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Equilibrium and kinetic studies of methyl violet sorption by agricultural waste

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Abstract

In this work, sunflower (*Helianthus annuus* L.) seed hull (SSH), an agricultural waste, was evaluated for its ability to remove methyl violet (MV) from aqueous solutions. Sorption isotherm of MV onto the SSH was determined at 30 °C with the initial concentrations of MV in the range of 25–300 mg/L. The equilibrium data were analyzed using the Langmuir, Freundlich and Temkin isotherm models. The equilibrium process was described well by the Freundlich isotherm model. The maximum SSH sorption capacity was found to be 92.59 mg/L at 30 °C. The kinetic data were studied in terms of the pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models. The pseudo-second-order model best described the sorption process. A single-stage batch-adsorber design of the adsorption of MV onto SSH was studied based on the Freundlich isotherm equation. The results indicated that sunflower seed hull was an attractive candidate for removing methyl violet from aqueous solution.
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Keywords: Sunflower seed hull; Methyl violet; Sorption; Equilibrium; Kinetics

1. Introduction

Synthetic dyes are widely used in a number of industrial processes, such as textile industries, paper printing and photography [1]. Waste effluent containing colour compounds causes serious environmental problems. Dyes can have acute and/or chronic effects on exposed organisms depending on the exposure time and dye concentrations. Dyes are inherently highly visible meaning that concentrations as low as 0.005 ppm capture the attention of both the public and the authorities [2]. Dyes absorb and reflect sunlight entering water and so can interfere with the growth of bacteria and hinder photosynthesis in aquatic plants [3]. Basic dyes have high brilliance and intensity of colours and are highly visible even in a very low concentration [4–10]. Repeated or prolonged exposure to the methyl violet (2B) can produce target organ (skin and eyes) damage. The methyl violet (2B) may be harmful if inhaled, swallowed or absorbed through skin. Contact may cause irritation to the skin and eyes [11]. Hence, the dye removal is of great importance.

Activated carbon, as an adsorbent has been widely investigated for the adsorption of basic dyes [12–15], but its high cost limits its commercial application. In recent years, extensive research has been undertaken to develop alternative and economic adsorbents.

An economic sorbent is defined as one which is abundant in nature, or is a by-product or waste from industry and requires little processing [16]. Such alternatives include palm ash and chitosan/oil palm [17,18], shale oil ash [19], *Posidonia oceanica* (L.) fibres [20], palm kernel fibre [21], sand [22], peanut hull [23] and soy meal hull [24].

In this work, we attempt to use sunflower seeds hulls, which are discarded as waste material from the food industry, as an alternative low-cost sorbent in the removal of methyl violet from aqueous solutions. Sunflower grains are botanically defined as fruits. They are composed of a thin outer shell, the pericarp, also known as "hull", that surrounds and contains the seed, usually named "kernel". The seed contains the largest proportion of oil that is found in a fruit [25]. The hull, which comprises between 20 and 30% of the seed, depending on the variety, contains mostly crude fibre and an insignificant quantity of fat [26]. Sunflower is the fifth most important source of edible oil after soybean, rapeseed, cotton, and peanut. The total world production of 25.8 million tonnes of sunflower seed go almost

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exclusively to oil extraction, providing 8.2% of total world volume, estimated at around 107 million tonnes [27]. Sunflower fruits are hulled before they enter in the industrial process of oil extraction. Thus a huge load of sunflower hulls is generated each year. Sunflower hulls have little commercial value and become a disposal problem owing to their low bulk density, thus occupying large storage areas. Hence, the utilization of such agriculture solid waste for wastewater treatment is most desirable. To our knowledge, the adsorption of dyes in the solutions using sunflower seed hull was little studied. Osma et al. [28] reported the adsorption of diazo dye reactive black 5 (RB5) from aqueous solutions on sunflower seeds shells. The validity of the results for basic dyes needs further investigation.

The aim of this study was to investigate the potential of sunflower seed hull, an agricultural waste, as an adsorbent in the removal of a basic dye, methyl violet, from aqueous solutions.

2. Materials and methods

2.1. Sorbate

Methyl violet (MV) supplied by Sigma–Aldrich (M) Sdn Bhd, Malaysia was used as received. The characteristics and chemical structure of this dye are listed in Table 1.

