Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick

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Abstract

This paper presents a study on the batch adsorption of basic dye, methylene blue, from aqueous solution ($40 \, mg \, L^{-1}$) onto cedar sawdust and crushed brick in order to explore their potential use as low-cost adsorbents for wastewater dye removal. Adsorption isotherms were determined at 20 °C and the experimental data obtained were modelled with the Langmuir, Freundlich, Elovich and Temkin isotherm equations. Adsorption kinetic data determined at a temperature of 20 °C were modelled using the pseudo-first and pseudo-second-order kinetic equations, liquid-film mass transfer and intra-particle diffusion models. By considering the experimental results and adsorption models applied in this study, it can be concluded that equilibrium data were represented well by a Langmuir isotherm equation with maximum adsorption capacities of 142.36 and 96.61 $mg \, g^{-1}$ for cedar sawdust and crushed brick, respectively. The second-order model best describes adsorption kinetic data. Analysis of adsorption kinetic results indicated that both film- and particle-diffusion are effective adsorption mechanisms. The Influence of temperature and pH of the solution on adsorption process were also studied. The extent of the dye removal decreased with increasing the solution temperature and optimum pH value for dye adsorption was observed at pH 7 for both adsorbents. The results indicate that cedar sawdust and crushed brick can be attractive options for dye removal from dilute industrial effluents.
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1. Introduction

Pollution caused by industrial wastewaters has become a common problem for many countries. The effluents from dye manufacturing and consuming industries are highly coloured coupled with high chemical and biochemical oxygen demands (COD and BOD). Discharge of such effluents imparts colour to receiving streams and affects its aesthetic value. Colour interferes with penetration of sunlight into waters, retards photosynthesis, inhibits the growth of aquatic biota and interferes with gas solubility in water bodies [1–3]. Dyes may also be problematic if they are broken down anaerobically in the sediment, as toxic amines are often produced due to incomplete degradation by bacteria [4]. Direct discharge of dyes laden wastewater into municipal wastewater plants and/or environment may cause the formation of toxic carcinogenic breakdown products. Today more than 9000 dyes are incorporated in colour index belonging to various chemical application classes.

Various techniques have been employed for the removal of dyes from wastewaters. Due to low biodegradability of dyes, a conventional biological treatment process is not very effective. Dyes laden wastewaters are usually treated by physical or chemical processes. All these methods have different colour removal capabilities, capital costs and operating rates. Among these processes, adsorption has been found to be superior to other techniques for wastewater treatment in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances. Activated carbon is the most widely used adsorbent with great success because of its high adsorption capacity. But its use is limited due to its high cost. This has led to search for cheaper substitutes. Several wastes and residues have been investigated for the adsorption of dyes with varying success [5–10]. New economical, easily available and highly effective adsorbents are still needed. In this work, cost-effective

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cedar sawdust and crushed brick were selected as adsorbents for the investigation of adsorption of methylene blue from aqueous solution.

Methylene blue is not strongly hazardous, but it can cause some harmful effects. Adsorption of methylene blue from the aqueous phase is a useful toll for product control of adsorbents. Some kinds of sawdust have been studied as adsorbents for removal of methylene blue from aqueous solutions [11–13]. However, no study has been regarded for the adsorption of methylene blue by cedar sawdust and crushed brick.

The aim of this work is to study the removal of methylene blue from aqueous solution by adsorption onto cedar sawdust and crushed brick in batch mode. Adsorption kinetics and isotherms were determined and modelled by rate and diffusion equations, and by The Langmuir, Freundlich, Elovich and Temkin models. The Influence of temperature and pH of the solution on adsorption process was investigated.

2. Materials and methods

2.1. Adsorbents and adsorbate

The two adsorbents used in this study: brick and cedar sawdust were obtained from local industries. They were used directly for adsorption experiments without any treatment. Cedar sawdust was dried in air and crushed to a fine powder. The other adsorbent were cleaned, dried to constant weight and crushed to pass through a 315 μm screen particle size. The resulting materials were sieved in the size range of 80–315 μm. The materials were placed in an airtight container for further use. The chemical composition of the crushed brick is summarized in Table 1. Values are expressed as percent w/w. No further characterization or analysis was performed on the adsorbents.

Methylene blue, a cationic dye, 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 concentration were prepared with bidistilled water.

2.2. Adsorption procedure

Adsorption experiments were carried out in batch conditions. For isotherm studies, accurately weighted amount (0.001–0.015 g) of adsorbent (crushed brick or cedar sawdust) were continuously stirred at 400 rpm with 10 mL of 40 mg L^{-1} methylene blue aqueous solution in thermostated bath. The tem-
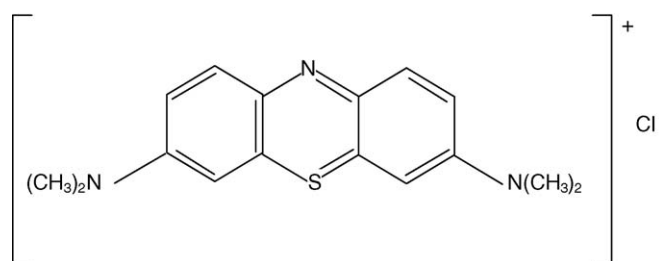

Fig. 1. The structure of methylene blue.

perature was controlled at 20 °C. Agitation was provided for 5 h, which is more than sufficient time to reach equilibrium. At the end of the equilibrium period the contents of the bottles were centrifuged for 15 min at 3000 rpm and the supernatant was subsequently analyzed for residual concentration of methylene blue.

