

Removal of Methylene Blue from Aqueous System Using Tobacco Stems Biomass: Kinetics, Mechanism and Single-Stage Adsorber Design

D. Damodar Reddy,^a Rakesh Kumar Ghosh,^b J. Purna Bindu,^a
M. Mahadevaswamy,^a and T.G.K. Murthy^a

^aICAR-Central Tobacco Research Institute, Rajahmundry, 533105, India

^bICAR-National Research Institute on Jute & Allied Fibre Technology, 12 Regent Park, Kolkata, 700040, India;
iarirakesh@gmail.com (for correspondence)

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This study investigated the technical feasibility of using the tobacco stems biomass (TSB), as a low-cost novel adsorbent for removal of methylene blue (MB) from water. TSB was characterized by pH zero-point-charge (pH_{ZPC}) and FTIR analysis. Batch adsorption studies were performed to evaluate process variables, kinetics and equilibrium of MB adsorption. Results showed that MB removal was higher at pH values >pH_{ZPC} of adsorbent, and for particle size <0.5 mm. The adsorption kinetics followed pseudo-second order ($k_2 = 0.008$ to 0.001 g mg⁻¹ min⁻¹), with intraparticle diffusion as one of the rate limiting steps. The Langmuir isotherm with maximum capacity of 169.5 mg g⁻¹ was statistically found a best fit model. A single stage batch adsorber was designed and quantity of TSB required for treating 1000-10,000 L of stained water was determined. The results imply that the TSB with could be a promising alternative adsorbent for remediation of cationic dye bearing wastewater. © 2017 American Institute of Chemical Engineers Environ Prog. 00: 000-000, 2017

Keywords: tobacco stem biomass, methylene blue removal, adsorption, adsorber design

INTRODUCTION

Contamination of aquatic systems with dyes is a burning environmental issue around the world. Effluent from textile, paper, leather, and other related industries contains residues of synthetic dyes and is often released untreated into the environment, particularly in developing countries. These dyes in effluent, if not removed, can pollute water bodies and adversely affect aquatic life, water quality and aesthetic value of receiving water systems, resulting in serious environmental problem [1]. Though an array of technologies is available to remediate dyes from stained waters, the adsorption method employing solid adsorbents is widely used because of its efficiency and practical feasibility [2,3]. The economics of adsorption technique depend mainly on the cost of the adsorbent materials. That is why the application of activated carbon for wastewater treatment in developing countries is still limited. This has prompted an exploration of renewable alternative adsorbents, especially of plant origin like coir pith carbon [4], coconut bunch waste [5],

sugarcane bagasse [6], *Typha* phytomass [7], *Eichhornia crassipes* biomass [8], crop residue ash [9], etc. Local availability, abundance, little/no processing and low cost are some obvious advantages of plant biomass based adsorbents. Until this study, there has been no information on tobacco stems biomass (TSB) as an adsorbent for treatment of dye-bearing wastewater.

Tobacco (*Nicotiana tabacum* L.) is an important commercial crop grown extensively in many countries of the world, including China, Brazil, India, and the United States of America. Since the crop is primarily grown for its leaves, the stem biomass part (TSB) is often neglected and treated as waste. Typically, a tobacco crop producing 2000 kg ha⁻¹ leaf yield also generates about 1000 kg ha⁻¹ of TSB. In India, such huge and renewable TSB has traditionally been discarded as solid waste or burned off in heaps. In an earlier study, it was found that even tobacco stem ash was capable of removing cationic dye, MB, from water [10]. However, burning of tobacco stems not only causes environmental pollution, but also represents wastage of renewable biomass. Therefore, valorization of this vast, renewable and locally available TSB for multiple beneficial purposes assumes economic and ecological significance. To the best of our knowledge, there exists no published report on the adsorptive potential of TSB for the removal of cationic dyes from contaminated water.

