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Fixed-bed dynamic column adsorption study of methylene blue (MB) onto pine cone

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ABSTRACT

The effectiveness of pine cone biomass in the removal of methylene blue (MB) dye from its aqueous solution was tested here by a fixed-bed column adsorption study. The adsorption column breakthrough curves (BTCs) indicated the favourable column dynamics and its dye adsorptive behaviour depends on feed flow rate, initial MB dye concentration and column bed height. The results showed that the amount of total sorbed dye, equilibrium dye uptake, mass transfer zone and total percentage of dye removal increased with increase in MB dye concentration and the height of the bed, but decreased with increase in initial flow rate. To determine the fixed-bed column adsorption kinetic parameters, Thomas, Yoon–Nelson and Bed Depth Service Time (BDST) models fitted the experimental BTC obtained from dynamic studies. All these parameters are required for the design of adsorption column and it was found that all three kinetic models were applicable. Thomas model showed that the value of maximum solid-phase concentration (q_0) decreased when the flow rate and the height of the bed increased but increased with increasing initial MB dye concentration. The value of Thomas kinetic rate constant (K_{Th}) increased with higher flow rate but decreased with increasing initial MB dye concentration and the height of the bed. Yoon–Nelson model showed that the time required to achieve 50% adsorbate breakthrough, τ fitted well with the experimental data ($\tau_{50\%\ exp.}$) in the entire column adsorption system. The rate constant K_{YN} increased with both increasing flow rate and initial MB dye concentration but decreased with increasing bed height. The BDST model showed that the rate constant (K_0) decreased when both the bed heights and the initial MB dye concentration increased, but increased with the increase in flow rate. The value of the volumetric sorption capacity of the bed (N_0) increased with increasing flow rate, initial MB dye concentration and bed height. Overall, all the three models were fitted well with the experimental data.

Keywords: MB adsorption; Fixed-bed column; BTC, Thomas model; Yoon–Nelson model

1. Introduction

Effluents from many industries contain one or more of toxic dyes [1]. A very little quantity of dye in water is visible and undesirable [2]. The removal of dyes from wastewater is of great interest in the field of water pollution which causes environmental degradation [3]. Methylene blue (MB) is the most general water-soluble dye, which is used for dyeing leather, cotton, printing, calico, tanning and for medical

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purposes [4]. The discharge effluents have these industries contain dye bearing effluents. Adsorption, which is one of the easiest and cost-effective physio-chemical treatment process in removing dyes from aqueous solution, was selected in this study [5,6]. Activated carbons are generally used as adsorbents because of their high adsorption capacities in the removal of inorganic/organic materials from aqueous solution. However, the cost of activated carbon is relatively high which limits their usage [7]. Cost-effective alternative technologies or adsorbents for this purpose are needed. Natural agricultural by-product materials that are locally available in large quantities or certain industrial solid wastes may have the potential to remove dyes as an inexpensive and effective adsorbent. Agricultural wastes are renewable and available abundantly with no or low cost [8]. There are many reported results on the removal of MB dye from aqueous solution using a wide range of adsorbents which has been reviewed by many investigators [9–13]. However, most of the earlier investigations on MB adsorption were restricted to batch equilibrium studies. The adsorption capacity of various adsorbents obtained from batch equilibrium experiments is useful to determine the effectiveness of adsorbents under various physio-chemical process conditions. It also provides the fundamental information of dye adsorption mechanism and kinetic parameters, and to determine the optimum value of various process parameters. However, the data may not be applicable to most of the treatment systems (such as column operations) where contact time is not sufficient for the attainment of equilibrium [14,15]. Further, batch experimental data are often not easy to apply directly to fixed-bed column performance because isotherms are unable to give accurate data for scale up since a flow column is not at equilibrium. Hence, there is a need to perform adsorption study using fixed-bed columns. This fixed-bed column with adsorbents offer easy, continuous operation and scale up which is an important aspect of adsorption process. But lesser number of adsorption results on column study compared to vast batch adsorption study, on inorganic/organic removal by various adsorbents, were reported which is also mentioned in recent review article by Yagub et al. [12]. Further, no research was reported about MB adsorption to pine cone biomass in column mode. Therefore, it is imperative to describe dynamic behaviour in a fixed-bed column condition. The major characteristics of fixed-bed adsorption are the history of effluent concentration [9–12,16]. These concentration-time curves (or their equivalent) are commonly referred to as the breakthrough curves (BTCs) and the time at which the effluent concentration reaches the threshold value is called the breakthrough time. The rational design of adsorption systems is based on accurate predictions of BTCs at specified condition. Despite the usefulness of fixed-bed mode, its analysis is usually complex [17]. The effectiveness of an adsorbent can be obtained from the BTC of effluent concentration where a typical S-shaped BTC is commonly observed [18]. Fixed-bed operation is influenced by equilibrium adsorption (isotherm and capacity), kinetics (diffusion and convection co-efficient) and hydraulic hold up, column geometry and mal-distribution factors [19].

The aim of the present work is to investigate the effects of process variables such as flow rate, bed depth and MB concentration on adsorption capacity of pine cone biomass in a dynamic fixed-bed column operation. Thomas, Yoon–Nelson, and Bed Depth Service Time (BDST) kinetic models were used to analyse the column performance for the removal of MB dye from aqueous solution using pine cone biomass. The results of the parameters obtained with modelling the continuous process can be scaled to an actual industrial column operation [18].

2. Materials and methods

2.1. Adsorbent and its characterization

Pine tree cones were collected locally from Curtin University located at Bentley campus, Perth, Western Australia. It was collected between April and May, 2010. The cones were washed several times with distilled water to remove impurity such as dirt, sand and then dried in an oven at 65˚C temperature for 24 h. Dried pine cone was then ground by using a crusher. The resultant powders were passed through British Standard Sieves and particles below 100 μm were collected in a plastic container and used as adsorbent for adsorption experiments. To determine the information of the surface morphological structure of pine cone before and after adsorption, pine cone biomass powder was then analysed by a scanning electron microscope (SEM) named EVO 40. A spectrum 100 FTIR spectrometer was used to determine the functional groups of pine cone adsorbent. Particle size of pine cone powder was measured by Malvern Hydro 2000S Master Sizer, Malvern Instruments Ltd., UK. The Brunaur Emmett Teller (BET) surface area of the adsorbent was measured using BET method.

2.2. Adsorbate and other chemicals

The basic cationic dye, MB, was tested as an adsorbate in this study. The formula of MB is $C_{16}H_{18}N_3SCl{\cdot}3H_2O$, and molecular weight is 319.85 g.

