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ENVIRONMENTAL CHEMISTRY, POLLUTION & WASTE MANAGEMENT | RESEARCH ARTICLE

Adsorptive capacity of sawdust for the adsorption of MB dye and designing of two-stage batch adsorber

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Abstract: The use of low-cost locally available adsorbent, sawdust for the removal of methylene blue (MB) dye in a batch adsorber system has been investigated. The experimental data fitted best in Langmuir isotherm as compared to Freundlich and Temkin isotherms, showing maximum adsorption capacity of 76.92 mg/g. The study revealed that the adsorption of MB dye onto sawdust follows pseudo-second-order kinetic model and the same has been used in design of a two-stage batch adsorber by minimizing total contact time to attain a fixed percentage of MB dye removal. The minimum contact time required for the removal of MB dye with 99% efficiency has been found as 37.54 min.

Subjects: Adsorption Science; Environmental Chemistry; Environmental Issues; Environmental Sciences; Pollution; Pollution Management

Keywords: sawdust; adsorption isotherm; adsorption kinetics; two-stage batch adsorber system

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S.P. Shukla, professor, Civil Engineering department, Institute of Engineering and Technology Lucknow has been known as an academician with good academic record. He has completed his PhD from Indian Institute of Technology Kanpur in 2007 and M.E. from IIT Roorkee in 1989. He has guided 21 M.Tech. theses in the field of Environmental Engineering and is guiding 7 PhD scholars on state-of-art topics. He has published 71 research papers including 23 in peer-reviewed International journals and National journals of repute having total Thomson Reuters ISI Impact factor based on JCR more than 14 (Citations: 74; h-index: 4; i10-index: 4 as per Google Scholar). He has also presented 44 research papers in National and International seminar/ workshop/ conferences. He has also co-authored 2 edited book chapters and 1 book titled "Foundation of Environmental Studies" which is a publication of the Uttar Pradesh Technical University, Lucknow.

PUBLIC INTEREST STATEMENT

About 10–20% of dyes in the textile sector are lost in residual liquors through incomplete exhaustion and washing operations, which inhibit sunlight penetration into the stream. Discharge of dye-bearing effluents into natural streams and rivers not only imparts toxicity to aquatic life, but also adversely affects the self-purification system and esthetics of the surroundings. Basic dyes can also cause allergic dermatitis, mutations, and skin diseases like cancer and psoriasis. This study focuses on searching low-cost adsorbent (sawdust) for dye removal from effluent and designing a two-stage batch adsorber model for the adsorption of methylene blue (MB) dye.

1. Introduction

The textile dyeing industry consumes large quantity of water and produces huge volume of colored wastewater from different steps in the dyeing and finishing processes (Hameed, 2009). The colored wastewater damages the esthetic nature of water, reduces the light penetration (Kisku, Tiwari, Shukla, Singh, & Murthy, 2015) and photosynthesis activity of aquatic organisms due to the presence of metals, chlorides, nitrate etc., in it (Farzana & Meenakshi, 2014). Basic dyes can also cause allergic dermatitis, mutations, and skin diseases like cancer and psoriasis. Therefore, it is necessary to remove dye from colored wastewater (El-Latif, Ibrahim, & El-Kady, 2010; Khan, Khan, Asiri, Azuma, & Rub, 2014; Kisku et al., 2015; Tiwari, Shukla, Bhargava, & Kisku, 2013). Pengthamkeerati, Satapanajaru, and Singchan (2008) and Vijayaraghavan and Yun (2008) suggested that the conventional methods for removing dye from wastewater such as coagulation/flocculation, chemical oxidation, and activated sludge process; are very difficult and ineffective.

Many of the small scale industries in India and developing countries are still discharging colored wastewater into surface water bodies due to high cost of color removal, although several studies have demonstrated adsorption process using various adsorbents for removal of dyes. Adsorption on activated carbon is the most widespread technology used in removal of dyes (Gurses, Hassani, Kiransan, Acisli, & Karaca, 2014), phenols (Kumar, Kumar, Kumar, & Gupta, 2007), pesticides (Daneshvar, Aber, Khani, & Khataee, 2007) and other hazardous chemicals (Dwivedi, Sahu, Mohanty, Mohan, & Meikap, 2008; Tsai, Chiang, Huang, & Chiang, 2008) from wastewater. The present study was performed to demonstrate the use of locally available low-cost adsorbent (sawdust) for removal of the dye from colored wastewater coming out from textile dyeing industry. Many researchers worked on low-cost adsorbents such as modified cenospheres (Tiwari, Shukla, Mohan, Bhargava, & Kisku, 2015), papaya seeds (Hameed, 2009), hydrolyzed wheat straw (Batzias, Sidiras, Schroeder, & Weber, 2009), bentonite (Bulut, Ozacar, & Sengil, 2008), rice husk (Han et al., 2008), untreated lignite (Gurses et al., 2014), activated sawdust (Banerjee, Chattopadhyaya, Srivastava, & Sharma, 2013; Kini, Saidutta, Murty, & Kadoli, 2013), pristine, acid-activated bentonite composite beads (Oladipo & Gazi, 2014), and multiwall carbon nanotubes (Shirmardi, Mesdaghinia, Mahvi, Nasseri, & Nabizadeh, 2012). Simultaneously, we have also given design of two-stage batch adsorber system for removing fixed percentage of the dye from colored wastewater by minimizing contact time for ready use by small scale industries. Li, Yue, Su, and Gao (2011) studied adsorption equilibrium and two-stage batch adsorber design for the removal of reactive and disperse dye to minimize adsorbent dose. The methylene blue (MB) dye was taken in this study because of its known strong adsorption nature onto solids (Hameed, 2009).