This study was, therefore, conducted to evaluate technical feasibility of using TSB as an adsorbent for removal of MB, a widely used basic dye, from its aqueous solution. Effects of different process variables, namely contact time, dye concentration, initial solution pH, adsorbent dose, and adsorbent's particle size on adsorption of MB onto TSB were investigated. Besides, the kinetics and equilibrium behavior of MB adsorption were evaluated using different kinetic and isotherm models. The favorability for MB adsorption onto TSB was also determined. Finally, a single stage batch adsorber design was developed to predict the amounts of TSB required for target levels of dye removal from aqueous solutions of varying MB concentration.

MATERIAL AND METHODS

Collection and Characterization of TSB (Adsorbent)

TSB was collected from the Research Farm, Central Tobacco Research Institute, Rajahmundry (16.98°N 81.78°E), Andhra

Pradesh, India. The collected TSB was cleaned thoroughly with distilled water to remove surface smeared soil, followed by slicing and drying at 70°C for 48 h. Subsequently, the dried TSB was crushed, sieved and stored without any further pretreatment for use in all adsorption experiments. The TSB was analyzed for pH (solid: water ratio at 1: 10) by using pH meter (Model 361, Systronics, India) and carbon content by the TOC Analyzer (Vario TOC Select, Elementar, Germany). The surface morphology was investigated by scanning electron microscopy (SEM) analysis (Carl Zeiss AG - EVO 40 Series, Germany). The surface property of TSB was determined by measuring pH at zero point of charge (pHzpc) by the potentiometric mass titration method [11] and functional groups were identified by Fourier transform infrared (FTIR) spectrum analysis (Bruker ALPHA FTIR/ATR system; range: 4000-400 cm⁻¹; resolution: 4 cm⁻¹).

MB (Adsorbent) and Other Reagents

MB was selected as a model cationic dye for this investigation. Analytical grade MB (MW: 373.91 g mol⁻¹; λ_{max}: 665 nm) was purchased from Qualigens®. Other required chemicals of analytical grades were procured from SdFine® (Mumbai, India). The MB stock solution (1000 mg L⁻¹) was prepared by dissolving 1 g MB in 1 L distilled water (pH 6.9), and subsequently diluted to obtain working solutions of desired dye concentrations for various adsorption experiments. Preliminary studies with blank dye (MB) solution showed no effect of solution pH (pH 3–11) on the λ_{max} (665 nm) of MB, which indicated stability of the cationic MB molecule within the studied pH range.

Batch Adsorption Studies

Batch adsorption experiments were performed to investigate the effects of process variables like contact time, initial dye concentration, solution pH, adsorbent dose, and adsorbent's particle size on adsorption of MB onto TSB at room temperature (27 ± 1°C). For, adsorption kinetics, 0.2 g TSB was agitated with 100 mL MB solution of varying concentrations (50, 100, and 250 mg L⁻¹; pH: 6.9) in a series of 250 mL Erlenmeyer flask on an orbital shaker (Optics Technology, India) at 150 rpm over a period of 240 min. The TSB-MB suspensions were centrifuged at 8000 rpm for 10 min, and the MB concentration in supernatant estimated by measuring absorbance with an UV-VIS spectrophotometer (Model- 2202, Systronics, India) at 665 nm against a standard calibration curve. The amount of dye adsorbed at time *t*, *q_t* (mg g⁻¹), at equilibrium, *q_e* (mg g⁻¹), and dye removal percentage were calculated as:

$$q_t = \frac{(C_i - C_t)W}{V} \quad (1)$$

$$q_e = \frac{(C_i - C_e)W}{V} \quad (2)$$

$$\% \text{ Dye removal} = \frac{100(C_i - C_t)}{C_i} \quad (3)$$

where *C_t* and *C_e* are MB concentrations (mg L⁻¹) at time *t*, and equilibrium; *V* is volume of the solution (L) and *W* is the mass of adsorbent (g).