The chemical structure of this dye is shown in Fig. 1. It was supplied by Sigma–Aldrich Pty. Ltd., NSW, Australia, and of analytical grade. It was used without further purification. The stock dye solution was prepared by dissolving 1 g of MB in 1,000 ml distilled water. The experimental solutions were obtained by diluting the stock dye solution with deionised water to give the appropriate concentration of the experimental solutions. The concentration of dye was measured using UV/visible spectrometer at wavelength of 660 nm. A calibration curve was plotted between absorbance and concentration of dye solution to obtain absorbance-concentration profile, which is not showed here. Unknown MB concentration was measured using the calibration curve.

2.3. Fixed-bed adsorption column design and experimental procedure

A fixed-bed adsorption column was used to evaluate dynamic behaviour of MB dye removal by pine cone biomass. The column studies were carried out using a Perspex glass column of 2.5 cm internal diameter and 30 cm long and are shown in Fig. 2. The column was packed with the adsorbent, pine cone powder between two supporting layers of pre-equilibrated glass wool as shown in Fig. 2. Both the ends of the column were connected with circular threaded caps. The column was packed with known quantity of pine cone biomass to obtain a particular bed height. Various packed-bed of pine cone packing materials were made by wet packing method as per Sen et al. [20]. Influent feed solution was injected into the column at a fixed discharge rate by a variable speed peristaltic pump which was placed at the bottom of the vertical column as shown in Fig. 2. The column was operated at room temperature. The bed porosity was measured by the following equation.

$$\varepsilon = 1 - m_p/\rho_p AH \quad (1)$$

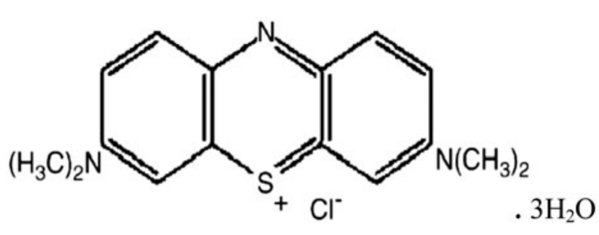
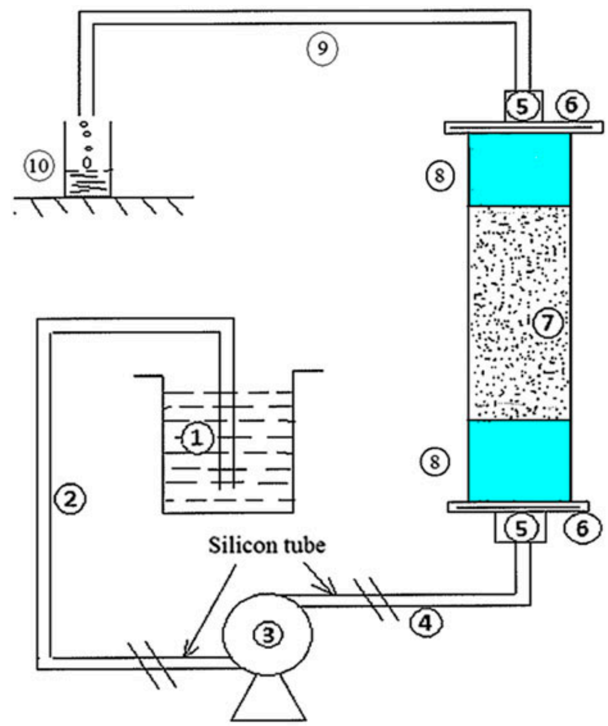


Fig. 1. Chemical structure of MB.



1. Reservoir
2. Inlet silicon tube
3. Peristaltic pump
4. Pump outlet silicon tube & column inlet
5. Nozzles
6. Circular threaded caps with 60 µm wire mesh
7. Packed column
8. Glass wool
9. Column outlet plastic tube
10. Effluent collector tubes

Fig. 2. Schematic diagram of the column.

where ε, H and A are the porosity, height (cm) and cross sectional area (cm^2) of the bed in column, respectively. m_p and ρ_p are the mass (g) and bulk density (g/cm^3) of pine cone, respectively. The initial MB dye concentration was in the range of 50–100 mg/L. The effluent samples were collected at certain time intervals and concentrations of dye were measured. Sampling of column effluent was done at certain time intervals in order to investigate the breakthrough point or column service time and shape of BTC. The effect of inlet flow rate (10, 12 and 15 ml/min), bed height (10, 12, and 15 cm) and initial

MB concentration (50, 70, and 100 mg/L) on BTC were evaluated. The obtained BTCs under various conditions were fitted with various column kinetic and mass transfer models and model parameters were determined.

2.4. Modelling and column adsorption process analysis

2.4.1. Theory of BTC

The performance of fixed-bed column was analysed using the theory of the BTC. The time for breakthrough appearance and shape of BTC are very important characteristics for determining the operation and the dynamic response of an adsorption column [14,17]. The shape of the concentration-time profile of BTC is the important characteristic for adsorption dynamic response and process design of an adsorption column [14]. A breakthrough plot is usually expressed in terms of adsorbed pollutant concentration, C_{ad} where C_{ad} = inlet pollutant concentration (C_0) —outlet pollutant concentration. (C_t) or normalized concentration is defined as the ratio of effluent dye concentration (C_t) to the inlet dye concentration (C_0) i.e. (C_t/C_0) as a function of time, t or volume of effluent for a given bed height [21]. A typical BTC is shown in Fig. 3.

Time equivalent to total or stoichiometric capacity is:

$$t_t = \int_{t=0}^{t=\infty} \left(1 - \frac{c_t}{c_0}\right) dt = A_1 + A_2 \quad (2)$$

Time equivalent to usable capacity is:

$$t_u = \int_{t=0}^{t_b} \left(1 - \frac{c_t}{c_0}\right) dt = A_1 \quad (3)$$

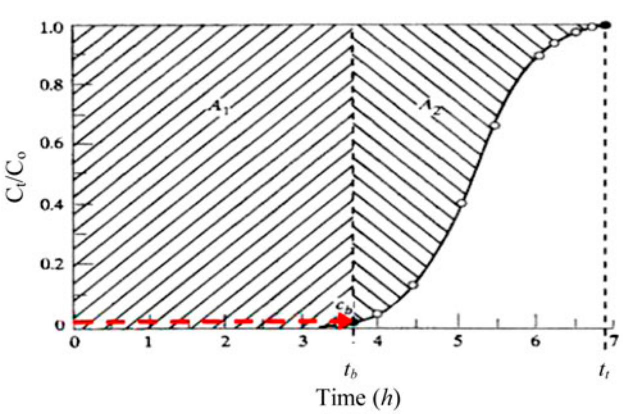


Fig. 3. Typical BTC.