2.2. Sorbent

Sunflower seed hulls (SSH) were removed from the sunflower seeds obtained locally, washed five times by hot water and finally with deionized water to remove any adhering dirt and oven dried at 70 °C for 24 h to constant weight. The dried materials were ground and sieved to obtain a particle size range of 0.5–1 mm and stored in plastic bottle for further use. No other chemical or physical treatments were used prior to adsorption experiments. The chemical composition of the SSH was 31.9% cellulose, 29.3%

lignin and 27.2% pentosan [29]. Scanning electron microscopy (SEM) analysis was carried out on the SSH sample before and after adsorption to study its surface texture.

2.3. Equilibrium studies

Adsorption experiments were carried out by adding a fixed amount of sorbent (0.30 g) into a number of 250 mL-stoppered glass Erlenmeyers flasks containing a definite volume (200 mL in each case) of different initial concentrations (25–300 mg/L) of dye solution without changing pH (pH 4.5 ± 0.3) and temperature 30 °C. The flasks were placed in a thermostatic water-bath shaker and agitation was provided at 130 rpm for 135 min to ensure equilibrium was reached. At time $t = 0$ and equilibrium, the dye concentrations were measured using a double beam UV–vis spectrophotometer (Shimadzu, Model UV 1601, Japan) at 586 nm wavelength. The amount of adsorption at equilibrium, q_e (mg/g), was calculated by:

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

where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V is the volume of the solution (L) and W is the mass of dry sorbent used (g).

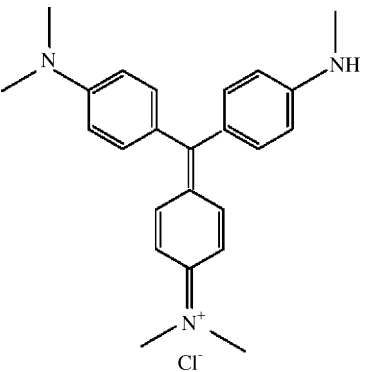The dye removal percentage can be calculated as follows:

$$\text{Removal percentage} = \frac{C_0 - C_e}{C_0} 100 \tag{2}$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively.

2.4. Effect of solution pH

In this study, 200 mL of dye solution of 100 mg/L initial concentration at different pH values (2.0–7.0) was agitated with

Table 1
The physical characteristics and molecular structure of methyl violet dye

Dye name	Methyl violet 2B
Abbreviation	MV
Generic name	Basic violet 1
General description	Methyl violet 2B is a mixture of polymethylated (4,5 and 6) pararosaniline chlorides
λ_{max}	586
Colour index number	42,535
Chemical formula	$C_{24}H_{28}ClN_3$
Molecular weight (g/mol)	393.95
Molecular structure	

0.30 g of SSH in a water-bath shaker at 30 °C. Agitation was made for 135 min at a constant agitation speed of 130 rpm. The pH was adjusted with 0.1 N NaOH and 0.1 N HCl solutions and measured by using a pH meter (Ecoscan, EUTECH Instruments, Singapore).

2.5. Batch kinetic studies

The procedures of kinetic experiments were basically identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals, and the concentrations of dye were similarly measured. All the kinetic experiments were carried out at pH 4.5 ± 0.3. The amount of sorption at time t, q_t (mg/g), was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{3}$$

where C_t (mg/L) is the liquid-phase concentrations of dye at any time.