The amount of methylene blue adsorbed, q_e (mg g^{-1}), was obtained as follows:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations of methylene blue (mg L^{-1}), respectively, V is the volume of solution (L) and W is the amount of adsorbent used (g).

Batch adsorption kinetic experiments were carried out by agitating at a speed of 400 rpm 0.5 g of adsorbent (cedar sawdust or crushed brick) with 1 L aqueous solution of methylene blue at a concentration of 40 mg L^{-1} in glass flasks placed in a temperature controlled water bath at a constant temperature of 20 °C. The schematic diagram of the experimental apparatus is shown in Fig. 2. After the desired contact time, solutions were centrifuged for 15 min at 3000 rpm and the supernatant solutions were analyzed for the final concentration of methylene blue by using a UV–vis spectrophotometer (Hewlett Packard 8453) set at a wave-length of 665 nm, maximum absorbance.

The amounts of methylene blue adsorbed were calculated from subtracting final solution concentrations from the initial concentration of aqueous solution. Blank solutions were used for each series of experiments.

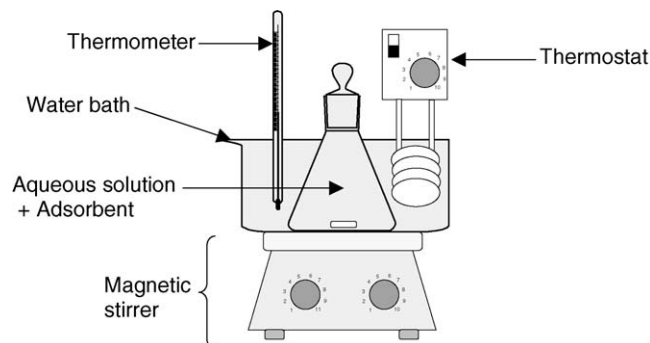Effect of pH was studied by adjusting the pH of dye solutions using dilute HCl and NaOH solutions.

Table 1
Chemical components of crushed brick

Component	Percentage (in weight)
SiO$_2$	78.99
Fe$_2$O$_3$	7.12
CaO	4.60
MnO	0.12
MgO	1.00
Al$_2$O$_3$	8.17

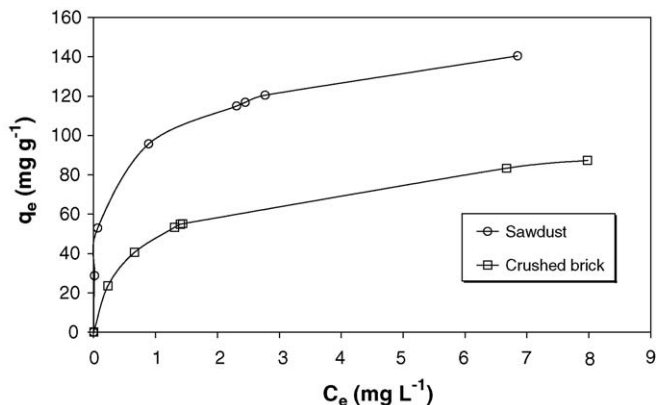Fig. 2. Experimental apparatus used for adsorption kinetic studies.

Fig. 3. Adsorption isotherms of methylene blue by cedar sawdust and crushed brick.

3. Results and discussion

3.1. Isotherms

The adsorption isotherms of methylene blue on cedar sawdust and crushed brick are shown in Fig. 3. The obtained results show a better adsorption of methylene blue on cedar sawdust. Isotherms showed the shape of type L according to the classification of Giles et al. [14]. The L or Langmuir shape of the isotherms means that there is no strong competition between the solvent and the adsorbate to occupy the adsorbent sites. In this case, the longitudinal axes of the adsorbed molecules are parallel to the adsorbent surface [14].

Adsorption isotherms are important for the description of how adsorbates will interact with an adsorbent and are critical in optimizing the use of adsorbent. Thus, the correlation of equilibrium data using either a theoretical or empirical equation is essential for adsorption data interpretation and prediction. Several models have been published in the literature to describe experimental data of adsorption isotherms. Four famous isotherm equations, the Langmuir, Freundlich, Elovich and Temkin, were employed for further interpretation of the obtained adsorption data.

The goal of this part is to apprehend the interactions methylene blue-adsorbents through the validity of the models and also to find parameters allowing comparison of the tested adsorbents.

The Langmuir model is given by the following relation:

$$\frac{q_e}{q_m} = \frac{bC_e}{1 + bC_e} \quad (2)$$

where C_e is the liquid-phase concentration of the adsorbate at equilibrium (mg L^{-1}), q_e is the amount of adsorbate adsorbed at equilibrium (mg g^{-1}), q_m is the maximum adsorption capacity (mg g^{-1}) and b is the Langmuir constant related to the energy of adsorption (L mg^{-1}).