2. Materials and methods

2.1. Adsorbate

MB dye used in the present investigation was procured from Himachal Futuristic Communications Limited, New Delhi. The chemical formula of MB dye is $C_{16}H_{18}ClN_3S.2H_2O$ having molecular weight 319 and structure as shown in Figure 1.

2.2. Adsorbent

The sawdust used in the present study was collected from 10 randomly selected local saw mills and it was mixed sawdust, i.e. not from a single wood type. After homogenous mixing, sawdust was continuously boiled with distilled water till a clear (without any color) solution appears. Thereafter it was dried at the temperature 60°C for 48 h (Hameed, 2009). The dried sample was grounded and sieved with sieve set containing 300 and 500 μ sieve. The treated mixed sawdust passing through 500 μ sieve and retained on 300 μ sieve was used in the present study by storing it in plastic bottles.

2.3. Adsorption isotherms and kinetic models

Adsorption experiments were carried out by adding a fixed amount of adsorbent (2 g sawdust) in 1 L flasks containing a definite volume (500 mL) of MB dye having different initial concentrations (50, 100, 150, 200, 250, 300 mg/L) at room temperature. The flasks were kept in Jar test apparatus (Model: JLT6; VELP Scientifica) and agitated at 150 rpm for 200 min to ensure equilibrium condition. Dye

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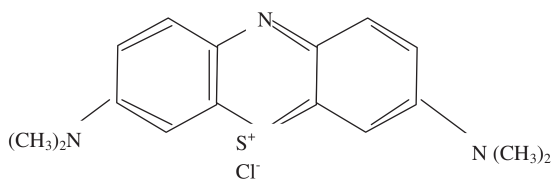


Figure 1. Chemical structure of MB dye.

concentrations were measured using a double-beam UV–vis spectrophotometer (Model: SP 3000 Plus; OPTIMA) at 675-nm wavelength. The amount of the adsorption at time t, q_t (mg/g), was calculated by equation:

$$q_t = \frac{(C_0 - C_t) \times V}{W} \tag{1}$$

where C_0 is the liquid-phase initial concentration of the dye in mg/L, C_t is the liquid-phase remaining concentration of the dye in mg/L at time t, V is the volume of the solution in L, and W is the mass of dry adsorbent in g.

The amount of the adsorption at equilibrium, q_e (mg/g), was calculated by equation:

$$q_e = \frac{(C_0 - C_e) \times V}{W} \tag{2}$$

where C_e is the remaining liquid-phase concentration of the dye in mg/L at equilibrium.

The dye removal percentage was calculated as per equation:

$$\text{Removal percentage} = \left(\frac{(C_0 - C_e)}{C_0}\right) \times 100 \tag{3}$$

The Langmuir isotherm is nonetheless the first choice for adsorption process and has many applications in surface kinetics and thermodynamics. Langmuir isotherm is expressed as equation:

$$q_e = \frac{\alpha \beta C_e}{(1 + \alpha C_e)} \tag{4}$$

A linear form of this expression can be written as:

$$\frac{1}{q_e} = \frac{1}{\beta} + \left(\frac{1}{\alpha\beta}\right) \times \left(\frac{1}{C_e}\right) \tag{5}$$

where β is the monolayer capacity of the adsorbent (mg/g) and α is the adsorption equilibrium constant (L/mg).

The Freundlich isotherm assumes that the adsorption of the dye molecule occurs layer by layer over the surface of adsorbent. Freundlich isotherm is expressed as:

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

where K_F is the Freundlich constant related to the adsorption capacity of adsorbents (mg/g), and n is the Freundlich constant related to the adsorption intensity of adsorbents.

The Temkin isotherm is represented by:

$$q_e = B_t \ln K_t + B_t \ln C_e \tag{7}$$

where K_t is the equilibrium binding constant (L/mg), and B_t is the variation of adsorption energy (kJ/mol).

The adsorption kinetic study has been performed to find out the possible mechanisms for the adsorption process and to determine the equilibrium time. The kinetic rate equation is one of the widely used adsorption rate equations for the adsorption of solute from a liquid solution. The pseudo-first-order kinetic model may be expressed as (Oladipo & Gazi, 2014; Shaker, 2014; Tiwari et al., 2015):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{8}$$

Integrating Equation 8 and applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, we get:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) \times t \tag{9}$$

where q_e and q_t are the amounts of dye adsorbed at equilibrium (mg/g) and time t, respectively, and k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}).

The pseudo-second-order kinetic model may be expressed as (Gurses et al., 2014; Lucaci & Duta, 2011; Tiwari et al., 2015):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{10}$$

After integration and using the boundary conditions, for $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the integrated form of Equation 10 becomes:

$$\frac{t}{q_t} = \frac{1}{(k_2 \times {q_e}^2)} + \left(\frac{1}{q_e}\right) \times t \tag{11}$$

Where k_2 is the rate constant of pseudo-second-order adsorption (g/mg min).

The intra-particle diffusion rate constant (k_p) at different initial concentrations are determined using equation (Ho & McKay, 2011; Shaker, 2014):

$$q_t = k_p \times t^{\frac{1}{2}} \tag{12}$$

where k_p is the intra-particle diffusion rate constant (mg/(g min$^{1/2}$)).

2.4. Design of two-stage batch adsorber

Two-stage batch adsorber has been designed by placing them in series, i.e. first the wastewater will pass through stage 1 and then through stage 2. Fresh adsorbent is added in both the stages. The total contact time in two-stage batch adsorber has been optimized for 99, 98, and 97% removal of MB dye from colored wastewater.