3. Results and discussion

3.1. Effect of solution pH on dye uptake

Numerous researchers have suggested the pH dependency of the basic dyes binding process on different materials [20,30–33]. In this work, the influence of pH on the dye adsorption onto SSH was studied while the initial dye concentration, shaking time, amount of SSH and temperature were fixed at 100 mg/L, 135 min, 0.30 g and 30 °C, respectively. The effect of pH on the adsorption of MV by the SSH is presented in Fig. 1. The effect of pH on adsorption of dye was studied within pH range 2–7. Solution pH would affect both aqueous chemistry and surface binding-sites of the adsorbent. The equilibrium sorption capacity was minimum at pH 2 (3.15 mg/g) and increased up to pH 4, reached maximum (54.00–53.55 mg/g) over the initial pH 4–7. The absence of sorption at low pH can be explained by the fact that at this acidic pH, H^+ may compete with dye ions for the adsorption sites of adsorbent, thereby inhibiting the adsorption of dye. At higher solution pH, the SSH may get negatively charged, which enhances the positively charged dye cations through electrostatic forces of attraction. Similar results of pH effect were also reported for the adsorption of methylene
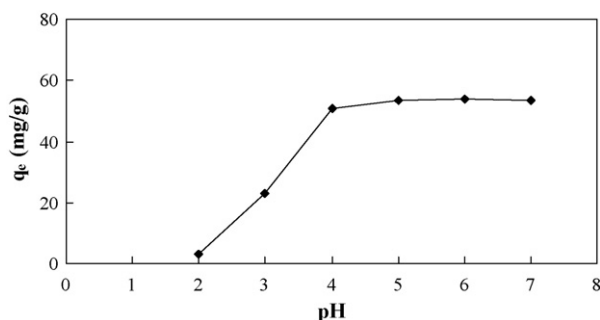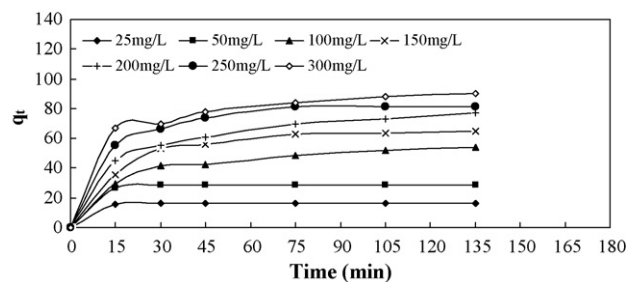

Fig. 2. Effect of contact time and initial concentration on the adsorption of MV onto SSH at 30 °C (pH 7, $W = 0.3$ g, stirring rate 130 rpm).

blue onto jute fibre carbon [34] and the adsorption of basic blue 9 from aqueous solution by dried activated sludge [35].

3.2. Effect of contact time and initial concentration

The adsorption of MV on SSH at different initial concentrations was studied as a function of contact time in order to determine the equilibrium time. Fig. 2 shows time course of the adsorption equilibrium of MV onto SSH. It can be observed that the dye uptake increased with time and, at some point in time, reached a constant value where no more dye was removed from the solution. At this point, the amount of dye being adsorbed onto the adsorbent was in a state of dynamic equilibrium with the amount of dye desorbed from the adsorbent. The time required to attain this state of equilibrium was termed the equilibrium time and the amount of dye adsorbed at the equilibrium time reflected the maximum dye adsorption capacity of the adsorbent under these particular conditions. It indicated that the contact time needed for MV solutions with initial concentrations of 25–50 mg/L to reach equilibrium was 30 min. For MV solutions with initial concentrations of 100–300 mg/L, equilibrium time of 105 min was required. However, the experimental data were measured at 135 min to make sure that full equilibrium was attained. The rapid adsorption observed during the first 15 min is probably due to the abundant availability of active sites on the SSH surface, and with the gradual occupancy of these sites, the sorption becomes less efficient.

Reported data on the sorption kinetics of basic dyes by various adsorbents have shown a wide range of adsorption rates. For example, the equilibrium time for the adsorption of rhodamine-B (basic dye) on waste orange peel was 20 min [36] and for methylene blue biosorption by *Posidonia oceanica* (L.) fibres was 10 min [20]. Senthilkumaar et al. [37] reported the adsorption rate of crystal violet (basic dye) on phosphoric and sulphuric acid activated carbons (PAAC and SAAC) at different time intervals and different initial dye concentrations and found the equilibrium time was 50, 80, 120 and 180 min for PAAC and 120, 150, 180 and 220 min for SAAC for the initial concentrations of 10, 20, 30 and 40 mg/L, respectively.

Fig. 2 also shows that the increase in the initial dye concentration increased the amount of dye adsorbed. It was clear that the removal of dye was dependent on the concentration of the dye. The amount of MV adsorbed increased from 16.592 to 90.07 mg/g as the concentration was increased from 25 to
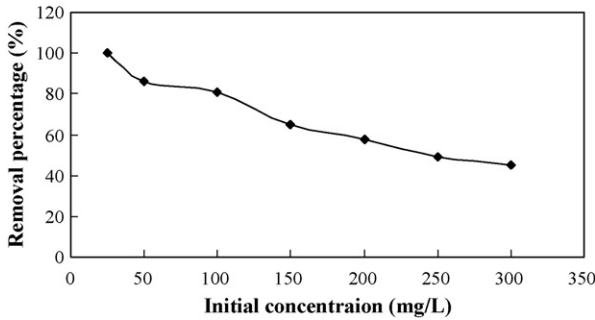

Fig. 1. Effect of initial pH on the equilibrium sorption capacity of SSH ($C_0 = 100$ mg/L, temperature 30 °C, stirring rate 130 rpm and $W = 0.30$ g).