Separate batch adsorption experiments were carried out to investigate the effect of process variable namely, initial solution pH, adsorbent dose and particle size of adsorbent on MB adsorption onto TSB. The effect of initial solution pH on MB adsorption was studied by shaking 0.2 g TSB in 100 mL MB solutions (50 mg L⁻¹; pH: 6.9) with a range of pH (3, 4, 5, 6, 7, 8, 9, 10, and 11) over a period of 120 min. The effect of dose was investigated by shaking different amounts of TSB (0.25, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, and 10.0 g L⁻¹) with 100 mL of MB solution (50 mg L⁻¹; pH: 6.9). The effect of particle size was investigated by shaking 0.2 g TSB

of different particle sizes (1–2 mm, 0.5–1 mm, 0.2–0.5 mm, and < 0.2 mm) with 100 mL of MB solution (50 mg L⁻¹; pH: 6.9). For adsorption equilibrium experiments, 0.2 g of TSB was agitated with 100 mL MB solution of different initial concentrations (50, 75, 100, 150, 200, and 250 mg L⁻¹; pH: 6.9) for 120 min.

Adsorption Kinetic Models

The adsorption kinetics of MB onto TSB was investigated by fitting the data to commonly used pseudo-first order (Eq. 4) [12], pseudo-second order (Eq. 5) [13], and intraparticle diffusion [14] models (Eq. 6).

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2.303}\right)t \quad (4)$$

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right)t \quad (5)$$

$$q_t = k_{id}t^{0.5} + C \quad (6)$$

where *k₁* (min⁻¹), *k₂* (g mg⁻¹ min⁻¹), and *k_{id}* (mg g⁻¹ min^{-0.5}) are rate constant for pseudo-first order, pseudo-second order, and intraparticle diffusion model, respectively. *C* reflects the boundary layer effect.

Adsorption Isotherm Models

The adsorption equilibrium data were tested by the isotherm models of Freundlich [15], Langmuir [16], Temkin [17], and Jovanoic [18] which can be represented as:

$$\log(q_e) = \log(K_f) + \frac{1}{n} \log(C_e) \quad (7)$$

$$\frac{C_e}{q_e} = \frac{1}{kb} + \frac{C_e}{b} \quad (8)$$

$$q_e = \alpha + \beta \ln C_e \quad (9)$$

$$q_e = \ln q_m + K_j C_e \quad (10)$$

where *K_f* (mg g⁻¹) and 1/*n* are Freundlich constants which indicate capacity and heterogeneity factor. *b* is the Langmuir maximum adsorption capacity (mg g⁻¹) and *k* (L mg⁻¹) is the Langmuir bonding energy coefficient. *α* and *β* are constants, representing adsorption capacity and retention intensity of Temkin adsorption. *q_m* is the maximum amount adsorbed (mg g⁻¹) and *K_j* (L mg⁻¹) is the constant related to the energy of Jovanoic adsorption.

The favorability for MB adsorption onto TSB was calculated by determining the dimensionless separation factor/equilibrium parameter (*R_L*), an essential characteristic of Langmuir isotherm. The value of *R_L* indicates the feasibility of dye adsorption. The value of *R_L* indicates either unfavorable (*R_L* > 1), linear (*R_L* = 1), favorable (0 < *R_L* < 1), or irreversible (*R_L* = 0) adsorption system. It was calculated as:

$$R_L = \frac{1}{(1 + kC_i)} \quad (11)$$

where *k* (L mg⁻¹) is the Langmuir bonding energy coefficient and *C_i* is the highest initial dye concentration (mg L⁻¹).

The Gibb's free energy change (Δ*G*) of adsorption was calculated from the Langmuir binding energy constant *k* (L mg⁻¹) after converting it to *K* (L mol⁻¹) using the molecular weight of MB before estimating the free energy change as:

$$\Delta G = -RT \ln(K) \quad (12)$$

where Δ*G* is free energy change of adsorption (kJ mol⁻¹), *R* is universal gas constant (8.3145 J mol⁻¹ K⁻¹), and *T* is temperature (K).