This relation can be linearized in two forms:

- According to Stumm and Morgan [15] representation (form I):

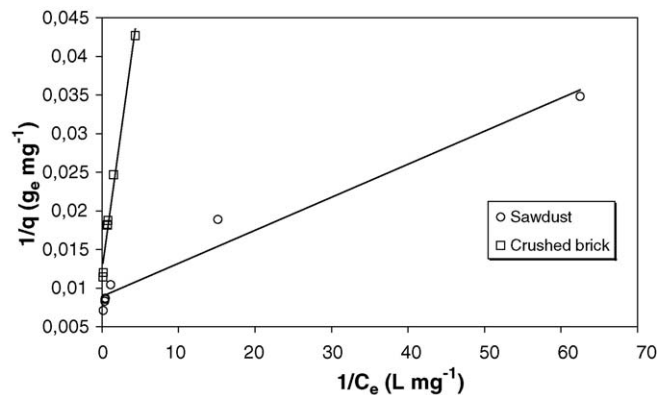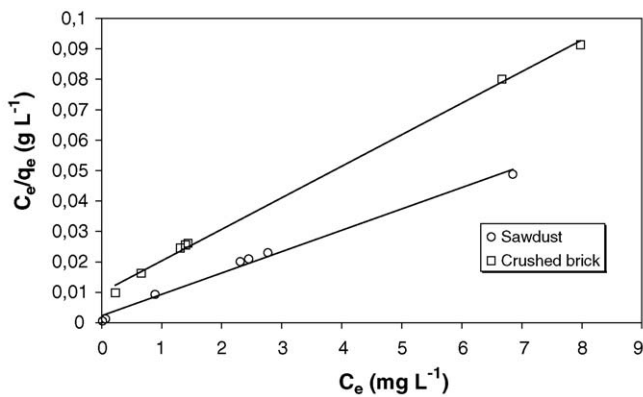$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C_e} \quad (3)$$

Fig. 4. Langmuir plots of methylene blue adsorption by cedar sawdust and crushed brick.

- According to the representation of Weber [16] (form II):

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (4)$$

If the adsorption obeys Langmuir equation, maximum adsorption capacity and Langmuir constant can be evaluated from the slopes and the intercepts of the plots C_e/q_e versus C_e (form II) or $1/q_e$ versus $1/C_e$ (form I).

The modelling of experimental results of the adsorption isotherms by the Langmuir equation (Fig. 4) presents considerable differences according to the mode of exploitation (linearization). It appears that the method of linearization thus intervenes in the estimation of the adsorption isotherms parameters. The obtained results (Table 2) show that the correlation coefficients for the Langmuir equation in the form II are higher than those of the form I. The values of the maximum adsorption capacity obtained by the linearized form II are higher than the experimental adsorbed amounts and correspond to the adsorption isotherms plateau. On the other hand, the monolayer adsorption capacities determined using the linearized form I are lower than experimental values. The values of the Langmuir constant determined using form I are higher than those obtained by form II.

The monolayer adsorption capacity, as calculated from Langmuir isotherms, for cedar sawdust is relatively higher in comparison to crushed brick. In addition, the Langmuir constant determined for cedar sawdust is higher than that obtained for crushed brick.

Table 2
Langmuir isotherm parameters and correlation coefficients

	Langmuir I			Langmuir II			
	q_m (mg g^{-1})	b (L mg^{-1})	r	q_m (mg g^{-1})	b (L mg^{-1})	r	R_L
Cedar sawdust	111.97	20.89	0.985	142.36	3.04	0.995	8.16×10^{-3}
Crushed brick	80.60	1.73	0.992	96.61	1.03	0.999	23.7×10^{-3}

All these observations demonstrate that Langmuir model shows goodness-of-fit for both adsorbents and prove that the best form of linearization of the Langmuir equation is that of Weber (form II).

The favourable nature of adsorption can be expressed in terms of dimensionless separation factor of equilibrium parameter, which is defined by [17]:

$$R_L = \frac{1}{1 + bC_0} \qquad (5)$$

where b is the Langmuir constant and C_0 is the initial concentration of the adsorbate in solution.

The values of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$). R_L values for methylene blue adsorption onto cedar sawdust and crushed brick were less than 1 and greater than zero indicating favourable adsorption (Table 2).

The Freundlich equation may be written as

$$q_e = K_F C_e^{1/n} \qquad (6)$$

K_F is a constant indicative of the adsorption capacity of the adsorbent (mg$^{1 - (1/n)}$ L$^{1/n}$ g^{-1}) and n is an empirical constant related to the magnitude of the adsorption driving force.

According to Halsey [18]:

$$K_F = \frac{q_m}{C_0^{1/n}} \qquad (7)$$

To determine the maximum adsorption capacity, it is necessary to operate with constant initial concentration C_0 and variable weights of adsorbent; thus, $\ln q_m$ is the extrapolated value of $\ln q$ for $C = C_0$.

If the adsorption obeys Freundlich equation, K_F and n can be obtained from the plot of $\ln q_e$ versus $\ln C_e$.

The Freundlich isotherms for the adsorption of methylene blue on cedar sawdust and crushed brick are presented in Fig. 5. The corresponding Freundlich parameters and the correlation coefficients are given in Table 3.

The values of maximum adsorption capacity, determined from Freundlich model, are much higher than experimental values. The correlation coefficients showed that the Langmuir

model (form II) fitted the results better than the Freundlich model. Similar results have been reported for the sorption of methylene blue and Basic Red 22 onto CaCl$_2$ treated beech sawdust [13]. The magnitude of the exponent n gives an indication of the favourability of adsorption. It is generally stated that values of n in the range 2–10 represent good, 1–2 moderately difficult, and less than 1 poor adsorption characteristics [19]. The studied materials are good adsorbents for methylene blue ($n > 2$).