Usable capacity of bed up to the breakthrough point time, t_b and A_2 area calculation gives unused bed height.

$t_u \approx t_b$

Area under the curve $\int_{t=0}^{t=\infty}(1 - \frac{c_t}{c_0})dt$, gives t_t value (total time), whereas area under curve $\int_{t=0}^{t_b}(1 - \frac{c_t}{c_0})dt$. gives, t_u value t_u/t_t is the fraction of the total bed capacity or length utilized up to break point. Area under the curve can be determined either graphically or by numerical integration.

The unused bed length (HUNB) or Mass Transfer Zone (MTZ) can be calculated as:

$$H_{UNB} = (1 - t_u/t_t)H_T = (1 - t_b/t_t)H_T \quad (4)$$

where H_T = total bed height

$$\text{MTZ} = H_{UNB} \quad (5)$$

The used bed length H_B (up to the break point) can be calculated as:

$$H_B = (t_b/t_t)H_T \quad (6)$$

whenever BTC is expressed, the following parameter calculations are applicable.

The total effluent volume (V_{eff}) can be estimated as follows:

$$V_{eff} = Q\, t_{total} \quad (7)$$

where Q and t_{total} are the volumetric flow rate (mL/min) and the total flow time (min), respectively.

The area under the BTC (A) is obtained by integrating the adsorbed concentration C_t/C_0 (mg/L) vs. t (min). The plot can be used to find the total adsorbed MB quantity (maximum column capacity). The total adsorbed MB quantity (q_{total}) in the column for a given feed concentration and flow rate is determined as per reference [21]:

$$q_{total} = QA/1000 = (QC_0/1000) \int_{t=0}^{t=t_{total}} \left(\frac{c_t}{c_0}\right) dt \quad (8)$$

The total amount of MB dye sent to column (m_{total}) is as follows:

$$m_{\text{total}} = C_0\ Q\ t_{\text{total}}/1000 \tag{9}$$

The total percentage removal of MB dye can also be found from the ratio of total adsorbed quantity (q_{total}) to the total amount sent to column (m_{total}) as:

$$\%\text{Removal} = (q_{\text{total}}/m_{\text{total}}) \times 100 \tag{10}$$

2.4.2. Modelling of fixed-bed column breakthrough

Various kinetic and mass transfer models have been developed to predict the dynamic behaviour of the column. These models have been utilized to determine breakthrough performance and also to calculate the column kinetic parameters and adsorption capacity of the fixed-bed column. These models are as follows:

2.4.2.1. Thomas model. Thomas model is one of the most generally and a widely used kinetic model in the column performance operations. The assumption of this model is that the process follows Langmuir kinetics of adsorption–desorption with no axial dispersion, and the driving force follows 2nd order reversible reaction kinetics. Thomas model also assumes that the constant separation factor is applicable to either favourable or unfavourable isotherm [22].

The adsorption rate constant for a continuous adsorption process in column and the maximum solid phase concentration of the solute on the sorbent was developed by the expression of Thomas equation which is as follows [22]:

$$\frac{C}{C_0} = \frac{1}{1 + \exp\left[K_{\text{T}}\left(\frac{q_0 m - C_0\ V}{Q}\right)\right]} \tag{11}$$

where K_{T} is the Thomas rate constant (mL/mg min), q_0 is the equilibrium adsorbate uptake (mg/g), m is the amount of adsorbent in the column (g), C_0 is inlet or initial concentration (mg/L), C effluent MB concentration (mg/L), Q is the flow rate (ml/min) and V is effluent volume (ml). The linearized form of Eq. (11) is given as:

$$\ln\left(\frac{C_0}{C} - 1\right) = \left(\frac{K_{\text{T}}\ q_0 m}{Q}\right) - \left(\frac{K_{\text{T}}\ C_0\ V}{Q}\right) \tag{12}$$

The kinetic coefficient K_{T} and the adsorption capacity of the bed q_0 can be determined from the plot of ln $[(Co/C)^{-1}]$ vs. t at a given flow rate.

2.4.2.2. Yoon–Nelson model. The Yoon and Nelson model [23] is judged the less complicated column model as it requires no detailed data concerning the characteristics of adsorbate, the type of adsorbent and the physical properties of adsorption bed. The assumption of this model is based on the rate of decrease in the probability of adsorption for each adsorbate molecule, is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. For a single component system, the Yoon and Nelson equation is expressed as [23]:

$$\frac{C}{C_0} = \frac{1}{1 + \exp[K_{\text{YN}}(\tau - t)]} \tag{13}$$

where K_{YN} is the Yoon and Nelson rate constant (min^{-1}), Co is the inlet or initial concentration (mg/L), C is the effluent MB concentration (mg/L), t is the breakthrough (sampling) time (min) and τ is the time required for 50% adsorbate breakthrough (min). The linearized form of Eq. (13) is given as:

$$\ln\left(\frac{C}{C_0 - C}\right) = K_{\text{YN}}\ t - K_{\text{YN}}\ \tau \tag{14}$$

The plot of ln $[C/(C_0 - C)]$ vs. sampling time (t) according to Eq. (14) will result in a straight line with slope of K_{YN} and intercept $K_{\text{YN}}\ \tau$.

2.4.2.3. BDST model. BDST approach is based on Bohart and Adams equation and it is a widely used model [24]. It gives an idea of the efficiency of the column under constant operating conditions for achieving a desired breakthrough level [15]. Service time is the time period for adsorbent that will be able to adsorb a specific amount of pollutant from solution before regeneration is needed. BDST model gives relationship between bed height (H_{T}) and service time (t) in terms of process concentrations and other adsorption parameters. A linear relationship between bed height (H_{T}) and service time (t) is given by [15]:

$$t = \left(\frac{N_0 H_{\text{T}}}{C_0 U}\right) - \left(\frac{1}{K_0 C_0}\right) \ln\left(\frac{C_0}{C_{\text{t}}} - 1\right) \tag{15}$$

where C_{t} = effluent concentration of solute in the liquid phase (mg/L), C_0 = inlet solute concentration (mg/L), U = influent linear velocity (cm/min), N_0 = adsorption capacity (mg/L), K_0 = rate constant in BDST model (L/mg min), t = time (min) and H_{T} = bed height of column (cm).

A plot of t vs. bed height H_T should yield a straight line where N_0 and K_0 can be determined. A simplified form of the BDST model is as follows:

$$t = az - b \tag{16}$$

where a = slope N_0/C_0U and b = intercept $(1/K_0C_0)$ ln $[(C_0/C_t)^{-1})]$.