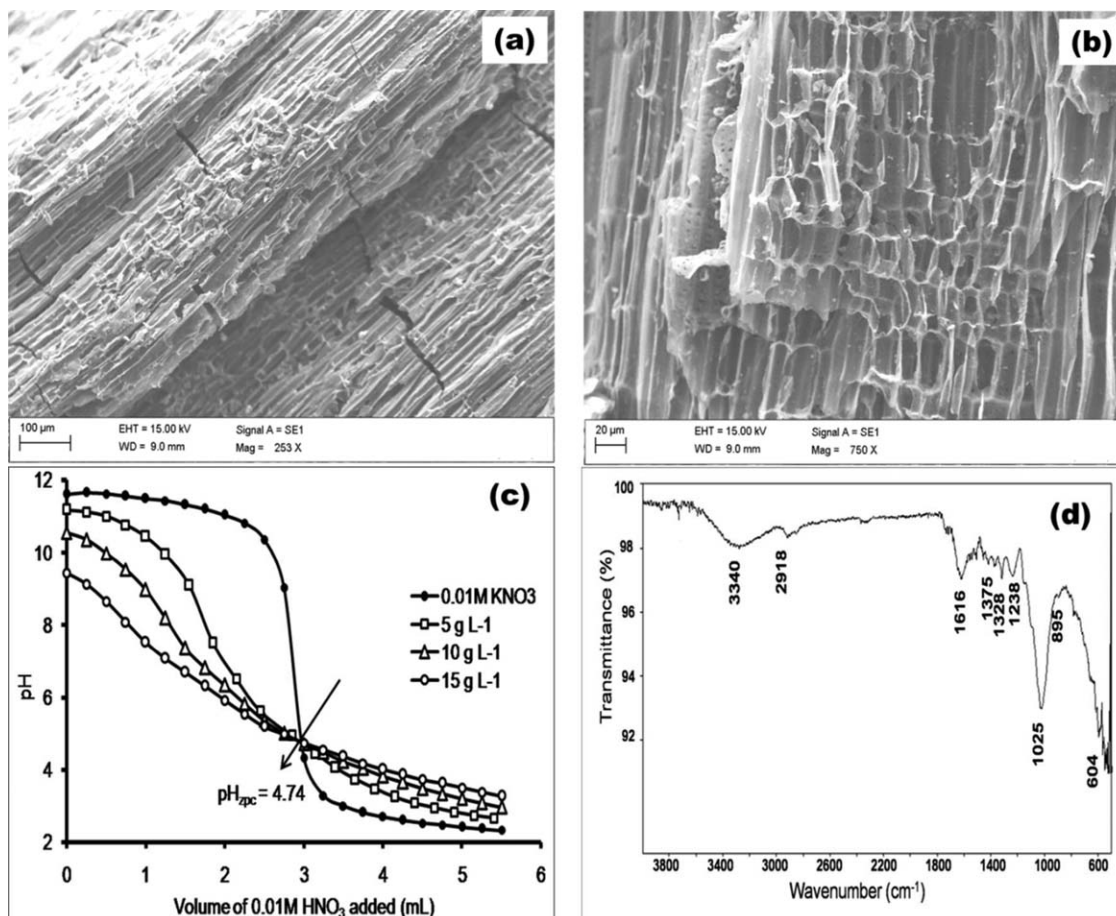


Figure 1. Characterization of TBS with SEM analysis at (a) 253X magnification; (b) 750X magnification; (c) pH Zero point charge; and (d) FTIR spectrum.

Error Analysis

The best-fit mathematical models were selected on the basis of error analysis through Chi-square (χ^2) test, which can be represented as follows:

$$\chi^2 = \frac{\sum (q_{e, \text{exp}} - q_{e, \text{cal}})^2}{q_{e, \text{cal}}} \quad (13)$$

where $q_{e, \text{exp}}$ (mg g^{-1}) and $q_{e, \text{cal}}$ (mg g^{-1}) are the amount of dye adsorbed at equilibrium from experiment and mathematical model, respectively.

