pH meter (WTW pH Meter 320, Germany).

Batch sorption experiments were carried out by shaking 1.0 g of perlite with 75 mL aqueous solution of methylene blue of known concentration in 250 cm^3-polyethylene flasks placed in a temperature controlled shaking water bath at different temperatures and a constant pH of 11. After the desired contact time, solutions were centrifuged for 15 min at 3000 rpm and the supernatant solutions were analyzed

Table 2
Some physical properties of perlite

Color	White
Size (mm)	0.07 (75%)–0.43 (25%)
Density (kg/m^3)	70–130
Specific surface area[a] (m^2/g)	1.88
Cation exchange capacity (CEC)[b] (meq/100 g)	34.25
Zeta potential (in water)[c] (mV)	−46.8
pH	6.6–8.0
Melting point (°C)	1300
Heat conductivity (kcal/M h °C)	0.034–0.045

[a] Calculated by BET N_2 adsorption.
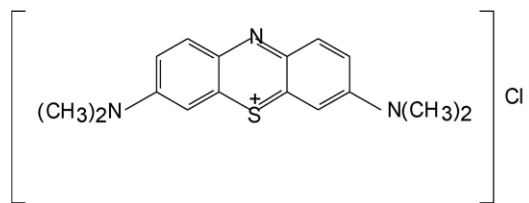[b] Calculated by NH_4^+ acetate method.
[c] From Ref. [23].

Fig. 1. The structure of methylene blue.

for the final concentration of methylene blue by using a UV–vis spectrophotometer (Shimadzu UV–vis 160 A spectrophotometer) set at a wave-length of 664 nm, maximum absorbance. The amounts of methylene blue sorbed were calculated from subtracting final solution concentrations from the initial concentrations of aqueous solutions. Blank solutions were used for each series of experiments.

3. Results and discussion

To analyse the sorption kinetics of methylene blue onto perlite, it would be useful to know its chemical structure and some physical properties. As was mentioned in Section 1, silicon atoms on the surface of perlite form different silanol groups, and these groups are responsible for adsorption of methylene blue. Also, the perlite samples have no point of zero charge (p.z.c.) and exhibits negative zeta potential value in the pH range 3–11 [22]. In alkaline medium, the surface of perlite becomes negatively charged, and therefore the sorption of dye cation by perlite increases at higher pH values and the sorption take places more easily [23]. A simple equation for sorption can be shown as follows [23]:

$$-MO^- + dye^+ \Leftrightarrow M\text{–}O\text{–}dye \tag{9}$$
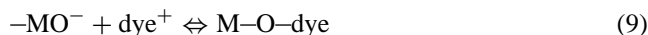
In this study, the pH for all the experiments was kept at a constant value of 11 in which the highest sorption of methylene blue occurred [23].

3.1. Equilibrium time

The sorption of methylene blue onto perlite was maintained as a function of time until the amount of methylene blue sorbed became constant, implying that equilibrium had been reached. Equilibrium time was 240 min in all concentrations and temperatures studied. In the case of agitation, equilibrium time decreased from 240 to 210 min when agitation speed was increased from 120 to 240 rpm (Fig. 2). This phenomenon may be probably attributed that dye molecules which are strongly attached onto the surface of the sorbent at higher agitation speed, causing decrease of equilibrium time. The amount of methylene blue sorbed per unit mass of perlite at equilibrium, i.e. equilibrium sorption capacity of perlite (q_e), increased with increasing initial dye concentrations, temperatures and agitation speeds. The values of equi-
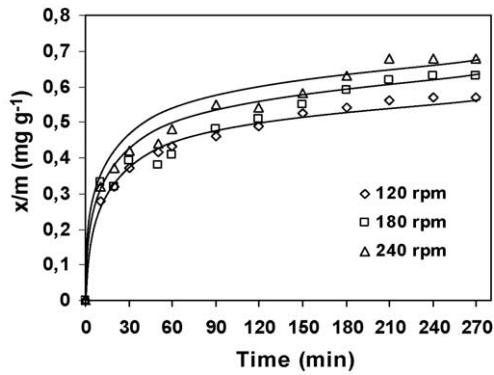
Fig. 2. Effect of agitation speed on the sorption of methylene blue by perlite. Conditions: 10 mg/L initial dye concentration, 30 °C.

librium sorption capacity obtained under all the experimental conditions are presented in Tables 3–5.

3.2. Effect of agitation speed on sorption kinetics

In all the experiments in which the effect of agitation speed was studied, the initial dye concentration and solution temperature were 10 mg/dm^3 and 30 °C, respectively. Fig. 2 shows the sorption of methylene blue by perlite at different agitation speeds. The amount of dye sorbed per unit mass of perlite at equilibrium, i.e. equilibrium sorption capacity, increases from 0.57 to 0.68 mg/g with increasing agitation speed from 120 to 240 rpm.