The equation defining the Elovich model is of kinetic nature. It is expressed by the relation

$$\frac{q_e}{q_m} = K_E C_e \exp\left(-\frac{q_e}{q_m}\right) \qquad (8)$$

where K_E is the Elovich constant (L mg^{-1}).

If the adsorption obeys Elovich equation, maximum adsorption capacity and Elovich constant can be calculated from the slopes and the intercepts of the plot $\ln(q_e/C_e)$ versus q_e (Fig. 6).

The values of the maximum adsorption capacity determined using the linear transformation of the Elovich equation (Table 4) are much lower than the experimental adsorbed amounts at equilibrium corresponding to the plateau of the adsorption isotherms, in spite of the good correlation coefficients (≥ 0.997). This means that the assumption of the exponential covering of adsorption sites is not in agreement with the experiment in the studied concentration range.

Temkin model is given by:

$$\frac{q_e}{q_m} = \frac{RT}{\Delta Q} \ln K_0 C_e \qquad (9)$$

where R is the universal gas constant (J mol^{-1} K^{-1}), T is the temperature (K), ΔQ is the variation of adsorption energy (J mol^{-1}) and K_0 is the Temkin constant (L mg^{-1}).

Table 3
Freundlich isotherm parameters and correlation coefficients

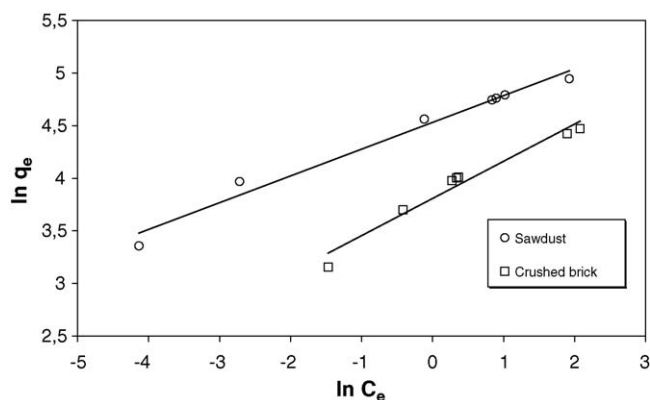|	Freundlich			
	K_F (mg$^{1 - (1/n)}$ L$^{1/n}$ g^{-1})	n	q_m (mg g^{-1})	r
Cedar sawdust	92.78	3.94	236.63	0.990
Crushed brick	44.93	2.83	165.44	0.981

Fig. 5. Freundlich plot for methylene blue adsorption onto cedar sawdust and crushed brick.

Table 4
Elovich and Temkin isotherms parameters and correlation coefficients

	Elovich			Temkin		
	q_m (mg g^{-1})	K_E (L mg^{-1})	r	ΔQ (kJ mol^{-1})	K_0 (L mg^{-1})	r
Cedar sawdust	24.11	259.96	0.999	19.58	286.86	0.998
Crushed brick	27.96	9.19	0.997	13.16	14.72	0.999

If the adsorption obeys Temkin equation, the variation of adsorption energy and the Temkin constant can be calculated from the slope and the intercept of the plot (q_e/q_m) versus ln C_e.

The maximum adsorption capacity obtained from the Langmuir equation (form II) was used for the plot of the Temkin equation (Fig. 7). The correlation coefficient showed a very good linearity (Table 4). The variation of the adsorption energy ΔQ obtained from the slope and the intercept of the linear regression is positive, which means that the adsorption reaction is exothermic.

The Langmuir model makes several assumptions, such as monolayer coverage and constant adsorption energy while the Freundlich equation deals with heterogeneous surface adsorption. The applicability of both Langmuir and Freundlich isotherms to both sorbent systems implies that both monolayer adsorption and heterogeneous surface conditions exist under the used experimental conditions.

Obtained results show that the adsorption of methylene blue onto cedar sawdust is better than that on crushed brick.

3.2. Adsorption kinetics

The adsorption of a solute by a solid in aqueous solution is a phenomenon whose kinetics is often complex. The adsorption rate is strongly influenced by several parameters related to the state of the solid, generally having very heterogeneous reactive surface, and to the physicochemical conditions under which adsorption is carried out.

The adsorption data for the uptake of methylene blue onto cedar sawdust and crushed brick versus contact time are presented in Fig. 8. The comparison of the kinetic curves shows that the rate of methylene blue adsorption onto cedar sawdust is higher than that obtained onto crushed brick. Differences between adsorption rates seem more marked at the beginning of adsorption; the observed variation decreases with time.

In order to interpret the experimental data, it is necessary to identify the step that governs the overall removal rate in the adsorption process. In general, adsorption may be described as a series of steps:

- transport of the adsorbate from the fluid to the external surface of the adsorbent across the boundary layer (film diffusion),
- diffusion of the adsorbate within the pores of the adsorbent (particle diffusion),
- adsorption itself onto the surface.