RESULTS AND DISCUSSION

Physico-Chemical Properties of TSB (Adsorbent)

The TSB was found to be acidic (pH- 6.03) in nature with an electrical conductivity of 2.12 dS m^{-1} . The alkaline earth metal contents were 0.65% Na, 0.68% Ca, and 1.31% K. the SEM analysis indicated uneven and porous structures in the TBS (Figures 1a and 1b). The pH_{zpc} of TSB was determined to understand the adsorbent's surface charge property (Figure 1c). The pH_{zpc} of TSB was 4.74. Figure 1d shows the FTIR analysis of TSB. The FTIR analysis shows several peaks, indicating presence of various functional groups which can help to understand the MB adsorption process [19]. The broad characteristic peak around 3340 cm^{-1} coupled with a weak peak at 604 cm^{-1} typically correspond to the O—H stretching vibration of free hydroxyl groups of cellulose and lignin and the out-of-plane deformation of O—H, respectively. The bands

around 2918 cm^{-1} are due to the stretching vibration of C—H bond in methylene ($-\text{CH}_2$) and methyl ($-\text{CH}_3$) groups. The peaks at 1375 , 1328 , and 1238 cm^{-1} indicate the in-plane symmetric deformation vibration of $-\text{CH}_3$ in lignin, the in-plane bending vibrations of O—H or stretching of C—O in cellulose, and the asymmetric stretching of $=\text{C}-\text{O}-\text{C}$ attached with aryl groups in lignin. The peak at 1616 cm^{-1} corresponds to vibration of C=O and C=C. A very weak peak observed at 895 cm^{-1} could be associated with the in-plane bending vibrations of C—H or out-of-plane deformation mode of C—H and O—H in pyranoid rings involved in cellulose [20]. A strong band at around 1025 cm^{-1} corresponding to C—O—C stretching vibration confirms the cellulose and lignin structures of TSB. The FTIR spectrum indicates the lignocellulosic nature of TBS coupled with various polar functional groups which may develop negative charges and participate in the adsorption of cationic MB molecules from aqueous solution.

Effect of Contact Time and Initial Dye Concentration on MB Adsorption by TSB

The adsorption of MB on TSB at three initial dye concentrations (50 , 100 , and 250 mg L^{-1}) was studied as a function of contact time (Figure 2a). In all initial dye concentrations, the MB adsorption increased rapidly with contact time for initial 15 min, and thereafter, it proceeded at a slower rate until reaching equilibrium. The initial rapid phase of MB adsorption is attributed primarily to the concentration gradient between MB in a solution and the TSB surface. As time proceeds, this concentration gradient diminishes gradually, leading to a decrease in the adsorption rate [6,8]. Though the time course of adsorption