A schematic diagram for a two-stage batch adsorption system is shown in Figure 2. For designing of two-stage batch adsorption system, "V" L solution was taken and the dye concentration was reduced from C_0 to C_1 mg/L in first stage and C_1 to C_2 mg/L in second stage. Initially at time $t = 0$, the amount of sawdust added was "W" g with a solid-phase MB dye concentration q_0 mg/g on it,

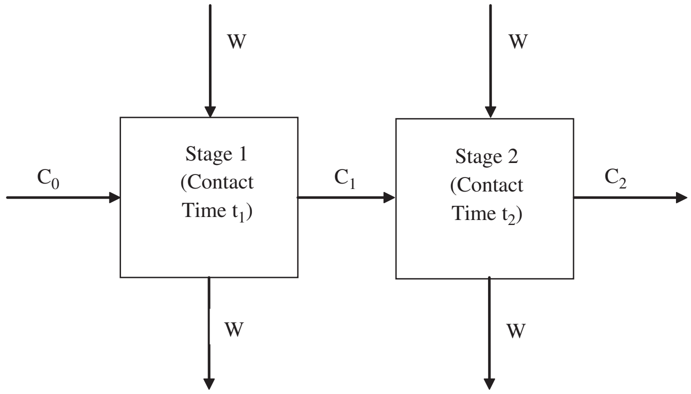


Figure 2. Schematic diagram of the two-stage batch adsorption process.

(usually q_0 = 0 mg MB dye/g sawdust) and finally MB dye concentration on the sawdust increased to q_t mg/g. This can be represented in the form of mass balance equation for *n*th stage as given below:

$$V(C_{n-1} - C_n) = W(q_{t_n} - q_0) \tag{13}$$

As the adsorption process in the present study fits best in pseudo-second-order kinetic model, Equations 11 and 13 have been combined to get mass balance equation as:

$$C_n = C_{n-1} - \frac{W(k_{2_n} q_{e_n}^2 t_n)}{V(1 + k_{2_n} q_{e_n} t_n)} \tag{14}$$

where *n* is stage number (*n* = 1, 2 for two-stage batch adsorber system).

Total MB dye removal for two-stage (*n* = 2) batch adsorber was calculated analytically by:

$$C_2 - C_0 = (C_2 - C_1) - (C_1 - C_0) = \frac{W(k_{2_2} q_{e_2}^2 t_2)}{V(1 + k_{2_2} q_{e_2} t_2)} + \frac{W(k_{2_1} q_{e_1}^2 t_1)}{V(1 + k_{2_1} q_{e_1} t_1)} \tag{15}$$

Percent MB dye removal, R_n, in each of the *n*th stages and total removal of MB dye were evaluated using following equations:

$$R_n = \frac{100(C_{n-1} - C_n)}{C_0} = \frac{100Wk_{2_n} q_{e_n}^2 t_n}{VC_0(1 + k_{2_n} q_{e_n} t_n)} \tag{16}$$

$$R = R_1 + R_2 = \frac{100(C_0 - C_1)(C_1 - C_2)}{C_0} = \frac{100W}{VC_0}\left(\frac{k_{2_1} q_{e_1}^2 t_1}{k_{2_1} q_{e_1} t_1} + \frac{k_{2_2} q_{e_2}^2 t_2}{k_{2_2} q_{e_2} t_2}\right) \tag{17}$$

where k_2 and q_e are expressed as a function of C_0 for MB dye:

$$k_2 = X_k C_0^{Y_k} \tag{18}$$

$$q_e = X_q C_0^{Y_q} \tag{19}$$

X_k, Y_k, X_q, and Y_q can be determined by plotting k_2 and q_e with respect to C_0 (initial dye concentration). For optimizing the total contact time (*T*) through both stages, contact time in first stage (t_1) was divided in 2-min interval and each interval has been designated as system number; *N* = 1, 2, 3, … and so on. We have varied the contact time, t_1, from 4 to 54 min with 2-min increment in first stage representing system numbers 1–26. The total contact time, T, required for achieving fixed percentage of MB dye removal and the contact times in the first and second stages of adsorber t_1 and t_2 min were calculated using following equations:

$$T = t_1 + t_2 \tag{20}$$

$$t_1 = 4 + (N - 1) \times 2\,\text{min} \tag{21}$$

Combining Equations 20 and 21, we get:

$$T = 4 + (N - 1) \times 2\,\text{min} + t_2 \tag{22}$$

3. Results and discussion

3.1. Adsorption study

3.1.1. Effect of pH on adsorption of MB dye

The effect of solution pH on MB dye adsorption has been studied by varying pH of MB dye solution from 2 to 12 using 1.0-N NaOH and 1.0-N HCl (Hameed, Krishni, & Sata, 2009). At different pH values, 250 mL of dye solution of 100 mg/L concentration was agitated for 180 min at 150 rpm.

The adsorption of dye increases with increase in solution pH from 2 to 4 and thereafter remains constant up to pH 10 (Figure 3). Kini et al. (2013) also studied the MB dye on acid-treated sawdust and found that the rate of removal of the dye seen under acidic conditions was more as compared to that under alkaline one. Slight reduction in adsorption has been observed with increase in pH from 10 to 12. Lower adsorption of MB at acidic pH is probably due to presence of excess H^+ ions competing with the cation groups on the dye for adsorption sites (Hameed, 2009). This, however, did not explain the slight decrease of dye adsorption at higher pH values. MB dye solution has natural pH 7.8 and at this pH, adsorption of MB dye is maximum with the sawdust. Hence, pH of MB dye solution has not been varied in further experiments.

3.1.2. Effect of adsorbent dose on the adsorption of MB dye

Different amounts of sawdust were added into 1,000 mL glass beakers containing 250 mL MB dye of 100 mg/L concentration. Mixture was stirred for 180 min (to ensure equilibrium was reached) at 150 rpm and then left for 2 min in rest position for settling of adsorbent particles. The variation in percentage removal of MB dye with adsorbent dose is shown in Figure 4. The percentage removal of MB dye increased from 65.6 to 97.4% with increase in adsorbent dose from 0.25 to 1.00 g. Kini et al. (2013) also studied MB dye on acid-treated sawdust and found that when adsorbent dose increases the removal of MB dye increased. After that there was slight increment in percent removal of MB dye. The increases in percentage removal were due to increase of available adsorption surface and availability of more adsorption sites. Banerjee et al. (2013) also reported that removal of MB dye from aqueous solution by biopolymer oak sawdust was increased as adsorbent dose increased.