If the process is controlled by the external resistance, the plot ln C versus time must be linear [20]. This kind of relation is
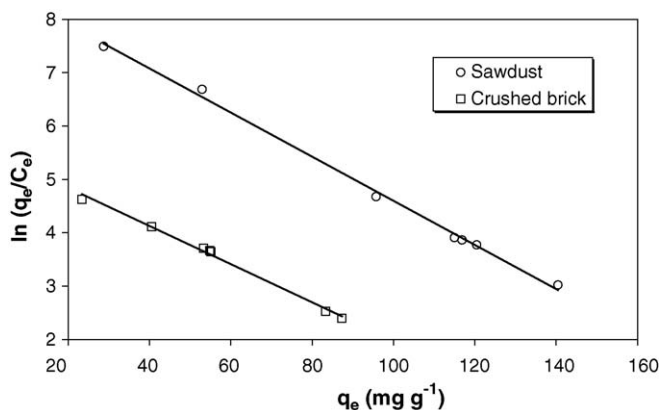

Fig. 6. Elovich plot of methylene blue adsorption by cedar sawdust and crushed brick.
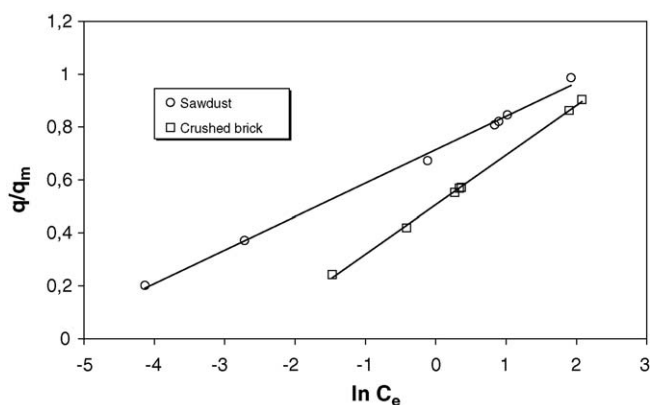

Fig. 7. Temkin plot of methylene blue adsorption by cedar sawdust and crushed brick.
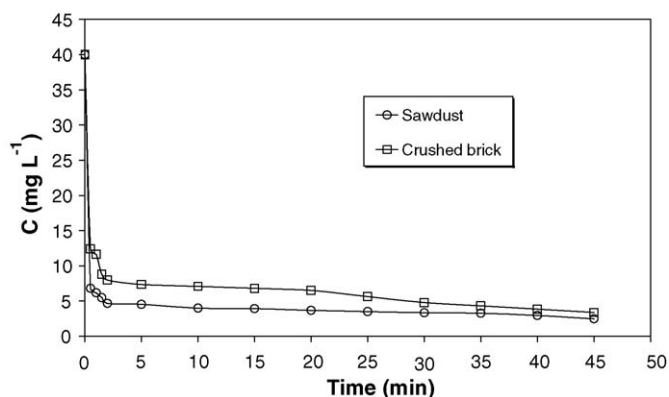

Fig. 8. Dynamics of methylene blue adsorption onto cedar sawdust and crushed brick.
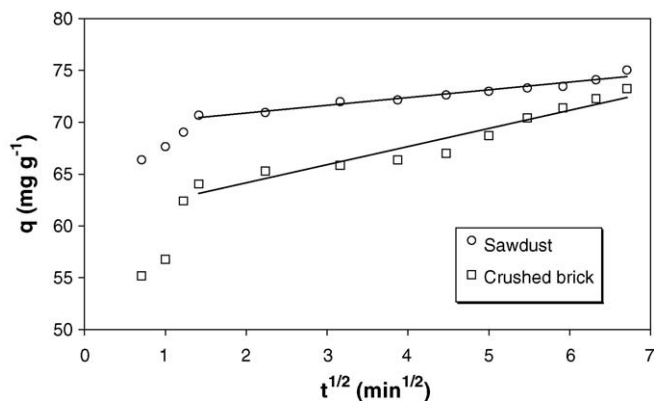
Fig. 9. Plots of methylene blue adsorption vs. square root of time.

Fig. 10. Plots of $\ln(1-F)$ vs. t.

shown for the first stage adsorption kinetics of methylene blue onto cedar sawdust and crushed brick. It seems that the external diffusion is the rate-controlling step of the initial fast adsorption of methylene blue onto cedar sawdust and crushed brick.

The kinetic results of Fig. 8 can be used to determine if particle diffusion is the rate-limiting step for methylene blue adsorption onto cedar sawdust and crushed brick. Some investigators [21,22] reported that if particle diffusion is involved in the sorption process then a plot of adsorbate uptake versus the square root of time would result in a linear relationship. Moreover, the particle diffusion would be the rate-controlling step if this line passes through the origin. As elucidated in Fig. 9, the plots have the same general features, initial curved portion followed by linear portion. The initial curved portion is attributed to the liquid-film mass transfer and the linear portion to the intraparticle diffusion. These phenomena have been reported for the adsorption of dye on activated carbon [23]. At a certain time limit, the curves reveal a linear characteristic that the intraparticle diffusion controls the adsorption process (Fig. 9). The plot of adsorbate uptake versus the square root of time can be represented by such a linear relationship but it does not pass through the origin. This indicates that intraparticle diffusion is involved in the sorption process but it is not the only rate-limiting mechanism and that some other mechanisms are involved. 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 stage of sorption [10,24]. Moreover, the intercept of the plot gives an idea about boundary layer thickness, the larger the value of the intercept, the greater is the boundary layer effect [10,25]. Namely, any increase in the intercept indicates the abundance of solute adsorbed on boundary layer. The value obtained for cedar sawdust is higher than that calculated for crushed brick.