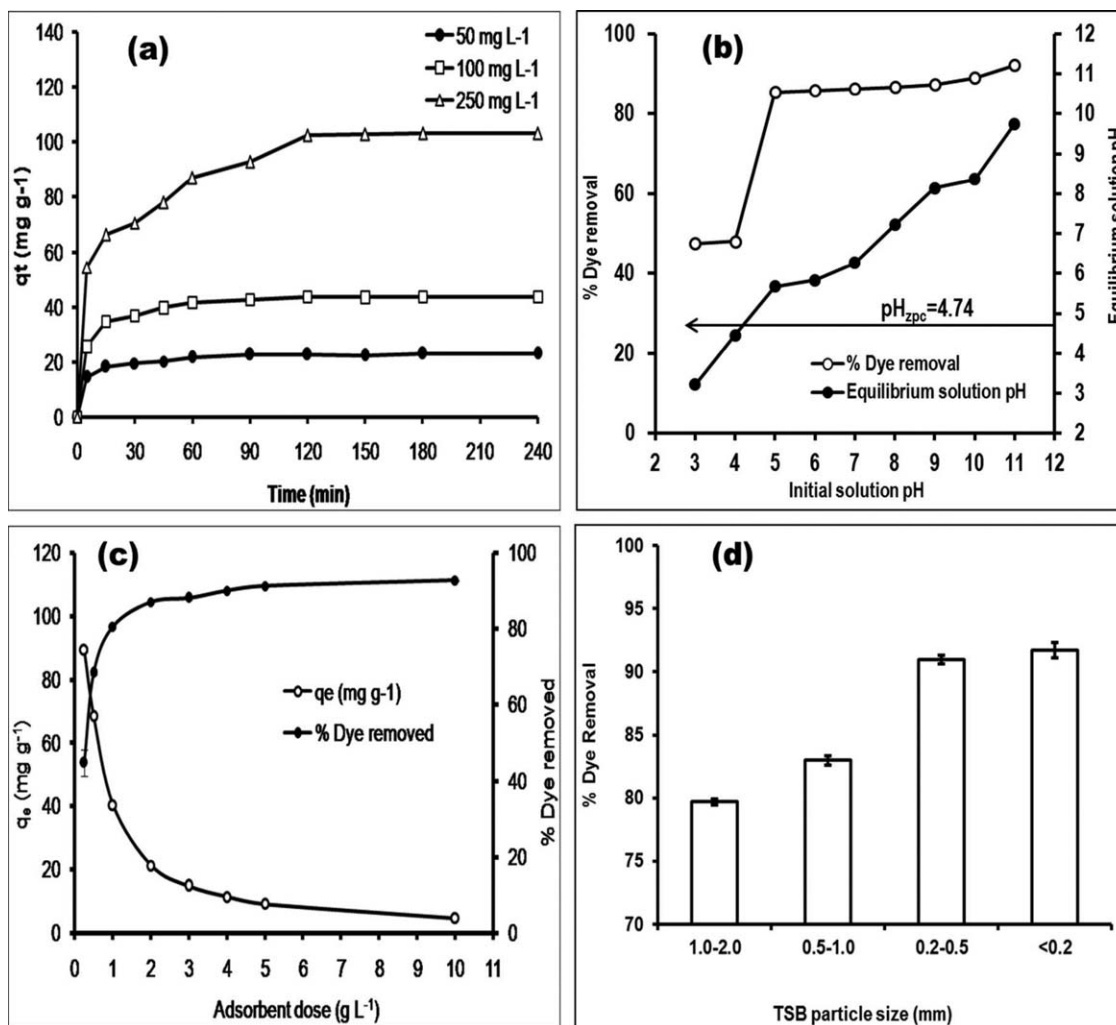


Figure 2. Effect of process variables on adsorption of MB onto TSB: (a) Contact time (2-240 min); (b) initial solution pH (pH: 3-11); (c) adsorbent dose (TBS: 0.25-10 g L^{-1}); and (d) particle size of adsorbent (size: <math><0.2</math> to 1-2 mm).

followed a similar trend for all initial dye concentrations, the q_t (mg g^{-1}) was dependent on C_i (mg L^{-1}), with the q_t values being greater at a higher initial MB concentration (Figure 2a). The system reached equilibrium first at about 90 min for low C_i values (50 and 100 mg L^{-1}), while it took longer time (120 min) to reach equilibrium for higher concentration (250 mg L^{-1}). This is so because the initial dye concentration provides the driving force to overcome the resistance to mass transfer of MB from the bulk solution to TSB. Based on these results, an optimum contact time of 120 min was selected for attaining equilibrium. It was noted that at equilibrium time of 120 min, MB removal was 91.4, 87.6 and 81.9% for C_i of 50, 100, and 250 mg L^{-1} , respectively.

Effect of Initial Solution pH on MB Adsorption by TSB

The pH of dye solution is an important factor which determines the dye removal efficiency of an adsorbent by influencing the ionization of dye molecules, and surface property of adsorbent. From the results presented in Figure 2b, it is evident that the MB removal increased from 47.5% to 92.2% with an increase in initial solution pH from 3 to 11. Further, Figure 2b also depicts the TSB-MB interaction induced changes in solution pH as evident from differences in pH values of initial and equilibrium solutions. The MB removal was low (47.5%–48.1%) at solution pH 3 and 4 for which the respective pH_e values were lower than pH_{zpc} , and increased sharply to attain