3.1.3. Effect of dye concentration on the adsorption of MB dye

The effect of dye concentration on MB dye removal has been summarized in Figure 5. While varying dye concentration, pH, adsorbent dose, and agitation speed were kept constant. Figure 5 shows that the adsorption of the dye increases with decrease in dye concentration from 300 to 50 mg/L. At lower initial concentration (50 mg/L) the removal of MB dye was observed maximum as compared to higher one (300 mg/L). Kini et al. (2013) observed that MB dye uptake was more at 50 mg/L of dye concentration onto activated sawdust. Shirmardi et al. (2012) studied the adsorption of acid red 18 onto multi-wall carbon nanotubes and observed that at lower concentration of the dye the removal was more as compared to higher concentration. Ansari and Mosayebzadeh (2010) studied adsorption of MB dye from aqueous solution using sawdust and sawdust coated with polypyrrole and observed that at lower concentration of the dye the removal was more as compared to higher concentration.

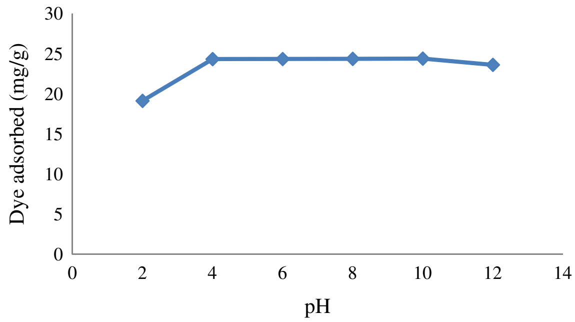


Figure 3. Effect of pH on the adsorption of MB dye on sawdust (C_0 = 100 mg/L, adsorbent dose = 4 g/L, stirring rate = 150 rpm).

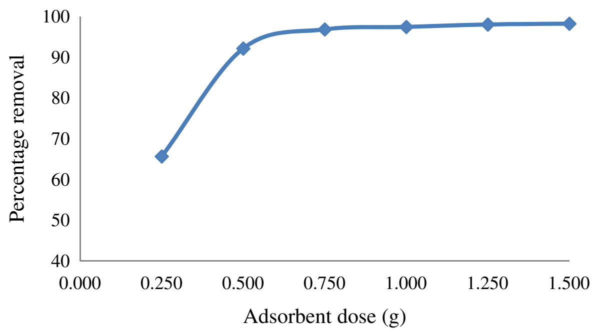


Figure 4. Effect of adsorbent dose on the adsorption of MB dye (C_0 = 100 mg/L, agitation speed = 150 rpm, time = 180 min and pH 7.8).

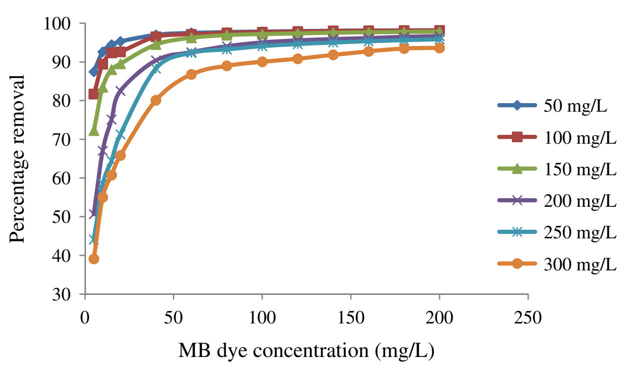


Figure 5. Effect of MB dye concentration on the adsorption of MB dye on sawdust (adsorbent dose = 4 g/L, agitation speed = 150 rpm and pH 7.8).

3.2. Desorption and reuse study

After the adsorption of MB dye onto sawdust where the residues of sawdust were exposed to 8 g/L of solution, collected and filtered, using Whatman filter paper No. 42. MB dye (1–2%) and the adsorbent (1%) were retained on the filter paper; these small variations due to filtration were neglected. Desorption experiments were comprehended by mixing the adsorbed materials, after adsorption, amount of MB dye and sawdust (0.05 g) mixed in aqueous solutions of 50 mL (same volume as in the adsorption step), pH (2–12) for 24 h (agitation speed = 150 rpm). To determine the reusability of the sawdust, five sequential adsorption–desorption processes were repeated, using the same adsorbents and following the experimental procedures described above in the optimum conditions found.

MB dye showed the strong acidic conditions favor desorption of the dye in high percentage (88%). In contrast, under alkaline conditions desorption is taking place in low percentages (18%). So, the pH value selected for the further reuse experiments (adsorption–desorption process) was two. To investigate the possibility of reuse of the low-cost adsorbent of the present study, sequential adsorption–desorption experiments in batch mode were conducted for five cycles. The reduction in adsorption percentages from the 1st to 5th cycle was 12%. El-Latif et al. (2010) observed that uptake capacity of

MB dye decreased from 22.4 to 11.9 mg/g in desorption study. From the above observation it is noted that reuse of the adsorbent will help in reducing amount of sludge generation in the process of removal of MB dye. Banerjee et al. (2013) also predicted that after reusing of adsorbent the amount of sludge generation was less.

The decrease of the adsorption efficiency can be attributed to several reasons as: (1) a progressive saturation of the active sites of sawdust by MB dye molecules; (2) a degradation of material due to extreme pH conditions. In addition, a progressive blocking of the active sites of the adsorbent by impurities in the case of untreated sawdust caused a slight decrease in the adsorption potential compared to the treated ones.