3. Results and discussion

3.1. Physical characterization of adsorbate biomass

The characterization of the surface chemistry and structure of pine cone is of considerable interest for the development of adsorption and separation processes. The ability of adsorption of pine cone depends upon porosity as well as chemical reactivity of functional groups on the surface. One important characteristic of pine cone is the presence of surface functional groups which are largely characterized by the FTIR spectroscopy method. The FTIR spectrum of pine cone is shown in Fig. 4. Numerous peaks were observed from the spectra (Fig. 4) indicating that pine cone is composed of various functional groups which are responsible for binding of cationic dye MB. The peak at 3,335.89 cm^{-1} represents O–H stretching vibrations, spectra band observed at 2,929.34 cm^{-1} indicates vibration of CH_n particularly due to C–CH_2 and C–CH bonds. The peak at 1,606.49 cm^{-1} indicates to C=O and vibration of C=C. The peak at 1,263.48 cm^{-1} corresponds to C–N stretching with amine or C–O vibration of carboxylic acid [25]. The peaks at 1,027.32 cm^{-1} are possibly assigned to the –C–C– stretching. Similar types of FTIR spectra of pine cone have been reported by few other investigators [25,26].

Scanning electron micrograph (SEM) of pine cone biomass before and after adsorption is shown in Figs. 5 and 6, respectively. The availability of pores and internal surface are evidently presented in the SEM pictures of the pine cone biomass before and after adsorption. The pores covered by the adsorbed MB

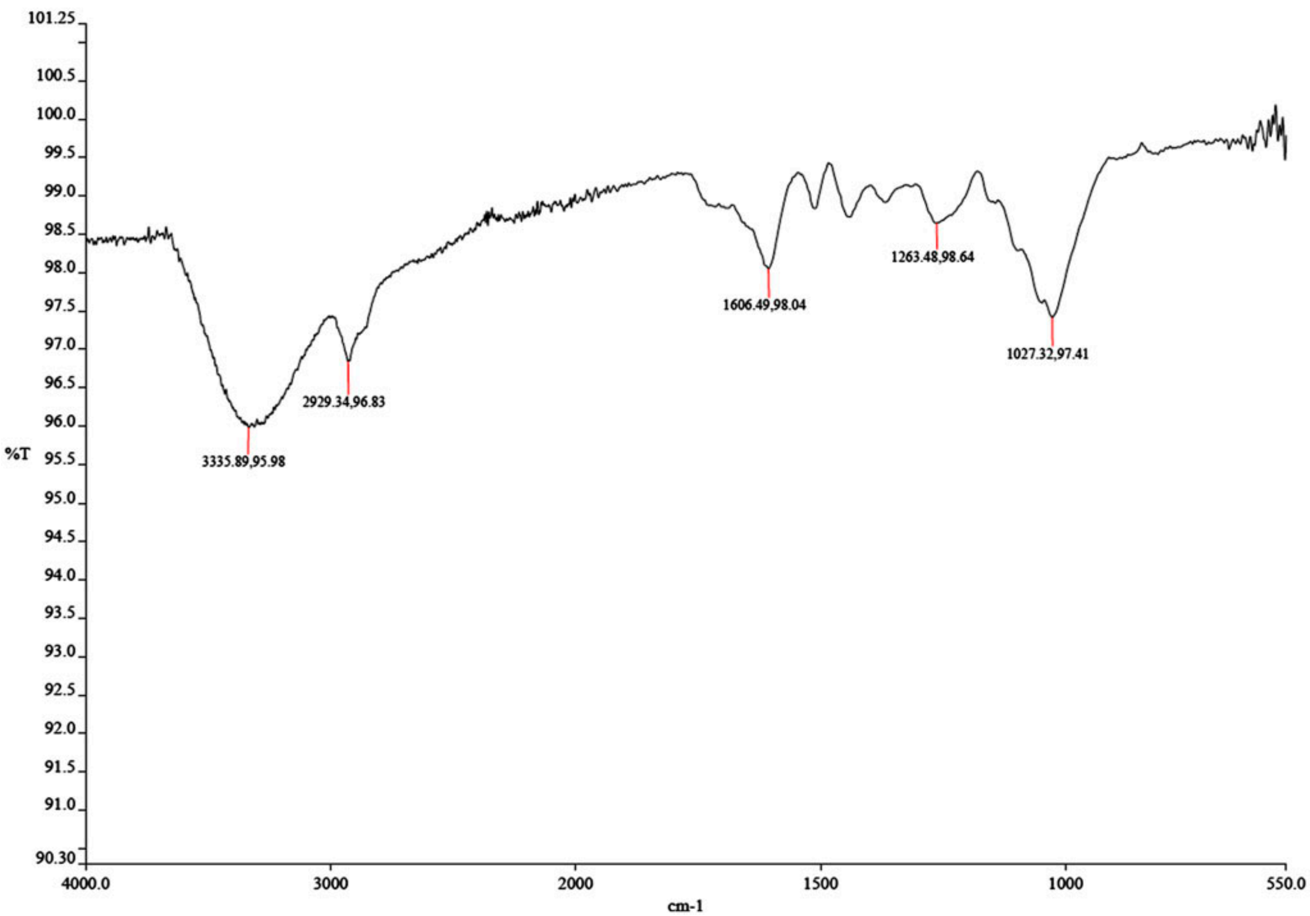


Fig. 4. FTIR spectra of pine cone biomass.

are also shown in Fig. 6. Essentially, the porous structure that is shown in Fig. 5 gets unclear in Fig. 6 because of adsorption.

3.2. Effect of initial flow rate on MB dye adsorption BTC

Flow rate is an important parameter for evaluating the efficiency of adsorbents in a continuous industrial scale packed-bed operation. The effect of the flow rate on the adsorption of MB dye using the raw pine cone was investigated by varying the flow rate (10, 12 and 15 ml/min) while the bed height and initial MB dye concentration was held constant at 12 cm and at 70 mg/L, respectively. The BTC of normalized dye concentration (C_t/C_0) vs. time (min) at different flow rates are shown in Fig. 7. From the BTCS, it was found that the breakthrough occurred faster with higher flow rate i.e. MB^{2+} eluted more rapidly as the velocity is increased. The breakthrough time decreased from 115 to 39 min for the flow rates ranging between 10 and 15 ml/min, respectively (Table 1). The various BTC parameters are also presented in Table 1. This may be due to the increase in speed of adsorption zone at increased flow rate which resulted in a decrease in the time required to reach the specific breakthrough concentration. Further from Table 1, it was observed that the adsorption capacity, q_{total} and dye removal percentage of column decreases with increase in flow rate. Similar type of observations was reported by various researchers for different systems [15,18,27]. As the velocity increases, the rate of mass transfer increases and thereby enhancing the rate of adsorption. As a result early breakthrough occurs at higher flow rates [20]. Further, retention time of dye molecules in the column depends on flow rate and decreases contact time between adsorbent and dye with increasing flow rate. Hence, MB dye molecules do not have sufficient time to penetrate and diffuse deeply into the pores of adsorbents. Therefore, lower adsorption capacity (q_{total}) was obtained at higher flow rate and equilibrium does not take place. This was further supported by unused (HUNB) or used beds (HB) which are presented in Table 1. At a lower flow rate, contact time between MB and pine cone was higher resulting in higher removal of MB in column (Table 1). This was also supported by MTZ (Table 1) or unused bed which increased with increasing flow rate. Overall, Table 1 indicates that the packed-bed column gives better performance in the removal of