Fig. 3 illustrates pseudo-first-order sorption kinetics of methylene blue by perlite at various agitation speeds. The values of rate constant, k_1, from the slopes of the plots of $\log(q_1 - q_t)$ versus t increases slightly from 1.24×10^{-2} to 1.51×10^{-2} min^{-1} with increasing agitation speed from 120 to 240 rpm. Correlation coefficients, r^2, obtained from the plots in Fig. 3 are 0.9589, 0.8898 and 0.9244 for 120, 180 and 240 rpm, respectively. The values of r^2 are lower than those of other rate laws, and equilibrium sorption capacity, q_1, does not agree with experimental data, q_e (see Table 1).

Fig. 4 shows intra-particle diffusion kinetics of the adsorption of methylene blue by perlite at various agitation speeds. Intra-particle diffusion rate was estimated from the slopes of the plots of q_t against square root of time. k_i, increases from 2.30×10^{-2} to 2.82×10^{-2} mg/g min$^{1/2}$ with an increase in agitation speed from 120 to 240 rpm as shown in Table 3.

Table 3
Kinetic parameters for methylene blue sorption by perlite at various agitation speeds

S^a	$q_e{}^b$	$q_2{}^c$	$k_2{}^d$	h^e	r_2^{2f}	$q_1{}^g$	$k_1{}^h$	r_1^{2i}	$k_i{}^j$	C^k	r_i^{2l}
120	0.57	0.59	0.087	0.0302	0.9957	0.352	0.0124	0.9589	0.0230	0.2338	0.9741
180	0.63	0.68	0.091	0.0420	0.9837	0.468	0.0147	0.8898	0.0269	0.2194	0.9764
240	0.68	0.71	0.097	0.0489	0.9879	0.430	0.0151	0.9244	0.0282	0.2493	0.9816

[a] Agitation speed (rpm).
[b] Equilibrium sorption capacity obtained as experimental (mg/g).
[c] Equilibrium sorption capacity obtained from pseudo-second-order equation (mg/g).
[d] The rate constant of pseudo-second-order reaction (g/mg min).
[e] The initial sorption rate from pseudo-second-order kinetics (mg/g min).
[f] Correlation coefficient from pseudo-second-order equation.
[g] Equilibrium sorption capacity obtained from pseudo-first-order equation (mg/g).
[h] The rate constant of pseudo-first-order reaction (min^{-1}).
[i] Correlation coefficient from pseudo-first-order equation.
[j] Intra-particle diffusion rate constant (mg/g min$^{1/2}$).
[k] Intercept from intra-particle diffusion equation.
[l] Correlation coefficient from intra-particle diffusion equation.

Table 4
Kinetic parameters for methylene blue sorption by perlite at different initial dye concentrations

$C_0{}^a$	$q_e{}^b$	$q_2{}^c$	$k_2{}^d$	h^e	r_2^{2f}	$q_1{}^g$	$k_1{}^h$	r_1^{2i}	$k_i{}^j$	C^k	r_i^{2l}
5	0.280	0.29	0.188	0.0158	0.9984	0.153	0.0140	0.9881	0.0130	0.1176	0.9412
10	0.570	0.59	0.087	0.0302	0.9957	0.352	0.0124	0.9589	0.0230	0.2338	0.9741
20	0.944	1.01	0.055	0.0561	0.9997	0.564	0.0179	0.9922	0.0407	0.3850	0.8800

[a] Initial dye concentration (mg/L).
[b] Equilibrium sorption capacity obtained as experimental (mg/g).
[c] Equilibrium sorption capacity obtained from pseudo-second-order equation (mg/g).
[d] The rate constant of pseudo-second-order reaction (g/mg min).
[e] The initial sorption rate from pseudo-second-order kinetics (mg/g min).
[f] Correlation coefficient from pseudo-second-order equation.
[g] Equilibrium sorption capacity obtained from pseudo-first-order equation (mg/g).
[h] The rate constant of pseudo-first order reaction (min^{-1}).
[i] Correlation coefficient from pseudo-first-order equation.
[j] Intra-particle diffusion rate constant (mg/g min$^{1/2}$).
[k] Intercept from intra-particle diffusion equation.
[l] Correlation coefficient from intra-particle diffusion equation.