Initially, the amount of methylene blue adsorbed onto adsorbents surface increases rapidly, but then the process slows down (Fig. 8). The adsorption kinetics of methylene blue onto cedar sawdust and crushed brick have been studied by applying the kinetic approximations proposed by McKay. The rate constants of the adsorption reactions can be calculated using the McKay equation [26]:

$$\ln(1 - F) = -kt \tag{10}$$
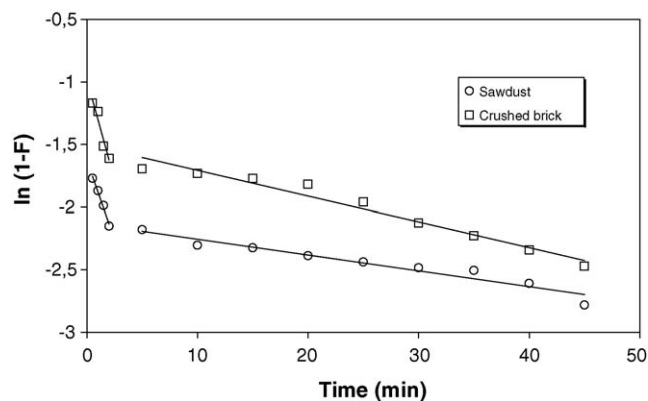
where F is the fraction of solute adsorbed and k is the rate constant.

The values obtained for $\ln(1 - F)$ as a function of time t, are plotted in Fig. 10. In order to analyze the curve, the final linear portion is extrapolated back to $t = 0$. Upon subtraction of the extrapolated line from the original curve, another straight line is obtained which represents the initial reaction. The overall adsorption is seen to consist of a fast initial process followed by a slower process that completes the adsorption. The rate constant of the initial fast reaction (k_1) is calculated from the slope of the first straight line (Fig. 10). The existence of two straight lines indicates two processes. A faster process corresponding to the residual curve, and a slower one corresponding to the later linear portion of the McKay plot, contribute to the overall rate of adsorption. As can be seen from Fig. 10, the rate constant of the slower reaction (k_2) is determined from the slope of the second linear portion.

It is evident that the initial fast reaction is controlled by film diffusion. The values of k_2 are approximately 16 (for crushed brick) to 20 (for cedar sawdust) times smaller than k_1 values. The obtained k_2 values are evidence of a particle diffusion mechanism in the second step of the adsorption [27].

The adsorption kinetics could be described by the Adam–Bohart–Thomas relation:

$$\frac{dq}{dt} = K_1 C (q_m - q) - K_2 q \tag{11}$$

where q is the amount of adsorbate adsorbed at time t (mg g^{-1}), t is the time (min), C is the concentration of adsorbate at time t (mg L^{-1}), q_m is the maximum adsorption capacity (mg g^{-1}), K_1 is the adsorption kinetic constant (L mg^{-1} min^{-1}) and K_2 is the desorption kinetic constant (min^{-1}).

At the initial stage of the adsorption reaction, when $t \to 0$, then $q \to 0$ and $C \to C_0$. The Eq. (11) could then be rewritten:

$$\left(\frac{dq}{dt}\right)_{t \to 0} = \left(\frac{d(C_0 - C)}{dt}\right)_{t \to 0} \frac{V}{W} = K_1 C_0 q_m \tag{12}$$

where W is the weight of adsorbent (g), V is the volume of solution (L) and C_0 is the initial concentration (mg L^{-1}).

Table 5
Kinetic and mass transfer coefficients

	γ (L mg^{-1} min^{-1})	k_{ads2} (g mg^{-1} min^{-1})	$k_S A$ (m^3 s^{-1})	K_W (mg m^{-3} s$^{-0.5}$)
Cedar sawdust	1.032×10^{-3}	53.33×10^{-3}	4.19×10^{-6}	154.54
Crushed brick	0.797×10^{-3}	20.15×10^{-3}	5.34×10^{-6}	70.89

It is possible to calculate the initial kinetic coefficient γ (L g^{-1} min^{-1}):

$$\gamma = K_1 q_m = -\frac{V}{C_0 W}\left(\frac{dC}{dt}\right)_{t \to 0} \tag{13}$$

The values of the kinetic coefficient, calculated taking into account the initial slopes of the kinetic curves, are given in Table 5. The velocity coefficient (γ) of cedar sawdust is greater than that of crushed brick, which is 1.3 times greater than that of crushed brick. The observed variation between the velocity coefficients is certainly due to differences in diffusion phenomena because of different nature of adsorbents.

The Lagergren rate equation was the first equation for the adsorption of liquid/solid system based on solid capacity. The Lagergren rate equation is one of the most widely used adsorption rate equations for the adsorption of solute from a liquid solution. The pseudo-first-order kinetic model of Lagergren may be represented by:

$$\frac{dq}{dt} = k_{ads}(q_e - q) \tag{14}$$

Integrating this equation for the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q$, gives:

$$\ln\frac{q_e - q}{q_e} = -k_{ads}t \tag{15}$$

where q_e is the amount of adsorbate adsorbed at equilibrium (mg g^{-1}), q is the amount of adsorbate adsorbed at time t (mg g^{-1}) and k_{ads} is the rate constant of pseudo-first order adsorption (min^{-1}).

The validity of the model can be checked by linearized plot of $\ln[(q_e - q)/q_e]$ versus t. The rate constant of pseudo-first order adsorption is determined from the slope of the plot.