strikingly higher values of 85.4%–92.2% at pH 5 and above for which the corresponding pH_e values were higher than pH_{zpc} . These results clearly indicate that greater proportion of MB could be removed when the pH_e is above pH_{zpc} of adsorbent (TSB). This behavior can be explained by the nature of adsorbent's surface charge and the ionization of MB molecule. The MB is a basic dye and exists as a cationic species in aqueous solution. The electrostatic attraction between the negatively charged adsorption sites of TSB and MB^+ molecules is mainly responsible for adsorptive removal of MB from its aqueous solution. When the solution pH_e is less than the pH_{zpc} of adsorbent, the adsorbent's surface becomes positively charged and repels the cationic MB molecule, resulting in low MB adsorption. As the solution pH_e raises more than the pH_{zpc} of adsorbent, the adsorbent's surface negative charge density increases, and results in higher adsorption of cationic MB because of electrostatic attraction. The pH_{zpc} of TSB, used in this study, was 4.74. When pH_e of the system (i.e., for initial solution pH 5 and above), was higher than the pH_{zpc} of TSB, the sorbent's surface negative charge density increased, and resulted in high MB adsorption [4,9].

Effect of Adsorbent Dose on MB Adsorption by TSB

The results depicted in Figure 2c showed that q_e (mg g^{-1}) values decreased from 89.4 to 4.63 mg g^{-1} with the increasing TSB dose from 0.25 to 10 g L^{-1} . Contrary to q_e , the %MB

Table 1. Comparison of kinetic model parameters for TSB-MB adsorption system.

Mathematical models	Model parameters	Initial concentration C_i (mg L ⁻¹)		
		50.00	100.00	250.00
Pseudo-first-order	R^2	0.892	0.983	0.894
	k_1 (min ⁻¹)	0.0555	0.0332	0.0189
	q_e (mg g ⁻¹) calculated	15.63	17.74	52.10
	q_e (mg g ⁻¹) experimental	22.85	43.80	102.4
	χ^2	3.333	38.29	48.57
Pseudo-second-order	R^2	0.999	0.999	0.986
	k_2 (g mg ⁻¹ min ⁻¹)	0.008	0.004	0.001
	q_e (mg g ⁻¹) calculated	23.75	45.45	107.5
	q_e (mg g ⁻¹) experimental	22.85	43.80	102.4
	χ^2	0.034	0.060	0.244
Intraparticle diffusion	K_{id} (mg g·min ^{-0.5})	0.920	1.895	5.359
	C (mg g ⁻¹)	13.87	25.36	43.20
	R^2	0.907	0.863	0.989

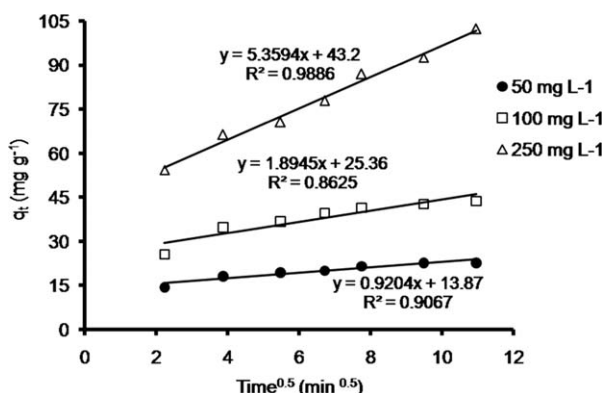


Figure 3. Intraparticle diffusion model for MB adsorption onto TSB at different initial dye concentrations. Conditions: (TSB: 2 g L⁻¹; MB: 50, 100, and 250 mg L⁻¹; pH: 6.9; temperature: 300 ± 1 K).