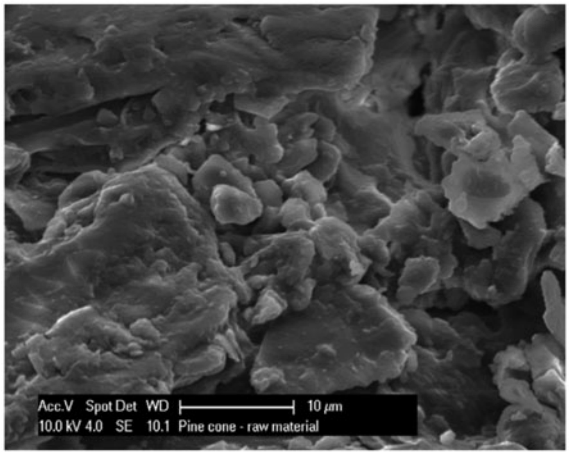


Fig. 5. SEM of pine cone biomass before adsorption.

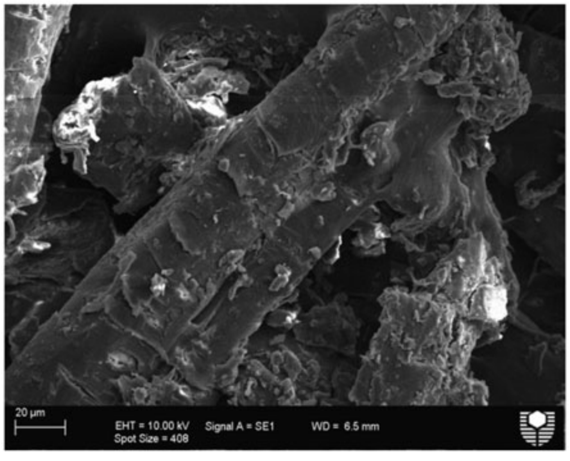


Fig. 6. SEM of pine cone biomass after adsorption.

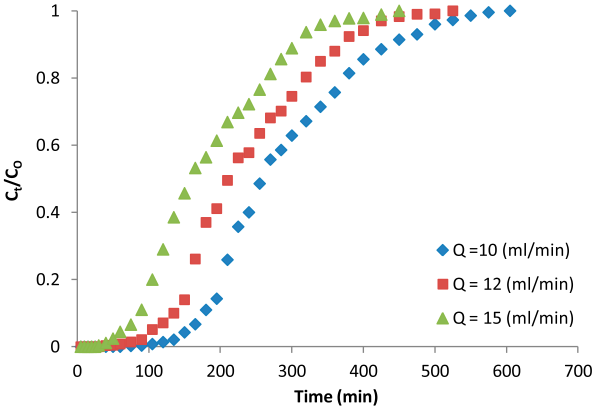


Fig. 7. Comparison of experimental BTCs of MB dye adsorption on raw pine cone at different flow rates. (Inlet MB dye concentration = 70 mg/L, bed height = 12 cm and temperature = 25 ± 1 ℃).

Table 1
Parameters obtained from BTCS of packed-bed column for MB removal by pine cone at different flow rates

Q (ml/min)	t_b (min)	V_{eff} (mL)	t_{total} (min)	m_{total} (mg)	q_{total} (mg)	% Removal	MTZ or HUNB (cm)	HB (cm)
10	115	2811.8	281.1	423.5	196.8	46.5	7.1	4.9
12	65	2650.8	220.9	441	185.5	42.1	8.5	3.5
15	39	2551.5	170.1	467.2	176.5	38.2	9.25	2.7

MB at lower solution flow rate, which is not favourable for large effluent treatment systems.

3.3. Effect of initial MB dye concentration on BTC

The effect of initial MB dye concentration on the BTCS at bed height of 12 cm and flow rate of 12 ml/min are shown in Fig. 8. The curves have relatively the same shape for all initial MB dye concentration and resulting in more shortened MTZ. As expected, a decreased initial dye concentration gave a slower BTC since the lower concentration gradient led to a slower transport due to lower diffusion coefficient or mass transfer. BTCS parameters of packed-bed column for the removal of MB by pine cone at different MB solution concentrations are presented in Table 2. Table 2 shows that the amount of total sorbed dye, equilibrium dye uptake, MTZ and total percentage removal increased with increasing initial MB dye concentration.

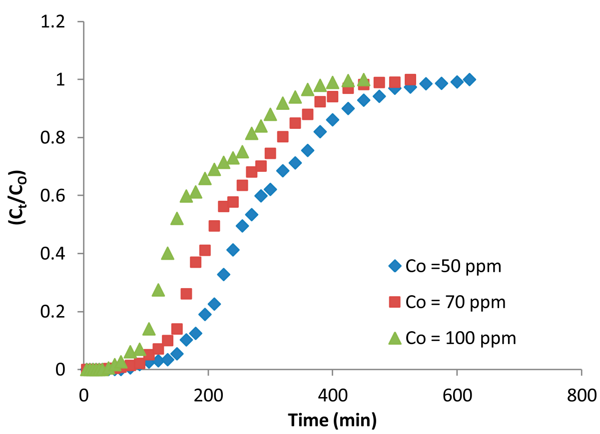


Fig. 8. Comparison of experimental BTCs of MB dye adsorption on raw pine cone at different initial MB dye concentration. (MB dye flow rate = 12 ml/min, bed height = 12 cm and temperature = 25 ± 1 °C).