Table 5
Kinetic parameters for methylene blue sorption by perlite at different temperatures of dye solution

T^a	$q_e{}^b$	$q_2{}^c$	$k_2{}^d$	h^e	r_2^{2f}	$q_1{}^g$	$k_1{}^h$	r_1^{2i}	$k_i{}^j$	C^k	r_i^{2l}
30	0.57	0.590	0.087	0.0302	0.9957	0.352	0.0124	0.9589	0.0230	0.2338	0.974
40	0.61	0.630	0.104	0.0412	0.9979	0.321	0.0150	0.9773	0.0219	0.2944	0.959
50	0.73	0.716	0.114	0.0584	0.9978	0.342	0.0152	0.9633	0.0227	0.3991	0.974

[a] The temperature of dye solution ($^{\circ}$C).
[b] Equilibrium sorption capacity obtained as experimental (mg/g).
[c] Equilibrium sorption capacity obtained from pseudo-second order equation (mg/g).
[d] The rate constant of pseudo-second-order reaction (g/mg min).
[e] The initial sorption rate from pseudo-second order kinetics (mg/g min).
[f] Correlation coefficient from pseudo-second-order equation.
[g] Equilibrium sorption capacity obtained from pseudo-first-order equation (mg/g).
[h] The rate constant of pseudo-first-order reaction (min^{-1}).
[i] Correlation coefficient from pseudo-first-order equation.
[j] Intra-particle diffusion rate constant (mg/g min$^{1/2}$).
[k] Intercept from intra-particle diffusion equation.
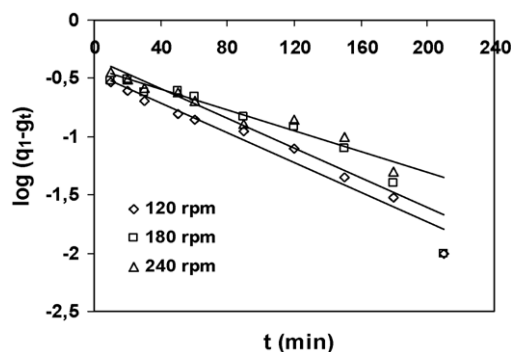[l] Correlation coefficient from intra-particle diffusion equation.

Fig. 3. Effect of agitation speed on pseudo-first-order sorption kinetics of methylene blue by perlite. Conditions: 10 mg/dm^3 initial dye concentration, 30 $^{\circ}$C.

The values of r^2 obtained are 0.9741, 0.9764 and 0.9816 for 120, 180 and 240 rpm, respectively. As shown in Fig. 4, the effect of a two-fold change in agitation speed from 120 to 240 rpm has only a small influence, indicating that external mass transfer has only a small influence on the sorption kinetics of methylene blue under these conditions. Similar results have been reported also for the sorption of Basic Blue 69 onto peat [10].
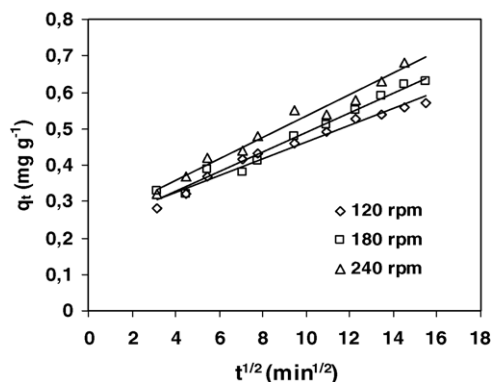

Fig. 4. Effect of agitation peed on intra-particle diffusion kinetics of methylene blue by perlite. Conditions: 10 mg/dm^3 initial dye concentration, 30 $^{\circ}$C.
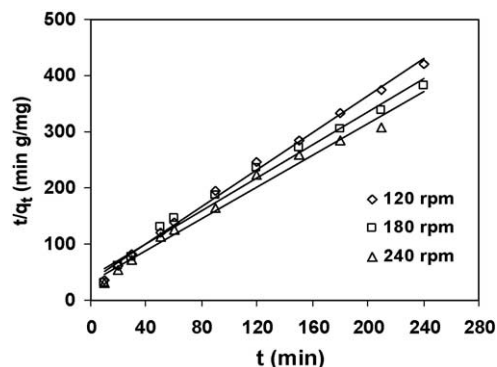

Fig. 5. Effect of agitation peed on pseudo-second-order sorption kinetics of methylene blue by perlite. Conditions: 10 mg/dm^3 initial dye concentration, 30 $^{\circ}$C.

Fig. 5 demonstrates pseudo-second-order sorption kinetics of adsorption of methylene blue by perlite at various agitation speeds. The values of the rate constant, k_2, from the linear plots of t/q_t versus t, increased slightly from 8.70×10^{-2} to 9.70×10^{-2} g/mg min with an increase in the agitation rate. The values of initial sorption rate, h, increase from 3.02×10^{-2} to 4.89×10^{-2} mg/g min, and the values of equilibrium sorption capacity, q_2, increase 0.59–0.716 mg/g, for an increase in agitation speed from 120 to 240 rpm. These values, q_2, are in agreement with experimental data, q_e, and the values of r^2 are also higher than 0.98.