3.3. Adsorption isotherm

In this study, the equilibrium data for MB on sawdust were fitted with the Langmuir, Freundlich and Temkin isotherms at different initial concentrations of MB dye (Figures 6–8). The experimental data fit more closely with Langmuir isotherm (Figure 9). Idris, Ndamitso, Iyaka, and Muhammad (2012) studied the adsorption of the MB dye onto activated carbon prepared from sawdust and found that the Langmuir isotherm better explains the adsorption process. This is also confirmed by the high value of R^2 in case of Langmuir (0.996) compared to Freundlich (0.945) and Temkin (0.985) isotherms. The adsorption of MB dye onto sawdust takes place as monolayer (adsorption capacity 76.92 mg/g; Table 1) adsorption on a surface that is homogenous in adsorption affinity. In case of Freundlich isotherm the value of n is greater than unity (n = 2.13) indicating that the dye is favorably adsorbed on sawdust. The

Figure 6. Langmuir isotherm plots for MB dye adsorption onto sawdust.

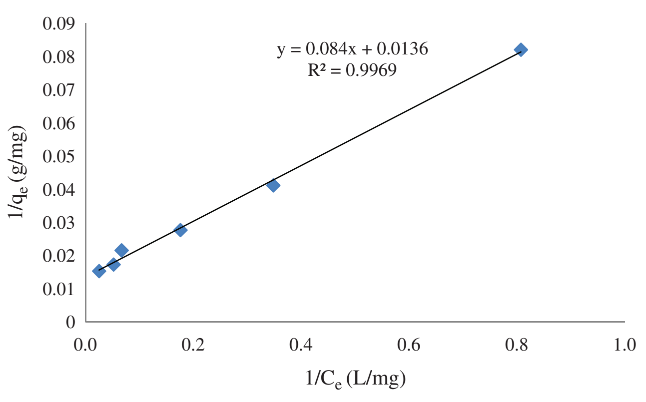


Figure 7. Freundlich isotherm plots for MB dye adsorption onto sawdust.

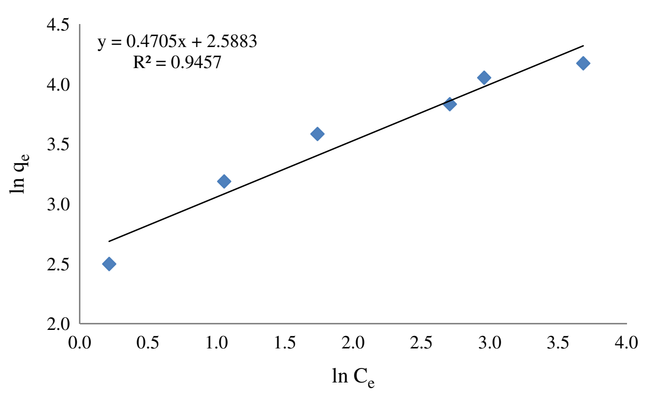


Figure 8. Temkin isotherm plots for MB dye adsorption onto sawdust.

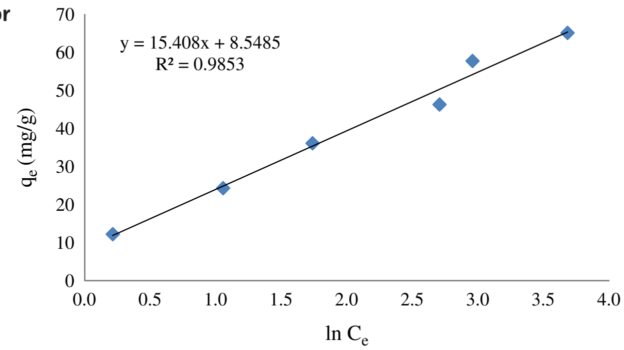


Figure 9. Comparison of different adsorption isotherms for best suitability of experimental data.

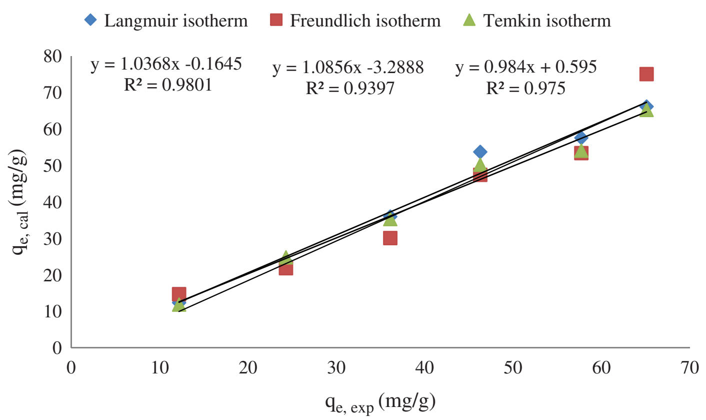


Table 1. Isotherm constants for MB dye adsorption onto sawdust

Languir constants		Freundlich constants		Temkin constants	
α	0.16	K_F	13.30	K_t	1.74
β	76.92	n	2.13	B_t	15.40
R^2	0.996	R^2	0.945	R^2	0.985

appropriateness of sawdust as compared to other adsorbents is shown in Table 2 which suggested the suitability of sawdust for removing MB dye.

3.4. Kinetic models

As seen in Figure 10, the adsorption rate of MB dye increases initially for 60 min but thereafter it slowed down at the stage of equilibrium. The equilibrium time was independent of the initial dye concentration. Figures 11 and 12 show plots of Equations 9 and 11 for the adsorption of dye (MB) onto sawdust for pseudo-first-order and pseudo-second-order kinetic models, respectively. From Table 3, it is clear that the values of $q_{e,\text{exp}}$ were more closer to the values of $q_{e,\text{cal}}$. Figure 13 and Table 3 reveal that pseudo-second-order equation fits better for the adsorption of MB dye onto sawdust which is also confirmed by higher R^2 values in plots between t/q_t and t. Observations of the present study are similar to the findings of Oladipo and Gazi (2015), in which the adsorption of acid red 25 dye from aqueous solution onto magnetic biomass fitted better in pseudo-second-order equation.