The increase in total amount of adsorbed MB (q_{total}) and hence percentage removal of MB (Table 2) was obtained with increasing MB dye concentration. This is because of increasing mass transfer concentration driving force and dye loading rate. These results are in agreement with many investigations for different system [28–30]. In many cases the diffusion process is concentration dependent [18]. On the other hand, decreasing the MB dye concentration increased the treated volume (V_{eff}) that can be processed and shifted the BTC to the right. The larger influent MB dye concentration, the steeper is the scope of BTC and smaller is the breakthrough time, t_b (Table 2) i.e. the diffusion process is concentration dependent. A decreased initial MB dye concentration gave an extended BTC, since the lower concentration gradient caused a slower transport due to reduced diffusion coefficient and reduced mass transfer coefficient. Available adsorbent sites are quickly filled at high initial dye concentration resulting in reduced breakthrough time. From Table 2, it was observed that the highest uptake and highest percentage removal of MB (47.6%) were obtained for the high dye concentration. However, percentage removal obtained from column study was lower than that obtained from batch study for the same initial dye concentration [12]. This may be due to insufficient contact time. Thus high dye

Table 2
Parameters obtained from BTCS of packed-bed column for MB removal by pine cone at different initial MB concentrations

C_0 (mg/L)	t_b (min)	V_{eff} (mL)	t_{total} (min)	m_{total} (mg)	q_{total} (mg)	% Removal	MTZ or HUNB (cm)	HB (cm)
50	85	3001.2	250.1	372	150.1	40.3	7.92	4.08
70	64	2650.8	220.9	441	185.5	42.1	8.5	3.5
100	46	2.286	190.5	480	228.6	47.6	9.16	2.84

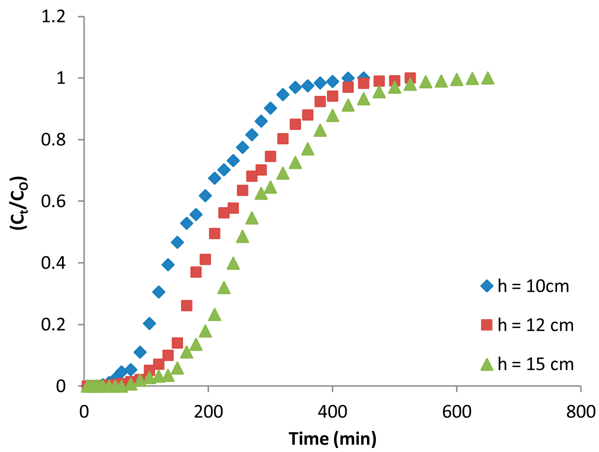


Fig. 9. Comparison of experimental BTCs of MB dye adsorption on raw pine cone at different bed height. (Inlet MB dye concentration = 70 mg/L, MB dye flow rate = 12 ml/min and temperature = 25 ± 1˚C).

loading rate and high concentration driving force resulted in a better column performance. Similar trends were obtained for adsorption of reactive black 5 dye by granular activated carbon [31], removal of MB dye using cedar sawdust and crushed brick [32].

3.4. Effect of bed height on BTC

Fig. 9 shows the BTCs obtained from MB adsorption on the pine cone for different bed heights of 10, 12 and 15 cm, with a constant flow rate of 12 ml/min and initial MB dye concentration of 70 mg/L, respectively.

BTCs parameters for MB column study were tabulated in Table 3. The results revealed that by increasing the bed height, the breakthrough time also shifted to increase. By increasing bed height from 10 cm to 15 cm, the percentage dye removal also increased from 38.9 to 46.1% (Table 3). This is also supported by used bed (HB). Detected breakthrough time (t_b) with increase in bed height is an expected result. As the bed height is increased, the adsorbent pine cone load also increased and hence total adsorption capacity of the bed increased. With the higher adsorbent loading, the contact time increased and in turn increases the "sweep efficiency" [20]. As a result, more adsorbent surface are exposed to flow and hence an increase in the removal of dye adsorption, q_{total} (Table 3). Further, it was supported by increased used bed (HB) from 2.19 to 4.47 cm (Table 3). Further, higher breakthrough time gives better intra-particle diffusion phenomena and higher will be the adsorption capacity of column [15]. Moreover, more volume of effluent (V_{eff}) can be treated with high MB removal efficiency by increasing bed height which is advantageous for adsorption column operation. Similar observation was reported by various researchers [29,33].

3.5. Kinetic modelling of fixed-bed column operation

3.5.1. Application of Thomas model

The BTC column experimental data were fitted to the Thomas model to determine the Thomas rate constant (K_{Th}) and maximum solid-phase concentration (q_0). The determined coefficients and relative constants were obtained using linear regression analysis according to Eq. (12).

The predicted curves of a linear plot of ln $(C_0/C_t)^{-1}$ against time (t), at various experimental conditions (different flow rate, different initial MB concentration and different bed height), according to the Thomas model are shown in Figs. 10–12 to determine values of K_{Th} and q_0 from the intercepts and slopes of the plot. The results of K_{Th}, q_0 and R^2 are given in Table 4. From the results in Table 4, it can be seen that the linear regression coefficient (R^2) value is high and hence the Thomas model fitted well with the experimental data. As shown in Table 4, with the initial MB dye concentration increased, the value of maximum solid-phase concentration (q_0) increased, but the value of Thomas rate constant (K_{Th}) decreased. This is because the driving force is the concentration difference between the dye in the solution and the dye on the biosorbent [34,35]. Thus, high driving force due to the higher MB concentration resulted in better column

Table 3
Parameters obtained from BTCs of packed-bed column for MB removal by pine cone at different bed height

h (cm)	t_b (min)	V_{eff} (mL)	t_{total} (min)	m_{total} (mg)	q_{total} (mg)	% Removal	MTZ or HUNB (cm)	HB (cm)
10	38	2088	174	378	147	38.9	7.81	2.19
12	65	2650.8	220.9	441	185.5	42.1	8.5	3.5
15	85	3427.2	285.6	520.8	239.9	46.1	10.53	4.47

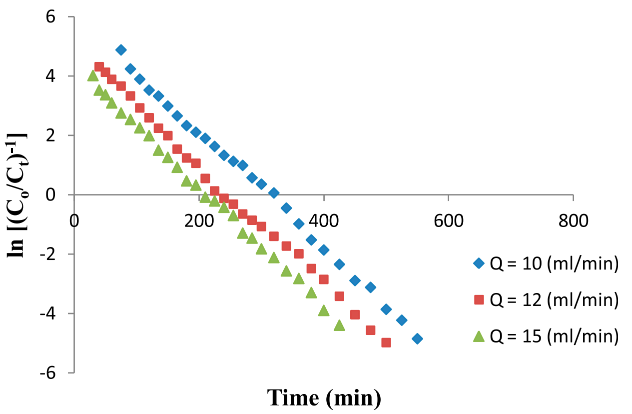


Fig. 10. Thomas kinetic plot for the adsorption of MB on pine cone: effect of flow rate (inlet MB dye concentration = 70 mg/L, bed height = 12 cm and temperature = 25 ± 1℃).