3.3. Effect of initial dye concentration on sorption kinetics

In all experiments, the temperature was maintained at 30 $^{\circ}$C and the agitation speed maintained at 120 rpm. Fig. 6 illustrates the sorption of methylene blue for different initial dye concentration at 30 $^{\circ}$C and 120 rpm as a function of contact time. When initial dye concentration was increased from 5.0 to 20 mg/dm^3, the equilibrium sorption capacity increased from 0.28 to 0.944 mg/g.
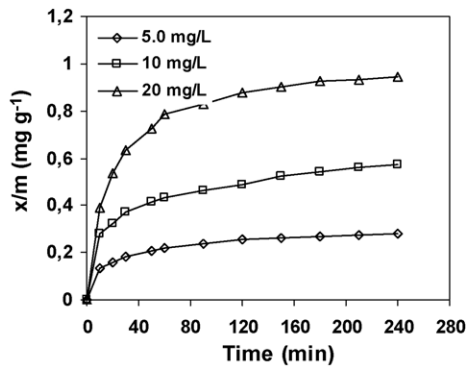
Fig. 6. Effect of initial dye concentration on the sorption of methylene blue by perlite. Condition: 30 °C, 120 rpm.

Fig. 8. Effect of initial dye concentration on intra-particle diffusion kinetics of methylene blue by perlite. Condition: 30 °C, 120 rpm.

Fig. 7 demonstrates pseudo-first-order sorption kinetics for the adsorption of methylene blue by perlite at different initial dye concentrations and 30 °C. The values of rate constant from the pseudo-first-order model increase with increasing initial dye concentration, and they are in the range of 1.40×10^{-2}, 1.24×10^{-2} and 1.79×10^{-2} min^{-1} for initial dye concentrations of 5.0, 10 and 20 mg/dm^3, respectively. Although the correlation coefficients, r^2, obtained for the plots in Fig. 7 have high values with the experimental data (>0.958), the values of equilibrium sorption capacity (q_1) from the intercept of the plots of $\log(q_1 - q_t)$ versus t are 0.153 and 0.352, 0.564 mg/g for initial dye concentrations of 5.0, 10 and 20 mg/dm^3, respectively. They are not in agreement with the experimental data (see Table 4).

Fig. 8 illustrates intra-particle diffusion kinetics of methylene blue by perlite at various initial dye concentrations and at a temperature of 30 °C and a stirring speed of 120 rpm. The values of intra-particle diffusion rates estimated from the slopes of the plots of q_t against $t^{1/2}$, k_i, increased from 1.30×10^{-2} to 4.07×10^{-2} mg/g min$^{1/2}$ with an increase in initial concentration from 5.0 to 20 mg/dm^3 (see Table 4). The values of r^2 obtained are 0.9412, 0.9741 and 0.88 for initial dye concentrations of 5.0, 10 and 20 mg/dm^3, respectively. As shown in Fig. 8,

with initial dye concentration increases, it is observed that deviations from intra-particle diffusion kinetics occur. These deviations may be attributed to some repulsion between adsorbent or adsorbate molecules due to concentration density.

Fig. 9 shows pseudo-second-order sorption kinetics of methylene blue by perlite for different initial dye concentrations and 30 °C and 120 rpm. The values of the rate constant obtained from pseudo-second-order kinetics, k_2, decrease from 18.80×10^{-2} to 5.50×10^{-2} g/mg min with increasing initial dye concentration. With increasing initial dye concentration, the values of initial sorption rate, h, increase in order of 1.58×10^{-2}, 3.02×10^{-2} and 5.61×10^{-2} g/mg min, respectively. This increase in initial sorption rate indicates that solute and sorbate molecules can be met more with each other in higher concentration. Similar results have been reported by Ho and McKay [10] for sorption of basic blue 69 and acid blue 25 onto peat. The values of r^2 obtained from the plots of pseudo-second-order kinetics given in Fig. 9 are higher than 0.99 for all initial dye concentrations. The values of equilibrium sorption capacity, q_2, increase from 0.29 to 1.01 mg/g with increasing initial dye concentration. These values, q_2, are in agreement with experimental data as to be in the effect of agitation speed.
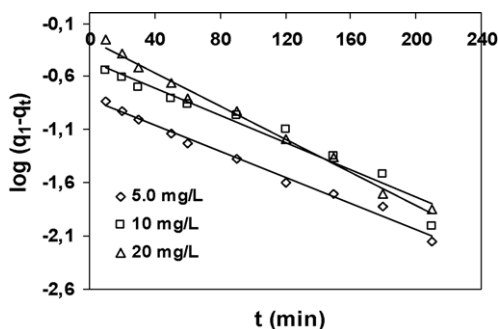