Fig. 3. Removal percentage versus initial concentration (pH 4.5 ± 0.3, $W = 0.3$ g, stirring rate 130 rpm).

300 mg/L. A similar phenomenon was observed for the adsorption of basic dyes from aqueous solution on activated carbons [12,13]. At low concentrations, adsorption sites took up the available dye more quickly. However, at higher concentrations, dye needed to diffuse to the sorbent surface by intraparticle diffusion. Also, the steric repulsion between the solute molecules could slow down the adsorption process. The percentage removal of MV adsorbed decreased from 99.9 to 45% as the initial concentration was increased from 25 to 300 mg/L as shown in Fig. 3.

3.3. Isotherm analysis

The purpose of the adsorption isotherms is to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface [38]. The equilibrium isotherms in this study have been described in terms of Langmuir, Freundlich and Temkin isotherms. The Langmuir theory assumes homogeneous type of adsorption within the biosorbent, meaning that once a dye molecule occupies a site, no further adsorption can take place at that site. The Langmuir adsorption isotherm has been successfully used to explain the adsorption of basic dyes from aqueous solutions [12–14]. The linear form of the Langmuir model is [39]:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \tag{4}$$

The linear plot of specific adsorption (C_e/q_e) against the equilibrium concentration (C_e) (mg/L) (Fig. 4) shows that the adsorption obeys the Langmuir model. The Langmuir constants Q_0 and b were determined from the slope and intercept of the plot and are presented in Table 2.
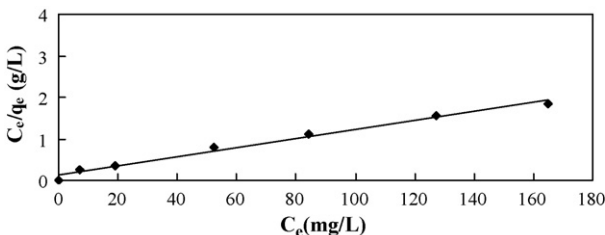
Table 2
Isotherm parameters for removal of MV by SSH at 30 °C

Isotherm	Parameters
Langmuir	
Q_0 (mg/g)	92.59
b (L/g)	0.0775
R^2	0.985
Freundlich	
n	4.218
K_F	26.196
R^2	0.996
Temkin	
B	10.131
A	19.66
R^2	0.943

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by Eq. (5) [40]

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

where C_0 is the highest initial concentration of adsorbate (mg/L) and b (L/mg) is Langmuir constant. The parameter R_L indicates the nature of shape of the isotherm accordingly:

$R_L > 1$ unfavorable adsorption
$0 < R_L < 1$ favorable adsorption
$R_L = 0$ irreversible adsorption
$R_L = 1$ linear adsorption

The value of R_L in the present investigation has been found to be 0.041, indicating that the adsorption of MV on SSH is favorable.

The Freundlich isotherm [41] is an empirical equation assuming that the adsorption process takes place on heterogeneous surfaces and adsorption capacity is related to the concentration of MV dye at equilibrium. A linear form of the Freundlich equation is generally expressed as follows:

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \tag{6}$$

where K_F (mg/g (L/mg)$^{1/n}$) is roughly an indicator of the adsorption capacity and $1/n$ is the adsorption intensity. The magnitude of the exponent, $1/n$, gives an indication of the favorability of adsorption. Values of $n > 1$ represent favorable adsorption condition [42,43]. The plot of $\ln q_e$ versus $\ln C_e$ (Fig. 5) is employed
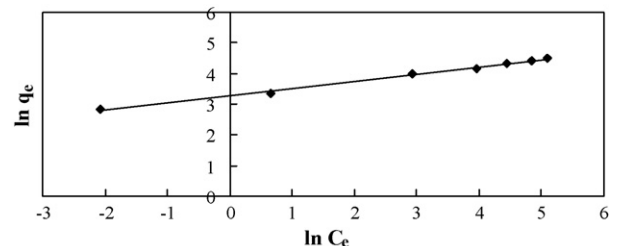

Fig. 4. Langmuir isotherm of MV adsorption onto SSH at 30 °C.
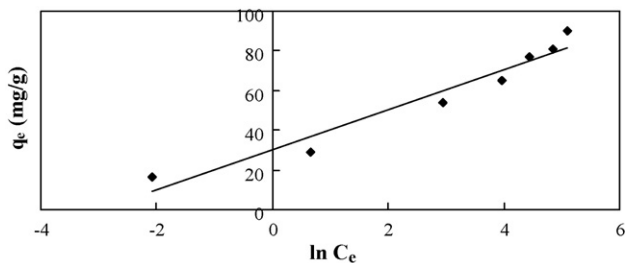

Fig. 5. Freundlich isotherm of MV adsorption onto SSH at 30 °C.