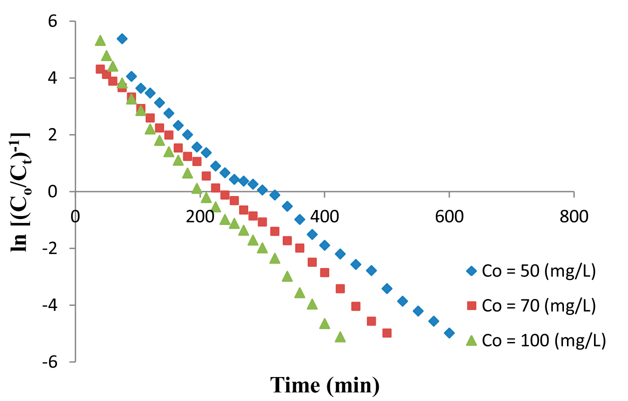


Fig. 11. Thomas kinetic plot for the adsorption of MB on pine cone: effect of initial dye concentration (MB dye flow rate = 12 ml/min, bed height = 12 cm and temperature = 25 ± 1℃).

performance. As flow rate increased, the value of Thomas rate constant (K_{Th}) increased but the value of maximum solid-phase concentration (q_0) decreased. With the bed depth increased, the value of maximum solid-phase concentration (q_0) increased, whereas the value of Thomas rate constant (K_{Th}) decreased. So

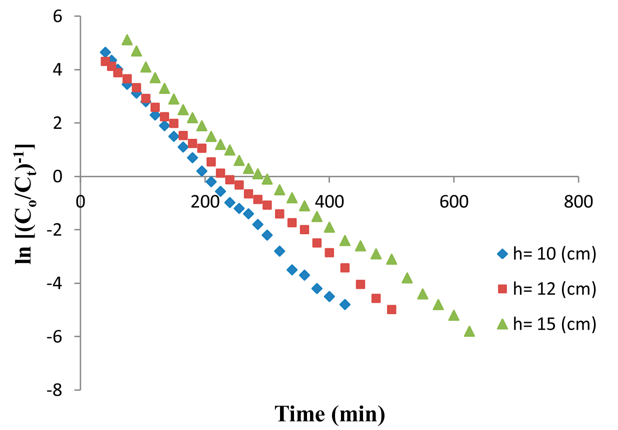


Fig. 12. Thomas kinetic plot for the adsorption of MB on pine cone: effect of bed height (inlet MB dye concentration = 70 mg/L, MB dye flow rate = 12 ml/min and temperature = 25 ± 1℃).

with higher initial MB dye concentration, lower flow rate and higher bed depth would increase the adsorption of MB onto pine cone powder column. Similar type of Thomas constants for different systems was reported by Han et al. [35] and Aksu and Gönen [34].

3.5.2. Application of Yoon–Nelson model

A simple theoretical model developed by Yoon–Nelson was used to study the breakthrough behaviour of MB dye on pine cone powder. The values of K_{YN} (a rate constant) and τ (the time required for 50% MB breakthrough) were obtained from ln $[C_t/(C_0 - C_t)]$ vs. t plots at different flow rates (10, 12 and 15 ml min^{-1}) and at different initial dye MB concentrations (50, 70 and 100 mg/L) and also at different bed heights varied between 10 and 15 cm according to Eq. (6). This plot will result in a straight line with slope of K_{YN} and intercept of τK_{YN} which are given in Figs. 13–15. The values of K_{YN} and τ are listed in Table 5.

Table 5 shows that the rate constant K_{YN} increased with both increasing initial MB dye concentration and flow rate, whereas the 50% breakthrough time τ

Table 4
Thomas kinetic model parameters at different experimental condition by non-linear regression analysis

	Flow rate (ml/min)			Initial MB dye concentration (mg/L)			Bed height (cm)		
Thomas parameters	10	12	15	50	70	100	10	12	15
K_{Th} (ml/min mg)	0.28	0.286	0.293	0.354	0.286	0.258	0.36	0.286	0.265
q_0 (mg/g)	55.35	44.39	38.23	38.95	44.39	55.68	48.75	44.39	42.49
R^2	0.997	0.997	0.998	0.985	0.997	0.989	0.995	0.997	0.99

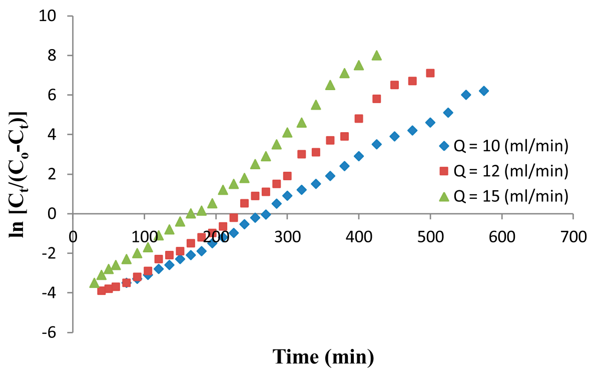


Fig. 13. Yoon–Nelson kinetic plot for the adsorption of MB on pine cone: effect of flow rate (inlet MB dye concentration = 70 mg/L, bed height = 12 cm and temperature = 25 ± 1℃).

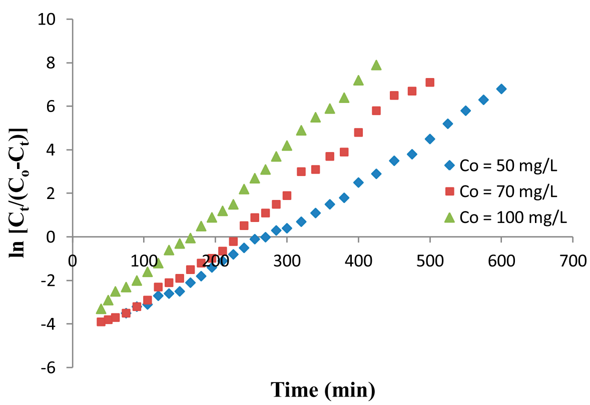


Fig. 14. Yoon–Nelson kinetic plot for the adsorption of MB on pine cone: effect of initial dye concentration (MB dye flow rate = 12 ml/min, bed height = 12 cm and temperature = 25 ± 1℃).

decreased with both flow rate and initial MB concentration. With the bed mass increasing, the values of τ increased while the values of K_{YN} decreased. This is due to the fact that increase in initial ion concentration increases the competition between adsorbate

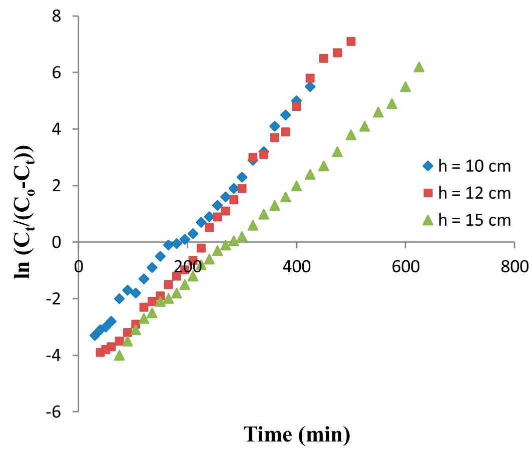


Fig. 15. Yoon–Nelson kinetic plot for the adsorption of MB on pine cone: effect of bed height (inlet MB dye concentration = 70 mg/L, MB dye flow rate = 12 ml/min and temperature = 25 ± 1℃).

molecules for the adsorption site, which ultimately results in increased uptake rate [29,32].