Fig. 7. Effect of initial dye concentration on pseudo-first-order sorption kinetics of methylene blue by perlite. Condition: 30 °C, 120 rpm.
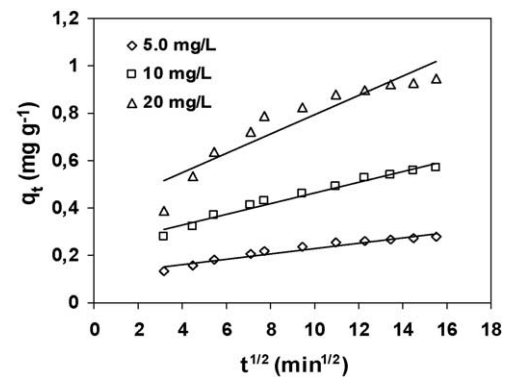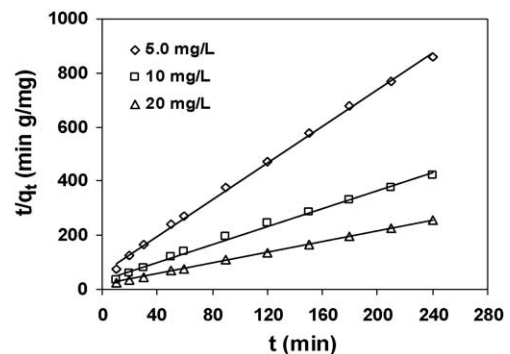

Fig. 9. Effect of initial dye concentration on pseudo-second-order sorption kinetics of methylene blue by perlite. Condition: 30 °C, 120 rpm.
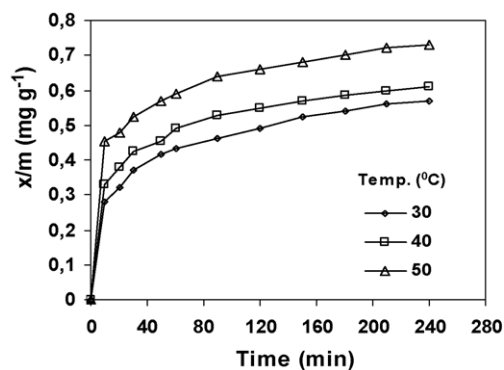
Fig. 10. Effects of temperature on the sorption of methylene blue by perlite. Conditions: $10\,mg/dm^3$ initial dye concentration, 120 rpm.

3.4. Effect of temperature on sorption kinetics

The temperature dependence of methylene blue sorption onto perlite was studied with a constant initial concentration of $10\,mg/dm^3$ at 120 rpm. Fig. 10 shows the effect of temperature on the sorption of methylene blue by perlite as a function of contact time. The equilibrium sorption capacity increases from 0.59 to 0.73 mg/g when the temperature of dye solutions increases from 30 to 50 °C. The fact that the sorption of dye is in favor of temperature indicates that the mobility of the dye molecule increases with a rise in the temperature, and it can be suggested that the dye molecule should interact more effectively with the functional groups on perlite mentioned beforehand.

Fig. 11 demonstrates the effect of temperature on pseudo-first-order sorption kinetics of methylene blue onto perlite. The values of rate constant estimated from the pseudo-first-order model increase with increasing solution temperature from 30 to 50 °C in order of 1.24×10^{-2}, 1.50×10^{-2} and $1.52 \times 10^{-2}\,min^{-1}$. Moreover, the effect of temperature on pseudo-first-order sorption kinetics of methylene blue is not considerably effective (i.e. plots for temperatures are almost overlapped) as shown in Fig. 11. Although the correlation coefficients, r^2, obtained have high values with the experimental data (>0.958), the values of equilibrium sorption capacity,
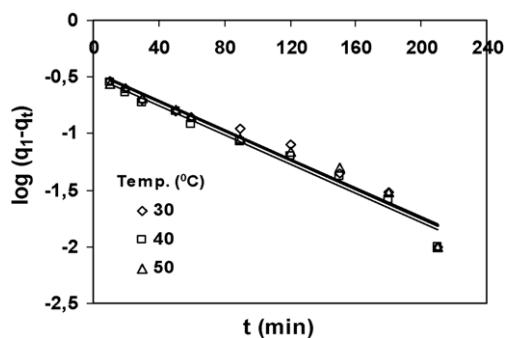