Fig. 6. Temkin isotherm of MV adsorption onto SSH at 30 °C.

Fig. 7. Pseudo-first-order kinetics for adsorption of MV onto SSH at 30 °C.

to evaluate the intercept K_F and the slope $1/n$. The values of K_F, n and the linear regression correlation (R^2) for Freundlich are given in Table 2.

Temkin and Pyzhev [44] considered the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The Temkin isotherm has been used in the following form:

$$q_e = \frac{RT}{b}\ln(AC_e) \tag{7}$$

Eq. (7) can be expressed in its linear form as

$$q_e = \frac{RT}{b}\ln A + \frac{RT}{b}\ln C_e \tag{8}$$

where

$$B = \frac{RT}{b}$$

The adsorption data can be analyzed according to Eq. (8). A plot of q_e versus $\ln C_e$ (Fig. 6) enables the determination of the constants A and B. The constant B is related to the heat of adsorption. The constant A and B together with the R^2 values are shown in Table 2.

Table 2 summarizes the results of the isotherm constants for the three different equilibrium isotherms tested. On the basis of the correlation coefficients (R^2), Freundlich isotherm seemed to represent the equilibrium adsorption data with better fit ($R^2 = 0.996$) as compared to the other isotherms. Similar result was reported in the literature for adsorption of methylene
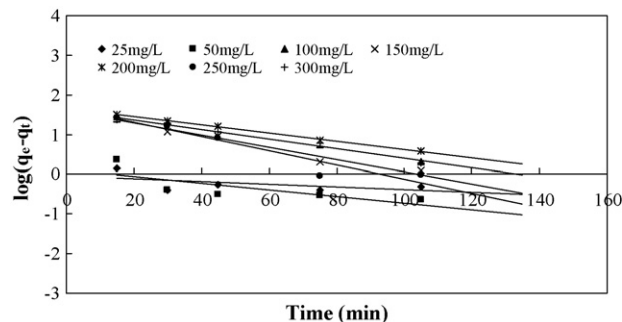
blue onto eggshells and eggshell membrane [45]. Conformation of the experimental data with the Freundlich isotherm model suggests that some heterogeneity in the surface or pores of the SSH sorbent will play a role in MV adsorption.

Table 3 compares the monolayer adsorption capacity Q_0 of different types of adsorbents used for removal of basic dyes. The value of Q_0 in this study is larger than those in most of previous works. This suggests that MV could be easily adsorbed on SSH.

3.4. Adsorption kinetics

Lagergren proposed a method for adsorption analysis which is the pseudo-first-order kinetic equation of Lagergren [51] in the form:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{9}$$

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

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{10}$$

where k_1 is the equilibrium rate constant (1/min), q_e the amount of dye adsorbed on the surface at equilibrium (mg/g), q_t the amount of dye adsorbed at any time (mg/g). The value of the adsorption rate constant (k_1) for MV sorption by SSH was determined from the plot of $\log(q_e - q_t)$ against t (Fig. 7). The parameters of pseudo-first-order model are summarized in Table 4.

Table 3
Comparison of monolayer equilibrium capacity for basic dye onto other low-cost sorbents

Dye	Adsorbent	Q_0 (mg/g)	T (°C)	Reference
Basic violet 1	Sunflower seed hull	92.59	30	This work
Rhodamine-B	Orange peel	3.23	29 ± 2	[36]
Methylene blue	Rice husk	40.58	32	[46]
Malachite green	Bentonite	5.858	35	[47]
Neutral red	Peanut hull	87.72	20	[23]
Methylene blue	Peanut hull	68.03	20	[23]
Methylene blue	Dehydrated peanut hull	123.5	30	[48]
Basic dye (Astrazon Blue FGRL)	Macroalga *Caulerpa lentillifera*	37.17	27	[49]
Methylene blue	Raw *Posidonia oceanica* fibres	5.56	30	[20]
Basic violet 1	Sugarcane dust	50.40	25	[50]
Basic violet 10	Sugarcane dust	13.90	25	[50]
Basic green 4	Sugarcane dust	20.60	25	[50]