Table 2. Comparison of maximum adsorption capacity of different adsorbents

Adsorbents	Capacity (mg/g)	Operating conditions			References
		Kinetic model	pH	Concentration	
Oak sawdust	38.46	Pseudo-second-order	12	200 mg/L	El-Latif et al. (2010)
Acid-activated bentonite clay	229.00	Pseudo-*nth*-order	8.0	100 mg/L	Oladipo and Gazi (2014)
Untreated lignite	35.30	Pseudo-second-order	7.0	100 mg/L	Gurses et al. (2014)
Saccharomyces cerevisiae spent waste	200.00	Pseudo-first-order	2.0	150 mg/L	El-Gendy, El-Salamony, and Nassara (2015)
Nanoparticles of chitosan-based biopolymers	17.40	Pseudo-second-order	5.5	200 mg/L	Shaker (2014)
Multiwalled carbon nanotubes	166.67	Pseudo-second-order	7.0	100 mg/L	Shirmardi et al. (2012)
Sawdust	76.92	Pseudo-second-order	7.8	200 mg/L	Present study

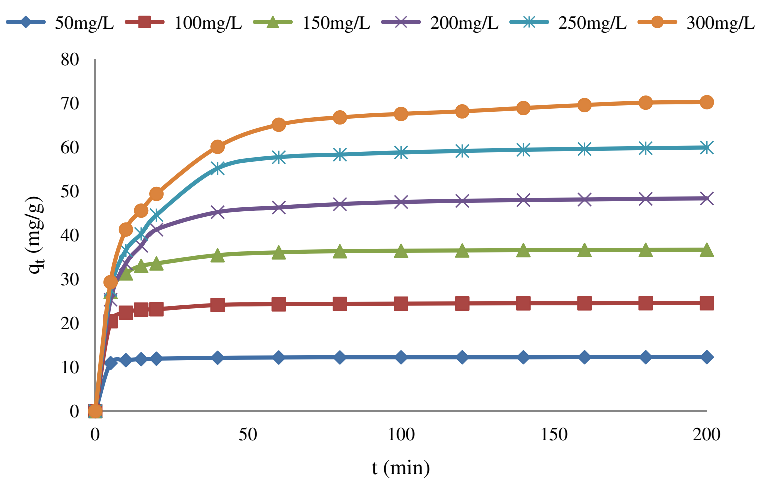


Figure 10. Effect of contact time and initial concentration of MB dye adsorption onto sawdust.

3.5. Intra-particle diffusion model

To assess the diffusion mechanism of MB dye, plots between q_t and $t^{1/2}$ were plotted. Plots will be linear if intra-particle diffusion occurs. The rate limiting process will only be due to intra-particle diffusion, if plot passes through the origin (0, 0). If these conditions are not met, some other mechanism along with intra-particle diffusion will also be involved. The different stages of rates of adsorption observed at different levels indicate that the adsorption rate was initially faster but with the passage of time it slowed down. From Figure 14, it was observed that the plots were not linear over the whole time range which implies that more than one process was affecting the adsorption process (Banerjee et al., 2013). Hameed et al. (2009) studied the adsorption capacity of cationic dye (MB) from aqueous solutions using pineapple stem (a novel agricultural waste) as adsorbent and observed that more than one step affected the adsorption process.

3.6. Two-stage batch adsorber

Two-stage batch adsorber system for the adsorption of MB dye using sawdust was designed with the help of Equations 13–22 given in methodology section. q_e and k_2 were plotted with respect to C_0

Figure 11. Pseudo-first-order kinetic model for different initial MB dye concentration onto sawdust.

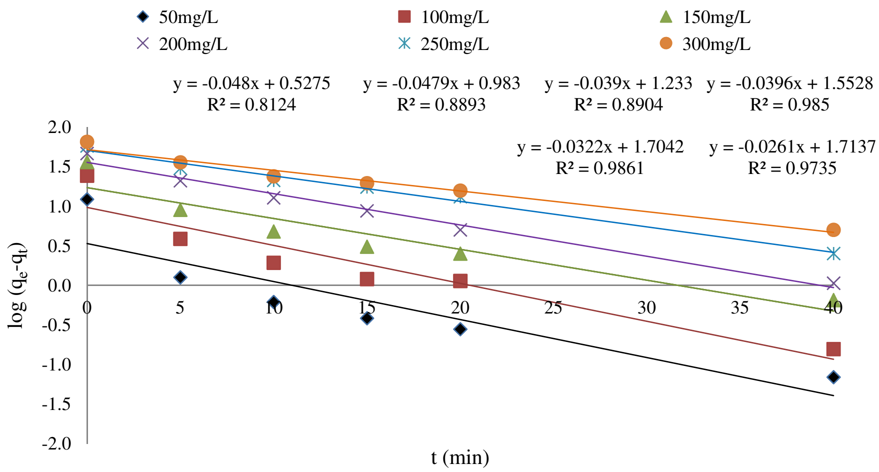


Figure 12. Pseudo-second-order kinetic model for different initial MB dye concentrations onto sawdust.