Fig. 11. Effect of temperature on pseudo-first-order sorption kinetics of methylene blue by perlite. Conditions: $10\,mg/dm^3$ initial dye concentration, 120 rpm.
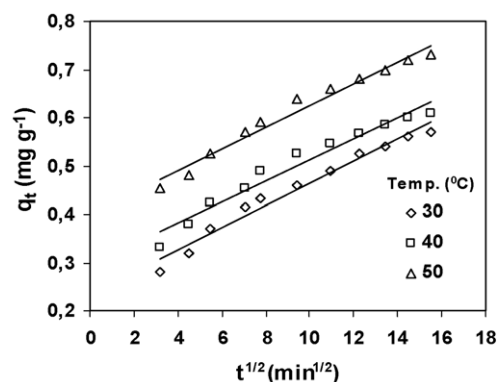

Fig. 12. Effect of temperature on intra-particle diffusion kinetics of methylene blue by perlite. Conditions: $10\,mg/dm^3$ initial dye concentration, 120 rpm.

q_1, calculated are 0.352, 0.321 and 0.342 mg/g for 30, 40 and 50 °C, respectively, and they close each other. These values are not in agreement with experimental data (see Table 5).

Fig. 12 shows the effect of temperature on intra-particle diffusion kinetics of methylene blue. The values of k_i estimated are 2.30×10^{-2}, 2.19×10^{-2} and $2.27 \times 10^{-2}\,mg/g\,min^{1/2}$ for 30, 40 and 50 °C, respectively. The values of r^2 from the plots given in Fig. 12 are found to be 0.974, 0.959 and 0.974 for 30, 40 and 50 °C, respectively. As shown in the plots (Figs. 4, 8 and 12), the linear plots of q_t versus $t^{1/2}$ do not pass through the origin. Such a deviation of the straight line from the origin may be due to the difference in the rate of mass transfer in the initial and final stage of sorption [33]. Moreover, the intercept C gives an idea about boundary layer thickness, the larger the value of the intercept the greater is the boundary layer effect [31]. Namely, any increase in the intercept C indicates the abundance of solute sorbed on boundary layer. The values of C obtained from intercept of the linear plots of q_t versus $t^{1/2}$ under all conditions studied are presented in Tables 3–5. As seen in these tables, while the value of C increases with increasing concentration and temperature, it exhibits a slight variation increasing agitation speed.

Fig. 13 illustrates the effect of temperature on pseudo-second-order sorption kinetics of methylene blue onto perlite. The values of k_2 increase from 8.70×10^{-2} to $11.40 \times 10^{-2}\,g/mg\,min$ with increasing temperature from 30 to 50 °C, respectively. Initial sorption rate, h, also increases in order of 3.02×10^{-2}, 4.12×10^{-2} and $5.84 \times 10^{-2}\,g/mg\,min$, respectively. Similar results have been reported by Ho and Mckay [10] for the sorption of basic blue 69 onto peat. The values of r^2 obtained are greater than 0.995 for all the temperatures. The values of equilibrium sorption capacity, q_2, are 0.59, 0.63 and 0.716 for 30, 40 and 50 °C, respectively, and these (q_2) are in agreement with experimental data, q_e (see Table 5).

As a result, it is clear that the values of correlation coefficients obtained for the linear plots from the pseudo-second-order equation are greater than those obtained for the first-
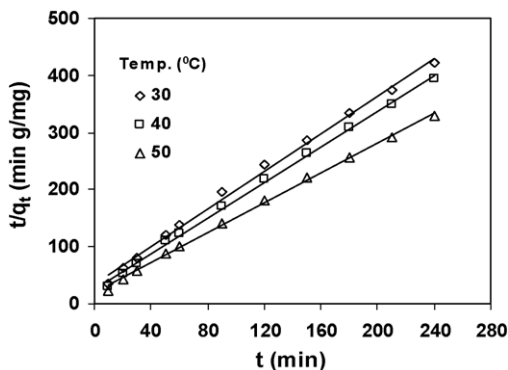
Fig. 13. Effect of temperature on pseudo-second-order sorption kinetics of methylene blue by perlite. Conditions: 10 mg/dm^3 initial dye concentration, 120 rpm.

Fig. 14. Arrhenius plot for sorption of methylene blue by perlite. Conditions: 10 mg/dm^3 initial dye concentration, 120 rpm.

order and intra-particle diffusion equations under all conditions studied as shown in Tables 3–5. Furthermore, the values of equilibrium sorption capacity, q_2, are in a good agreement with experimental data, q_e. This indicates strongly an activated sorption between the dye and functional groups on perlite [10,29], involving valency forces through sharing or exchange of electrons between sorbent and sorbed. It has also been reported that kinetics of cadmium adsorption onto perlite complies best with the pseudo-second-order model due to the higher correlation coefficients [34]. Also, the kinetics data derived using the intra-particle diffusion model indicate that intra-particle diffusion rate is one of the rate determining steps. This is also confirmed by the activation energy values shown below.