On the other hand, the pseudo-second-order kinetic equation of Ho based on adsorption capacity may be expressed in the form:

$$\frac{dq}{dt} = k_{ads2}(q_e - q)^2 \tag{16}$$

where k_{ads2} is the rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}) and q_e is the amount of solute adsorbed at equilibrium (mg g^{-1}). Integrating Eq. (16) for boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q$ gives

$$\frac{t}{q} = \frac{1}{k_{ads2}q_e^2} + \frac{t}{q_e} \tag{17}$$

It is noted that k_{ads2} and q_e in Eq. (17) can be obtained from the intercept and slope of the plot of t/q versus t and there is no need to know any parameter beforehand. Because here the adsorption

capacity is directly calculated from Eq. (17), rather than from adsorption equilibrium experiments.

As discussed above, the validity of the model of Lagergren and the pseudo-second-order kinetic model of Ho can be checked by each linearized plot. Figs. 11 and 12 illustrate the fitting results.

The first portion of adsorption kinetics can be described adequately by the model of Lagergren because of the relatively high values of the correlation coefficients (0.987 and 0.971 for, respectively, cedar sawdust and crushed brick). Similar observations were previously reported by Ho and McKay [28] and Kumar et al. [29]. These authors reported that the sorption data were represented well by the Lagergren first-order model only for the rapid initial phase. This confirms that it is not appropriate to use the Lagergren kinetic model to predict the adsorption kinetics of methylene blue onto cedar sawdust and crushed brick for the entire sorption period. The plots drawn according to Lagergren equation did not pass through the ori-
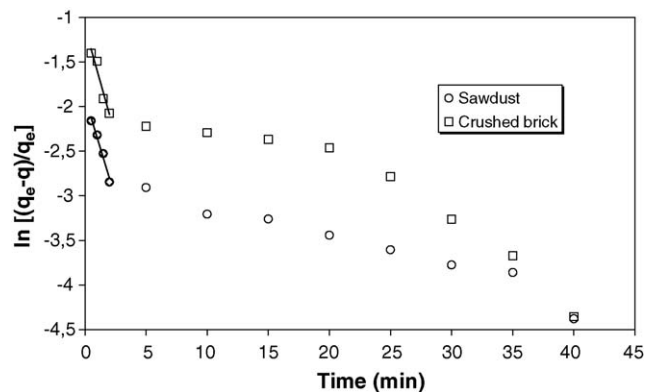

Fig. 11. Lagergren plots for methylene blue adsorption onto cedar sawdust and crushed brick.
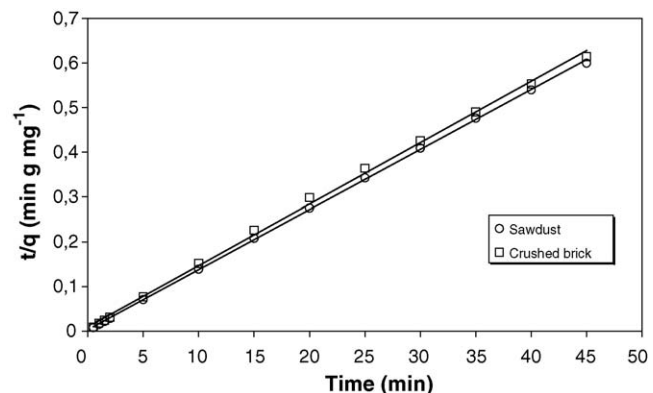

Fig. 12. Test of pseudo-second-order equation for methylene blue adsorption onto cedar sawdust and crushed brick.

gin possibly because the rapid initial phase of the adsorption of methylene blue onto cedar sawdust and crushed brick is more complex which cannot be approximated by a pseudo-first-order rate expression.

Regressing the observed values of t/q on t afforded lines with coefficients of correlation better than 0.999 allowing estimation of the amount of adsorbate adsorbed at equilibrium and the rate constant. It is clearly found that the adsorption of methylene blue onto cedar sawdust and crushed brick can be better described by the pseudo-second order equation (Fig. 12). The adsorption rate constant of pseudo-second-order obtained for cedar sawdust is almost three times more significant than that determined for crushed brick (Table 5).

The initial estimation of liquid-film mass transfer coefficient for batch system was made using the film diffusion model given by [30]

$$V\frac{dC}{dt} = -k_S A(C - C_S) \tag{18}$$

During the initial stage of adsorption of an adsorbate onto fresh adsorbent, C_S is very close to zero (C_S being in equilibrium with $q = 0$). Integrating Eq. (18) for $C_S = 0$ yields

$$-\ln\frac{C}{C_0} = k_S\frac{A}{V}t \tag{19}$$

with k_S the liquid-film mass transfer coefficient ($m^2\,s^{-1}$) and A the surface area of the adsorbent (m^2).

The value of liquid-film mass transfer coefficient can be obtained from Eq. (19) and the concentration versus time data.

Modelling of the adsorption kinetics by the equation of Spahn and Schlunder [30] is applied to the first terms of the kinetic curves, when t tends towards zero. We will consider in this study the global external transport coefficient ($k_S A$). Indeed, it is possible to standardize the liquid-film mass transfer coefficient by the total surface area of the adsorbent using ($k_S A$) rather than k_S. The external mass-transfer coefficients for the both adsorbents are tabulated in Table 5. The correlation coefficient determined for cedar sawdust (0.994) is better than that calculated for crushed brick (0.97). The external mass-transfer coefficient determined for crushed brick is 1.3 times greater than that obtained for cedar sawdust.