Table 4
Comparison of the pseudo-first-order, pseudo-second-order adsorption rate constants and calculated and experimental q_e values obtained at different initial MV concentrations

Initial concentration (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		k_1 (1/h)	$q_{e,cal}$ (mg/g)	R^2	k_2 (g/mg h)	$q_{e,cal}$ (mg/g)	R^2
25	16.59	0.0078	0.88	0.654	0.0588	17.02	0.999
50	28.68	0.0085	0.46	0.046	0.0407	29.16	0.999
100	54.03	0.0050	34.21	0.974	0.0167	59.88	0.998
150	65.01	0.0070	40.35	0.959	0.0011	71.43	0.998
200	77.10	0.0050	45.87	0.998	0.0007	85.47	0.999
250	81.09	0.0415	46.60	0.988	0.0013	87.72	0.999
300	90.07	0.0050	40.89	0.979	0.0012	95.24	0.999

The pseudo-second-order kinetics may be expressed as [52,53]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{11}$$

where k_2 is the rate constant of adsorption, q_e is the amount of dye adsorbed at equilibrium (mg/g) and q_t is the amount of dye adsorbed at time t (mg/g). Separating the variables in Eq. (11) gives:

$$\frac{dq_t}{(q_e - q_t)^2} = k_2\, dt \tag{12}$$

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

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{13}$$

which is the integrated rate law for a pseudo-second-order reaction. Eq. (13) can be rearranged to obtain:

$$q_t = \frac{t}{(1/k_2 q_e^2) + (t/q_e)} \tag{14}$$

which has a linear form of:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{15}$$

where the equilibrium adsorption capacity (q_e), and the second-order constants k_2 (g/mg min) can be determined experimentally from the slope and intercept of plot t/q_t versus t (Fig. 8).
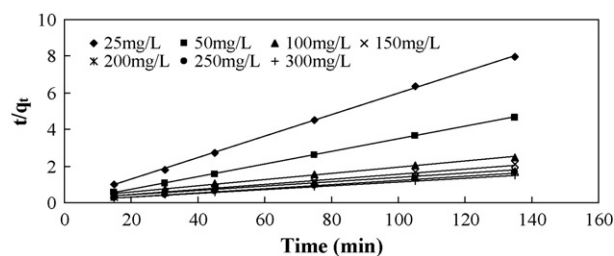

Fig. 8. Pseudo-second-order kinetics for adsorption of MV onto SSH at 30 °C.

Table 4 presents the coefficients of the pseudo-first- and second-order adsorption kinetic models. The R^2 values of the pseudo-second-order model exceeded 0.99 and the q values ($q_{e,cal}$) calculated from pseudo-second-order model were more consistent with the experimental q values ($q_{e,exp}$) than those calculated from the pseudo-first-order model. Hence, the pseudo-second-order model better represented the adsorption kinetics and this suggests that the overall rate of the MV adsorption process appeared to be controlled by chemical process. These results are in good agreement with that reported in literature (Table 5).

Since neither the pseudo-first-order nor the second-order model can identify the diffusion mechanism, the kinetic results were analyzed by the intraparticle diffusion model. Since the particles are vigorously agitated during the adsorption period, it is assumed that the rate is not limited by mass transfer from the bulk liquid to the particle external surface. The rate-limiting step may be film or intraparticle diffusion. The intraparticle diffusion

Table 5
A comparison of kinetic studies for the adsorption of basic dyes onto different adsorbents