3.5. Activation energy

Generally, a rise in temperature of a chemical reaction increases the rate of the reaction, and the temperature dependence results in a change in the rate constant. Activation energy of the sorption for methylene blue/perlite system can be estimated by Arrhenius equation providing the relationship between rate constant and temperature as shown in the following:

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right) \tag{10}$$

where k is the rate constant of sorption (g/mg min), k_0 the Arrhenius constant which is a temperature independent factor (g/mg min), E_a the activation energy (kJ/mol), R the gas constant (8.314 J/mol K) and T is the solution temperature in Kelvin (K).

In this work, activation energy of sorption process has been calculated using the values of rate constant from a pseudo-second-order kinetic equation and using the appropriate solution temperatures. An Arrhenius plot drawn of $\ln k_2$ versus $1/T$ is shown in Fig. 14. The value of E_a from the slope of the plot is 10.31 kJ/mol and k_0 is 5.25 g/mg min. Therefore, the Arrhenius equation for the methylene blue/perlite sorption
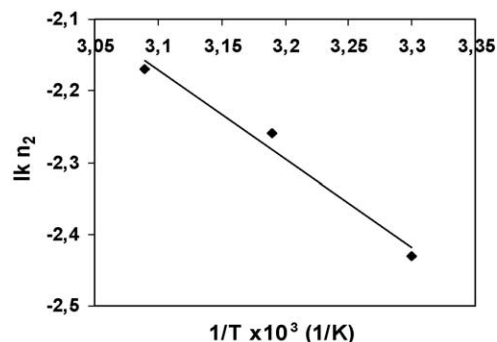
system can be written as follows:

$$k_2 = 5.25 \exp\left(-\frac{10.31 \times 10^3}{RT}\right) \tag{11}$$

The E_a obtained is very low, and thus the sorption of methylene blue by perlite may involve not only an activated process but a physical sorption. At the same time, a small value of E_a with 10.31 kJ/mol indicates that the sorption process is controlled by an intra-particle diffusion mechanism. A similar result has been reported for the sorption of Victoria blue by fly ash in a work done by Khare et al. [35]. Moreover, a similar value of E_a has also been reported as 13.20 kJ/mol for methyl violet/perlite sorption system by Dogan and Alkan [27].

4. Conclusion

The amount of methylene blue adsorbed onto perlite increased with increasing initial dye concentrations, solution temperatures and agitation speeds. The equilibrium time was 240 min for concentrations and temperatures, but it was 210 min with an increase in the agitation speed. The kinetics of sorption process were best described by a pseudo-second-order rate equation. The activation energy of sorption was calculated using the pseudo-second-order rate constants, and it was found to be 10.31 kJ/mol. From the value of the activation energy, it was seen that the intra-particle diffusion kinetics is one of the rate determining steps as well as pseudo-second-order kinetics.

References

[1] D. Ozer, A. Ozer, G. Dursun, Investigation of zinc(II) adsorption on *Cladophora crispate* in a two-staged reactor, J. Chem. Technol. Biotechnol. 75 (2000) 410–416.
[2] D.S. Kim, B.Y. Park, Effect of the removal of Pb^{2+} from aqueous solution by crab shell, J. Chem. Technol. Biotechnol. 76 (2001) 1179–1184.

[3] P. Nigam, G. Armour, I.M. Banat, D. Singh, R. Marchant, Physical removal of textile dyes from effluents and solid-state fermentation of dye-adsorbed agricultural residues, Bioresource Technol. 72 (2000) 219–226.

[4] R. Apak, K. Guclu, M.H. Turgut, Modeling of copper(II), cadmium(II) and lead(II) adsorption on bentonite, J. Colloid Interface Sci. 203 (1998) 122–130.

[5] G. Bereket, A.Z. Aroguz, M.Z. Ozel, Removal of Pb(II), Cd(II), Cu(II) and Zn(II) from aqueous solution by adsorption on bentonite, J. Colloid Interface Sci. 187 (1997) 338–343.

[6] K.P. Yadava, B.S. Tyagi, V.N. Singh, Effect of temperature on the removal of lead(II) by adsorption on china clay and wollastonite, J. Chem. Technol. Biotechnol. 51 (1991) 47–60.

[7] K.K. Panday, G. Prasad, V.N. Singh, Copper(II) removal from aqueous solution by fly ash, Water Res. 19 (7) (1985) 869–873.

[8] T. Viraraghavan, K.R. Ramakrishna, Fly ash for colour removal from synthetic dye solutions, Water Qual. Res. J. Can. 34 (1999) 505–517.

[9] B. Acemioglu, Adsorption of Congo red from aqueous solution onto calcium-rich fly ash, J. Colloid Interface Sci. 274 (2004) 371–379.