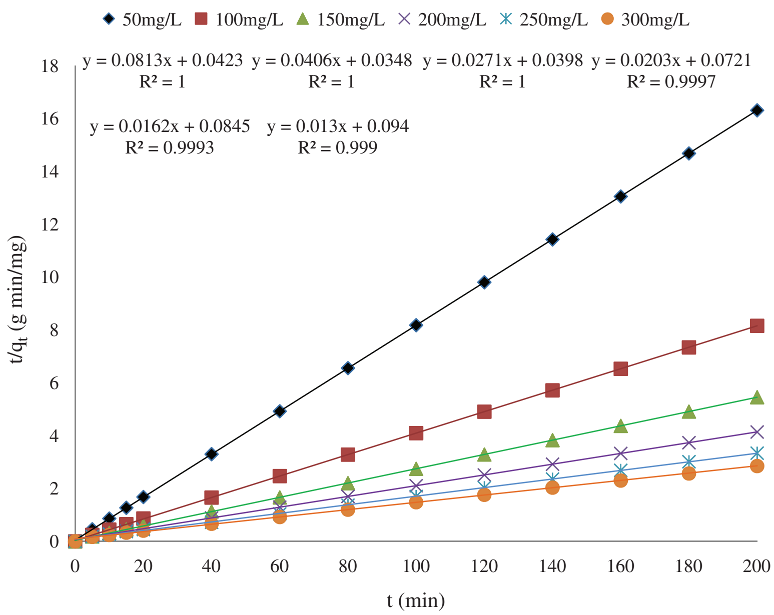


Table 3. Comparison of the pseudo-first-order, pseudo-second-order adsorption rate constants and calculated and experimental q_e values obtained at different initial MB dye concentrations onto sawdust

Initial concentration (mg/L)	$q_{e, exp}$ (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		k_1	$q_{e, cal}$(mg/g)	R^2	$k_2 \times 10^{-3}$	$q_{e, cal}$ (mg/g)	R^2
50	12.19	0.069	3.79	0.739	156.214	12.35	0.999
100	24.28	0.069	10.17	0.792	47.059	25.00	0.999
150	36.08	0.058	18.88	0.813	18.692	37.04	0.999
200	47.26	0.048	37.58	0.921	5.797	50.00	0.999
250	57.19	0.051	57.02	0.914	3.012	62.50	0.999
300	65.08	0.039	55.72	0.903	1.798	76.92	0.999

Figure 13. Comparison of different adsorption kinetic models for best suitability of experimental data.

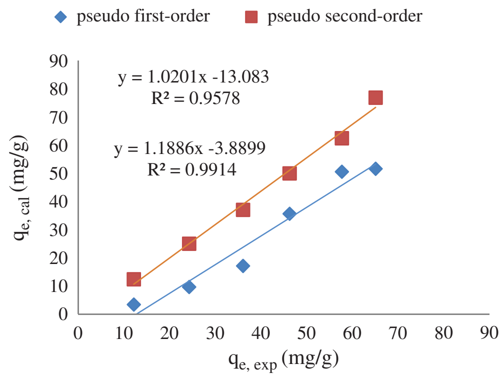


Figure 14. Intra-particle diffusion model for MB dye adsorption onto sawdust.

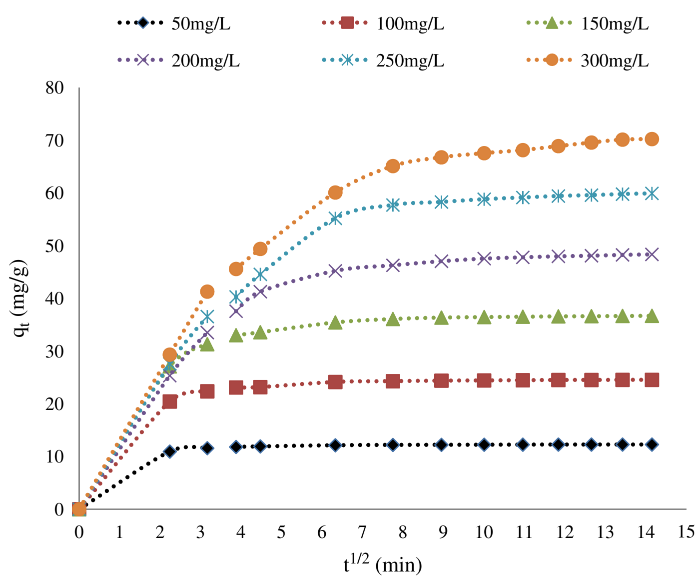


Figure 15. Plot between q_e and initial concentrations (C_0) of MB dye adsorption onto sawdust for two-stage batch adsorber design.

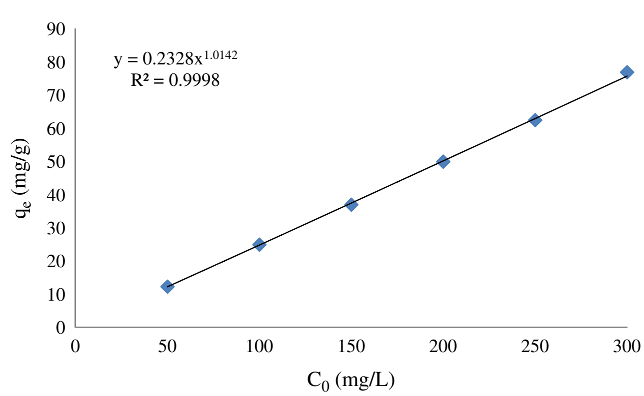


Figure 16. Plot between k_2 and initial concentrations (C_0) of MB dye adsorption onto sawdust for two-stage batch adsorber design.