The intraparticle diffusion coefficient can be determined using Weber and Morris model [21,31]:

$$C = C_0 - K_W t^{1/2} \tag{20}$$

or

$$q = \frac{K_W}{w}t^{1/2} \tag{21}$$

with

$$w = \frac{C_0 - C}{q} \tag{22}$$

where C_0 is the initial concentration ($mg\,L^{-1}$), C is the concentration at any time t ($mg\,L^{-1}$), t is the time (min), q is the amount adsorbed at any time t ($mg\,g^{-1}$), w is the weight of adsorbent per

volume of solution ($g\,L^{-1}$), K_W is the Weber intraparticle diffusion coefficient ($mg\,L^{-1}\,min^{-1/2}$). To determine the intraparticle diffusion coefficient, (wq) is fitted against $t^{1/2}$. The values of K_W determined from the slope of plots are tabulated in Table 5. The value of the intraparticle diffusion coefficient determined for cedar sawdust is two times greater than that obtained for crushed brick.

3.3. Effects of pH and temperature

To study the effect of pH on methylene blue adsorption on cedar sawdust and crushed brick, the experiments were carried out at $40\,mg\,L^{-1}$ initial dye concentration with 0.05 g/10 mL adsorbent mass at 20 °C for 5 h equilibrium time. The dye adsorption was minimum at the pH of 2 (Fig. 13). The dye adsorption by cedar sawdust and crushed brick was affected over the pH range of 2–5. At higher pH values of 9.5–11 the dye adsorption decreased. Optimum pH value for dye adsorption was observed at pH 7 for both adsorbents. Low pH (2–5) was unfavourable for methylene blue adsorption by cedar sawdust and crushed brick. As pH of the system decreased, the number of negatively charged adsorbent sites decreased and the number of positively charged surface sites increased, which did not favour the adsorption of positively charged dye cations due to electrostatic repulsion. Also, lower adsorption of methylene blue at acidic pH is due to the presence of excess H^+ ions competing with dye cations for the adsorption sites. This, however, did not explain the slight decrease of dye adsorption at higher pH values. There might be another mode of adsorption (ion exchange or chelatation for example). It is also important to point out that cedar sawdust and crushed brick might be subject to hydrolysis, which creates positively charged sites [12]. This may be one of the reasons for the adsorption decrease at high pH values.

The temperature dependence of methylene blue adsorption onto cedar sawdust and crushed brick was studied with the same experimental conditions presented above. Adsorption of methylene blue was carried out for a temperature range of 20–55 °C. Adsorption decrease with the increase of solution temperature. Same results were obtained by various authors for the adsorption
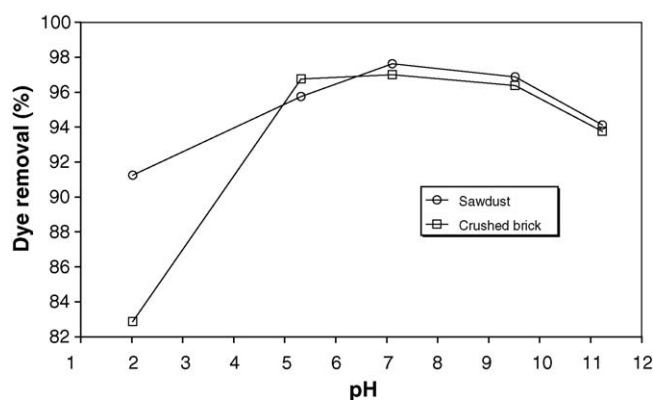

Fig. 13. Effect of pH on methylene blue removal by cedar sawdust and crushed brick (initial dye concentration = $40\,mg\,L^{-1}$, adsorbent weight = 0.05 g, volume = 10 mL, temperature = 20 °C, contact time = 5 h).

of dyes on various adsorbents [32–35]. This can be explained by the exothermicity and spontaneity of the adsorption process and by the weakening of bonds between dye molecules and active sites of adsorbents for high temperatures.

4. Conclusions

The results of present investigation show that cedar sawdust and crushed brick, low cost materials, have suitable adsorption capacity with regard to the removal of methylene blue from its aqueous solution.

The experimental equilibrium data obtained were applied to the Langmuir, Freundlich, Elovich and Temkin isotherm equations to test the fitness of these equations. By considering the experimental results and adsorption models applied in this study, it can be concluded that adsorption of methylene blue obeys Langmuir isotherm, the linearization mode of the Langmuir equation influences the estimation of parameters, cedar sawdust show better adsorption capacity than crushed brick, the Freundlich model is less suitable than that of Langmuir, the Elovich representation does not lead to a correct determination of the maximum adsorption capacity and the Temkin model shows that the reaction of adsorption is exothermic.

Adsorption kinetics follows pseudo-second order kinetic model. Kinetic results showed that both film- and particle-diffusion are effective adsorption mechanisms. The adsorption is a two-stage process comprising a fast initial phase and a slower second phase. In the first phase, methylene blue molecules are adsorbed at the outer sites of the adsorbent particles in a fast process that dominates the initial kinetics of adsorption. In the second phase, dye molecules slowly diffuse inward and adsorb to the inner sites of the adsorbents. The extent of the dye removal decreased with increasing the solution temperature and optimum pH value for dye adsorption was observed at pH 7 for both adsorbents.

Further experiments need to be conducted to test the dynamic adsorption of methylene blue in fixed bed onto cedar sawdust and crushed brick.

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