It was found that, the time required to achieve 50% of adsorbate breakthrough τ from the Yoon–Nelson model seemed to agree well with the experimental data ($\tau_{50\%\ exp.}$) in the entire column adsorption system, thus indicating Yoon and Nelson model fitted well to the experimental data. This was further supported by high value of linear regression coefficient R^2 (Table 5).

3.5.3. Application of BDST model

The BTC data obtained from the experimental column studies between MB dye and pine cone also fitted well to the BDST model (Table 6 where $R^2 > 0.99$). The parameters of K_0 and N_0 as calculated from the plots between ln $((C_0/C_t)^{-1})$ vs. t at different experimental conditions (different flow rate, different initial MB dye concentration and different bed heights) are listed in Table 6.

Table 5
Yoon–Nelson kinetic model parameters at different experimental condition by non-linear regression analysis

	Flow rate (ml/min)			Initial MB dye concentration (mg/L)			Bed height (cm)		
Yoon–Nelson parameters	10	12	15	50	70	100	10	12	15
K_{YN} (min^{-1})	0.020	0.025	0.029	0.019	0.025	0.29	0.029	0.025	0.017
τ (min)	263.2	217	159.4	269.1	217	158.	183.0	217	282.6
$\tau_{50\%\ exp.}$(min)	260	212	158	255	212	150	165	212	265
R^2	0.997	0.997	0.998	0.99	0.997	0.99	0.99	0.997	0.99

Table 6
BDST model parameters at different experimental condition

	Flow rate (ml/min)			Initial MB dye concentration (mg/L)			Bed height (cm)		
BDST parameters	10	12	15	50	70	100	10	12	15
K_0 (L/mg min)	0.281	0.285	0.292	0.353	0.285	0.257	0.362	0.285	0.264
N_0 (mg/L)	1555.9	1615.2	1673.8	1362.9	1615.2	1941.4	1551.2	1615.2	1699.6
R^2	0.997	0.997	0.996	0.997	0.995	0.998	0.996	0.994	0.995

As the initial MB dye concentration increased, the value of the volumetric sorption capacity of the bed (N_0) increased but the value of the rate constant (K_0) decreased. As the bed height increases, the rate constant (K_0) decreases while the volumetric sorption capacity of the bed (N_0) increases. This is because, the residence time of the fluid inside the column increases, allowing the MB dye molecules to diffuse deeper inside the pine cone [35]. Thus, the bed capacity changes with bed height. Furthermore, as seen in Table 6, K_0 did not change much with change in flow rate. These results indicate that the BDST model can be used to predict the adsorption performance at other operation conditions for adsorption of MB dye onto pine cone biomass.

4. Conclusion

Pine cone biomass was found to be an efficient media for the continuous removal of MB from aqueous phase by adsorption in a fixed-bed column. The effect of various operation parameters such as flow rate, initial MB dye concentration and height of packed-bed on the adsorption column has been reported. As the flow rate decreased the breakthrough time increased. This is because MB dye had more contact time with pine cone resulting in higher percentage removal of MB at lower flow rate. MB removal by pine cone increased with increasing initial MB dye concentration and the highest percentage removal of MB dye was obtained with the highest initial dye concentration. With the increase in the height of packed-bed, the breakthrough time increased, and the total percentage removal of MB dye was also increased. This is because of more exposed surface of adsorbent to MB flow. The application of Thomas model showed that the value of maximum solid-phase concentration (q_0) decreased when the flow rate and the height of the bed increased but increased with increasing initial MB dye concentration. The value of Thomas rate constant (K_{Th}) increased with increase in flow rate but decreased with increasing initial MB dye concentration and the height of the bed. The results from Yoon–Nelson model showed that the time required to achieve 50% adsorbate breakthrough τ seemed to agree well with the experimental data ($\tau_{50\%\ exp.}$) and also the results showed that the rate constant K_{YN} increased with both increasing flow rate and initial MB dye concentration but decreased with increasing the bed height. From BDST model, the value of the rate constant (K_0) decreased when both the bed heights and the initial MB dye concentration increased, but increased with the flow rate changes. However, the value of the volumetric sorption capacity of the bed (N_0) increased with increasing flow rate, initial MB dye concentration and bed heights. All three kinetic models are applicable to BTC obtained under various process conditions.

Symbols

A	—	cross-sectional area of bed in column, cm^2
A_1	—	used bed area, cm^2
A_2	—	unused bed area, cm^2
A	—	slope (N_0/C_0U)
b	—	intercept ($1/K_0C_0$) ln [$(C_0/C_t)^{-1}$)]
C	—	effluent MB concentration, mg/L
C_t	—	outlet pollutant concentration, mg/L
C_0	—	inlet pollutant concentration, mg/L
H	—	height of bed in column, cm
H_B	—	used bed length up to break point, cm
H_T	—	bed height of column, cm
H_{UNB}	—	unused bed length, cm
K_0	—	rate constant in BDST model, L/mg min
K_T	—	Thomas rate constant, mL/mg min
K_{YN}	—	Yoon–Nelson rate constant, min^{-1}
MTZ	—	mass transfer zone, cm
m	—	amount of adsorbent in the column, g
m_p	—	mass of pine cone, g
m_{total}	—	total amount of methylene blue dye sent to column, g
N_0	—	adsorption capacity, mg/L
Q	—	volumetric flow rate, mL/min
q_{total}	—	total adsorbed methylene blue dye quantity, g
q_0	—	equilibrium adsorbate uptake, mg/g
t	—	breakthrough (sampling) time, min
t_t	—	total time, min
t_{total}	—	total flow time, min

t_b — usable capacity of bed up to the breakthrough point time, min
t_u — time equivalent to usable capacity, min
U — influent linear velocity, cm/min
V — effluent volume, ml
V_{eff} — total effluent volume, mL
τ — time required for 50% adsorbate breakthrough, min
ρ_p — bulk density of pine cone, g/cm^3
ε — porosity

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