| Adsorbent	Dye	Kinetic model	Reference
Bagasse fly ash	Orange-G, methyl violet	Pseudo-second-order kinetic equation	[54]
Sepiolite	Methyl violet (MV), methylene blue	Pseudo-second-order kinetic equation	[55]
Wheat shells	Methylene blue	Pseudo-second-order kinetic equation	[56]
Granular kohlrabi peel	Cationic dyes, methylene blue (MB), neutral red (NR) andacridine orange (AO).	Pseudo-first-order kinetic equation	[57]
Fly ash	Methylene blue	Pseudo-second-order kinetic equation	[58]
Algal biomass based materials	Methylene blue	Pseudo-first-order and pseudo-second-order model	[59]
Nonconventional organomineral sorbent—iron humate	Basic dyes (methylene blue, malachite green, rhodamine-B, crystal violet)	Pseudo-second-order kinetic equation	[60]
Adsorbents prepared from *Prosopis cineraria* sawdust	Malachite green	Lagergren first-order kinetics model	[61]
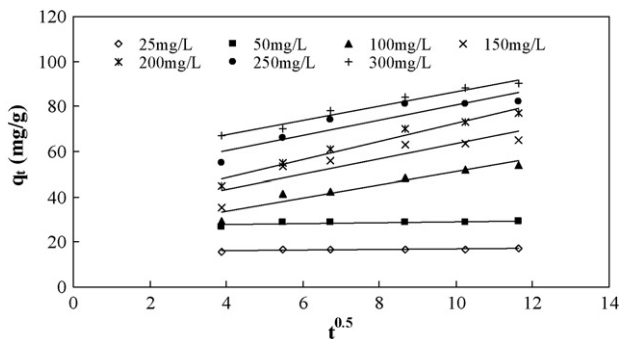
Fig. 9. Plots for evaluating intraparticle diffusion rate constant for sorption of MV onto SSH.

model is expressed as [62]:

$$q_t = k_{id}t^{1/2} + C \qquad (16)$$

where C is the intercept and k_{id} is the intraparticle diffusion rate constant (mg/g min$^{0.5}$), which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$ (Fig. 9). The k_{id} values were obtained from the slope of the linear portions of the curve of different initial concentrations and shown in Table 6. According to this model, the plot of uptake, q_t, versus the square root of time ($t^{1/2}$) should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate controlling step. When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and this further shows that the intraparticle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously. The values of intercept give an idea about the boundary layer thickness such as the larger the intercept, the greater the boundary layer effect.

3.5. Design of batch sorption from isotherm data

Fig. 10 shows a schematic diagram for a batch sorption system. The effluent contains V of water and an initial MV concentration C_0, which is to be reduced to C_1 in the adsorption process. The design is based on the experimental condition of 50 mg/L initial dye concentration at 30 °C and pH 4.5 ± 0.3. In this process, a mass of W (g) of fresh SSH sorbent is added to solution and the dye concentration on the solid changes from $q_0 = 0$ to q_1. The mass balance for the dye in the single stage is
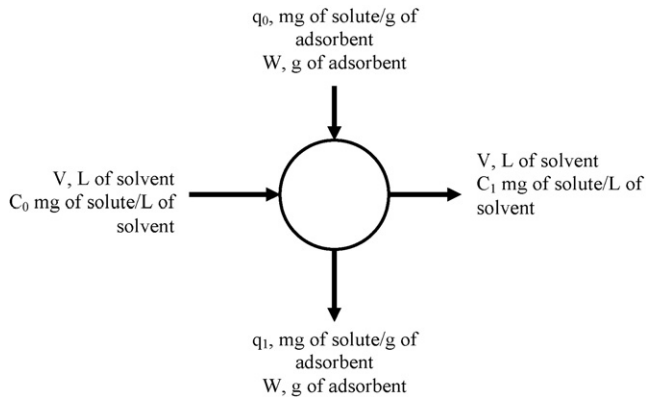

Fig. 10. A single-stage batch adsorption system.

given by

$$V(C_0 - C_1) = W(q_0 - q_1) \qquad (17)$$

Under equilibrium conditions,

$$C_1 \rightarrow C_e \quad \text{and} \quad q_1 \rightarrow q_e$$

Thus

$$VC_0 + Wq_0 = VC_e + Wq_e \qquad (18)$$

For the adsorption of MV on SSH, the Freundlich isotherm gives the best fit to experimental data (Table 2). Thus

$$\frac{W}{V} = \frac{C_0 - C_1}{q_e} = \frac{C_0 - C_e}{K_F C_e^{1/2}} \qquad (19)$$