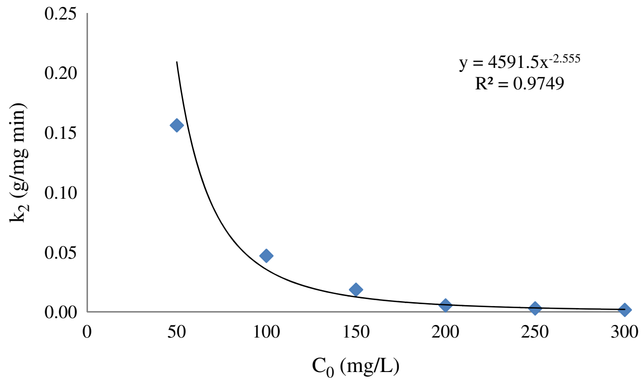
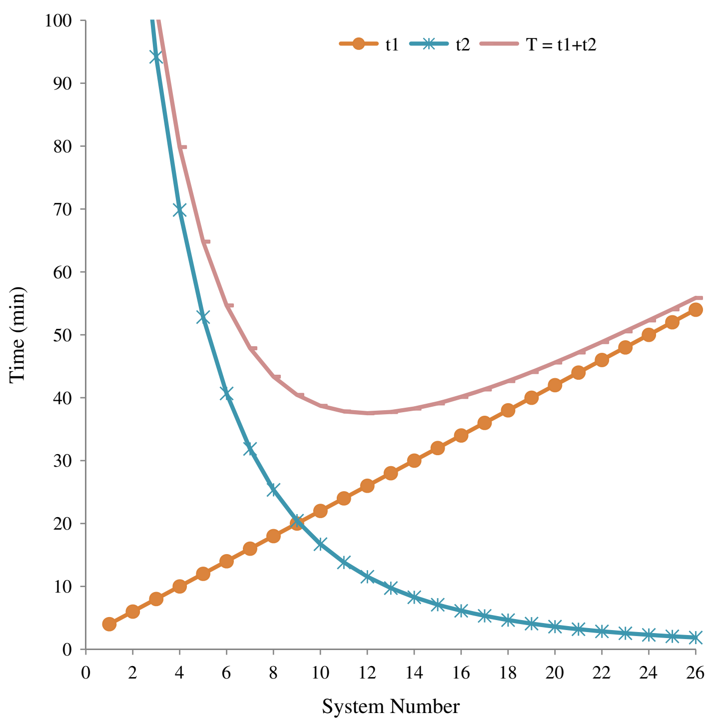


Table 4. Two-stage batch adsorber design parameter values

Adsorbent	X_k	Y_k	R^2	X_q	Y_q	R^2
Sawdust	4,591	−2.55	0.974	0.232	1.014	0.999

Figure 17. Contact time required in stage 1 (t_1), stage 2 (t_2) and overall ($T = t_1 + t_2$) for overall 99% MB dye removal in two-stage batch adsorption (initial dye concentration = 300 mg/L; fresh sawdust (4 g) for 1 L aqueous solution in each stage).



(initial dye concentration) (Figures 15 and 16) to get values of X_k, Y_k, X_q and Y_q (Table 4). For 99, 98, and 97% overall removal of MB dye, total contact time was determined with respect to system numbers 1–26 of first stage. First of all the amount of dye removal was calculated for each system number using the assigned t_1 value against a particular system number. Thereafter, contact time t_2 was calculated based on the requirement of dye removal in second stage. First stage, second stage and total contact time were plotted for each system number to determine system number with minimum contact time for given values of overall percent dye removal, initial dye concentration and adsorbent dose (Figure 17). Table 5 shows various system numbers to be used for 99, 98, and 97%

Table 5. Minimum contact time (min) to achieve different predefined overall percent MB dye removal by sawdust for a series of two-stage batch adsorption systems

Overall MB dye removal (%)	Initial MB dye concentration (mg/L)	System No.	Minimum contact time (min)		
			Stage 1 (t_1)	Stage 2 (t_2)	Total ($t_1 + t_2$)
99	300	12	26	11.54	37.54
	350	15	32	14.37	46.37
	400	20	42	14.18	56.18
	450	21	44	21.55	65.55
	500	25	52	23.79	75.79
98	300	7	16	12.02	28.02
	350	10	22	12.36	34.36
	400	13	28	13.55	41.55
	450	15	32	17.21	49.21
	500	18	38	19.23	57.23
97	300	6	14	9.28	23.28
	350	9	20	9.00	29.00
	400	11	24	11.20	35.20
	450	13	28	13.75	41.75
	500	15	32	16.65	48.65

overall dye removal with 4 g/L sawdust in each stage and initial dye concentrations varying from 300 to 500 mg/L. The minimum contact time varied from 37.54 to 75.79 min for 99%, 28.02–57.23 min for 98%, and 23.28–48.65 min for 97% overall removal of MB dye with initial dye concentrations varying from 300 to 500 mg/L and sawdust concentration 4 g/L, respectively. Oladipo and Gazi (2014) studied the removal of the acid red 25 from magnetic biomass and revealed that 96% removal of the dye occurs in system number 16 having the first-stage contact time as 180 min and the total contact time as 400 min. Ozacar (2006) studied removal of phosphate onto alunite and revealed that 95% removal of phosphate occurs in system number 17 having first stage contact time as 44 min and total contact time 89.7 min.

4. Conclusions

The present study has established the suitability of locally available sawdust as low-cost adsorbent for effective removal of MB dye from aqueous solutions. The adsorption process follows Langmuir isotherm with high value of R^2 (0.996) as compared to Freundlich (0.945) and Temkin (0.985) isotherms with the adsorption capacity of 76.92 mg/g. The equilibrium time was found to be independent of initial MB dye concentration. Pseudo-second-order kinetic model fits better for the adsorption of MB dye onto sawdust. Intra-particle diffusion study suggests that more than one process was affecting the adsorption process. The minimum contact time to achieve 99, 98, and 97% overall removal of MB dye from aqueous solution by adsorption using a fixed mass of fresh sawdust (4 g) for 1 L aqueous solution in each stage of two-stage batch adsorber was found to be 37.54, 28.02, and 23.28 min, respectively for initial MB dye concentration of 300 mg/L.

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