[10] Y.S. Ho, G. Mckay, Sorption of dye from aqueous solution by peat, Chem. Eng. J. 70 (1998) 15–124.

[11] T. Gosset, J.L. Trancart, D.R. Thevenot, Batch metal removal by peat kinetics and thermodynamics, Water Res. 20 (1986) 21–26.

[12] G. Mckay, J.F. Porter, Equilibrium parameters for the sorption of copper, cadmium and zinc ions on peat, J. Chem. Technol. Biotechnol. 69 (1997) 309–320.

[13] R. Gündogan, B. Acemioglu, M.H. Alma, Copper(II) Adsorption from aqueous solution by herbaceous peat, J. Colloid Interface Sci. 269 (2003) 303–309.

[14] Y.S. Ho, G. McKay, Kinetic models for the sorption of dye from aqueous solution by wood, Trans. IChemE Part B 76 (1998) 183–191.

[15] H.M. Asfour, O.A. Fadali, M.M. Nassar, M.S. El-Geundi, Equilibrium studies on adsorption of basic dyes on hardwood, J. Chem. Technol. Biotechnol. 35A (1985) 21–27.

[16] M. Dakiky, M. Khamis, A. Manassra, M. Mereb, Selective adsorption of chromium(VI) in industrial wastewater using low-cost abundantly available adsorbents, Adv. Environ. Res. 6 (2002) 533–540.

[17] M. Villaescusa, N. Miralles, Heavy metals uptake from aqueous by cork and yohimbe bark wastes, J. Chem. Technol. Biotechnol. 75 (2000) 812–816.

[18] A.M. Marganda, B.C.G. Ganzales, C.R. Guedes, Chromium removal in tannery wastewaters polishing pine sylvestris bark, Water Res. 27 (1993) 1333–1338.

[19] B. Acemioglu, A. Samil, M.H. Alma, R. Gundogan, Copper(II) removal from aqueous solution by organosolv lignin and its recovery, J. Appl. Polym. Sci. 89 (2003) 1537–1541.

[20] The Brochures of Perlite Mining Management, Eti Holding A.S. Menderes, Izmir, Turkey, 2001 (in Turkish).

[21] M. Polatli, M. Erdinc, E. Erdinc, E. Okyay, Perlite exposure and 4-years change in lung function, Environ. Res. Sec. A 86 (2001) 238–243.

[22] M. Dogan, M. Alkan, U. Cakir, Electrokinetic properties of perlite, J. Colloid Interface Sci. 192 (1997) 114–118.

[23] M. Dogan, M. Alkan, Y. Onganer, Adsorption of methylene blue from aqueous solution onto perlite, Water Air Soil Pollut. 120 (2000) 229–248.

[24] M. Dogan, M. Alkan, Adsorption of copper(II) onto perlite, J. Colloid Interface Sci. 243 (2001) 280–291.

[25] G. Antonocci, G. Goretti, A. Lagana, B.M. Petronio, Adsorption of organic solutes from water by modified perlite, Ann. Chim. 66 (7–8) (1976) 477–483.

[26] F. Conti, G. Goretti, A. Lagana, B.M. Petronio, Extraction of organic compounds from water by means of modified perlite-active charcoal mixture, Ann. Chim. 68 (9–10) (1978) 783–789.

[27] M. Dogan, M. Alkan, Adsorption kinetics of methyl violet onto perlite, Chemosphere 50 (2003) 517–528.

[28] S. Lagergren, Above the theory of so-called adsorption of soluble substances, Kungliga Suenska Vetens kapsakademiens, Handlingar 24 (1898) 1–39.

[29] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[30] W.J. Weber, Kinetics of adsorption on carbon from solution, J. Saint. Eng. Div. ASCE 89 (SA2) (1963) 31–39.

[31] N. Kannan, M. Meenakshısundaram, Adsorption of Congo red on various activated carbons, Water Air Soil Pollut. 138 (2002) 289–305.

[32] O. Inel, F. Tumsek, The measurement of surface areas of some silicates by solution adsorption, Turk. J. Chem. 24 (2000) 9–19.

[33] K.K. Panday, G. Prasad, V.N. Singh, Use of wollastonite for the treatment of Cu(II) rich effluents, Water Air Soil Pollut. 27 (1986) 287–296.

[34] T. Mathialagan, T. Viraraghavan, Adsorption of cadmium from aqueous solution by perlite, J. Hazard. Mater. B94 (2002) 291–303.

[35] S.K. Khare, K.K. Panday, R.M. Srivastava, V.N. Singh, Removal of victoria blue from aqueous solution by fly ash, J. Chem. Technol. Biotechnol. A: Chem. Technol. 38 (1987) 99–104.