Eq. (19) allows analytical calculation of the sorbent solution ratio for a given change in solution concentration, C_0 to C_e. Fig. 11 shows a series of plots (60, 70, 80 and 90% dye removal at different solution volumes, i.e., 1–16 L) derived from Eq. (19) for the adsorption of MV on SSH. From Fig. 11, the amount of SSH required for the 90% removal of MV solution of concentration 50 mg/L was 1.17, 5.86, 11.73 and 18.77 g for dye solution volumes of 1, 5, 10 and 16 L, respectively.
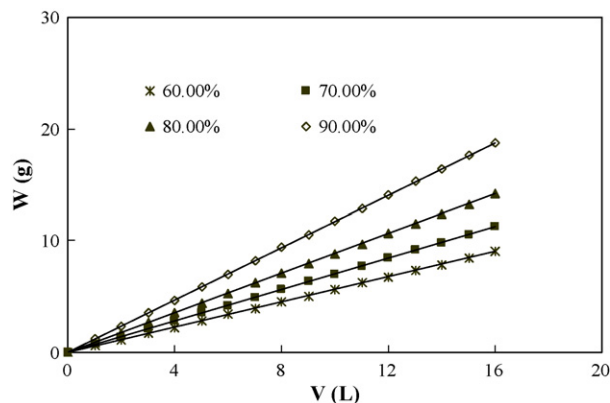
Table 6
Intraparticle diffusion constants for different initial MV concentrations

Initial concentration (mg/L)	k_{id} (mg/g h$^{1/2}$)	C	R^2
25	0.1248	15.486	0.6210
50	0.1936	26.972	0.4387
100	2.9476	21.703	0.9148
150	3.3619	30.045	0.7945
200	4.0732	31.985	0.9680
250	3.3844	46.930	0.8504
300	3.1778	54.886	0.9688

Fig. 11. Adsorbent mass (W) against volume of effluent (V) treated for different percentages of methyl violet removal ($C_0 = 50$ mg/L, $T = 30$ °C).
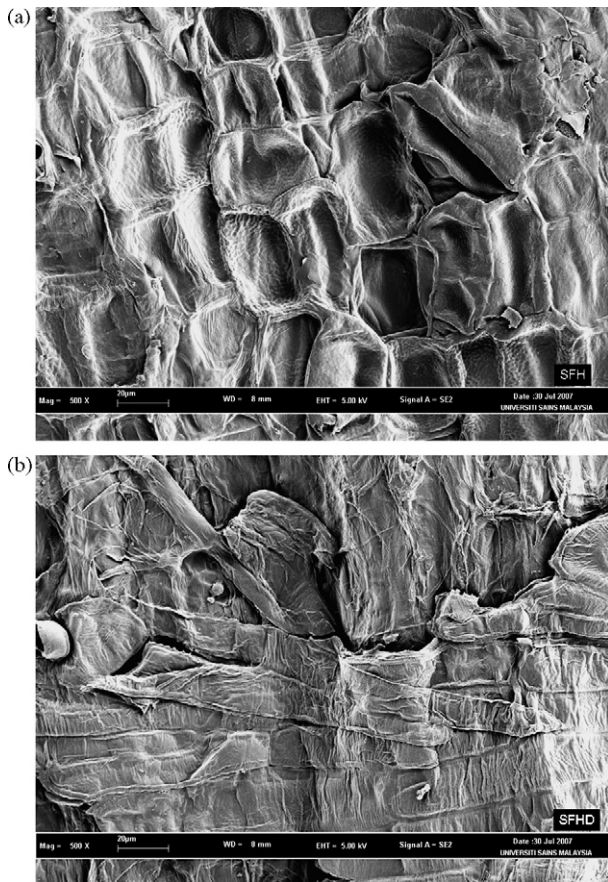
Fig. 12. Typical SEM micrograph of SSH particle (magnification: 500): (a) before dye sorption and (b) with dye sorbed.

3.6. Characterization of SSH

The surface structure of SSH was analyzed by scanning electronic microscopy (SEM) before and after MB sorption (Fig. 12a and b). The textural structure examination of SSH particles can be observed from the SEM photographs at 500× magnification (Fig. 12a). This figure reveals that the surface of SSH is rough surface. After dye adsorption, a significant change is observed in structure of the SSH (Fig. 12b) as a result of dye adsorption.

4. Conclusions

The results obtained show that sunflower seed hull waste is an efficient sorbent in the removal of MV from aqueous solutions. Equilibrium adsorption data for MV is in good agreement with Freundlich isotherm. The monolayer adsorption capacity of SSH was evaluated as 92.59 mg/g. Kinetics of MV sorption on SSH waste follows pseudo-second-order rate expression. Since sunflower seed hull, waste material from the food industry, used in this work is freely, abundantly available and the sorbent does not require an additional pretreatment step such as activation before its application, the sorbent is expected to be economically viable for removal of basic dye from aqueous solution.

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