removal increased (44.7%–88.2%) with increasing TSB dosage (from 0.25 to 2 g L⁻¹). Further, increase in TSB dosage from 2 to 10 g L⁻¹ caused only a marginal improvement in dye removal from 88.2% to 92.7%. The reason is that a known mass of adsorbent has fixed number of adsorption sites, and hence, it can adsorb only a fixed amount of MB from the dye solution. With the increase in adsorbent dose, the number of adsorption sites increases, which consequently increase adsorption of more dye molecules resulting increase in %dye removal. The amount of MB adsorbed per unit mass of adsorbent, q_e (mg g⁻¹), decreased from 89.4 to 4.63 mg g⁻¹ with an increase in dose from 0.25 to 10 mg L⁻¹. This is because a fixed volume of dye solution with known initial dye concentration has a defined number of total dye molecules, and under this condition adsorbent's dose becomes very important. Similar trends were reported for the adsorptive removal of MB by coconut bunch waste [5], tobacco stem ash [10] etc. With the increase in the adsorbent dose, number of adsorption sites increases and become over numbered as compared to the number of dye molecules. Hence, many adsorption sites of adsorbent remain vacant, which results in decreasing q_e [21]. Thus selection of appropriate dose becomes a very important factor for effective, efficient, and economic treatment process [3]. Therefore, the TSB dose of 2 g L⁻¹ was selected all batch adsorption studies.

Effect of TSB Particle Size on MB Adsorption

The results illustrated in Figure 2d showed that MB removal increased (79.7%–91%) with decreasing particle size

of TSB (from 1–2 mm to 0.2–0.5 mm) which could be due to increase in surface area. A further decrease in particle size from 0.2–0.5 mm to >0.2 mm led to only a slight improvement in the MB removal (91.0%–91.7%). Based on these results, TSB particle size of >0.5 mm was considered optimum with efficient MB removal. The study showed that TSB, even with larger particle size (>1 mm–< 2 mm), can remove 79% MB from the dye solution (50 mg L⁻¹). This indicates the practical feasibility of TSB to treat MB contaminated water with less restriction on the selection of adsorbent's particle size.

Adsorption Kinetics and Mechanism

In order to evaluate the kinetics of MB adsorption onto TSB and elucidate the mechanisms involved therein, the experimental kinetic data obtained at different initial dye concentration were fitted to pseudo-first order and pseudo-second order model [9,22]. Model parameters along with coefficient of determination (R^2) and χ^2 values of kinetic models are presented in the Table 1. The pseudo-second order kinetic model with highest R^2 values (0.986–0.999) along with smaller χ^2 values (0.034–0.244) indicated better fit as compared to the Lagergran first order model ($R^2 = 0.892$ – 0.983 ; $\chi^2 = 3.333$ – 48.57). Higher R^2 coupled with low χ^2 values indicated better model predictability with less error for pseudo-second order kinetic model. Data presented in Table 1 indicated that the adsorption capacity, $q_{e,exp}$ (mg g⁻¹), increased with increase in C_i levels. In contrast, the rate constant, k_2 , showed a decreasing trend with increase in C_i . The reason could be that at lower C_i , the competition for active sites of TSB is low. But at higher C_i , the competition for the TSB's surface active sites would be high, resulting in lower k_2 values [19]. To elucidate the mechanism involved in MB adsorption onto TSB, the kinetic data were fitted to the intraparticle diffusion model. The k_{id} and C values are presented in the Table 1. When the linear regression of q_t versus $t^{0.5}$ passes through the origin ($C = 0$), then intraparticle diffusion is the sole rate-controlling step (Figure 3). Table 1 clearly shows that the regression lines do not pass through origin and $C \neq 0$. Thus intraparticle diffusion is not the only rate-controlling step, and both boundary layer and intraparticle diffusion may have influenced the process [5,19,22]. The fast adsorption in the initial stage might have been controlled mainly by boundary layer diffusion, while at the later stage of slow adsorption intraparticle diffusion became major process. The value of C increased (13.87–43.20 mg g⁻¹) with an increase in C_i (50–250 mg L⁻¹) (Table 1), indicating the dependence of boundary layer thickness on initial MB concentration.

Adsorption Isotherm

A state of equilibrium is obtained when the amount of dye adsorbed onto an adsorbent is equal to the amount of dye desorbed from the same adsorbent. At such equilibrium point, the solution concentration remains constant. Adsorption equilibrium study indicates the adsorbate-adsorbent interaction and adsorption capacity of an adsorbent [10,23]. The equilibrium adsorption behavior of MB-TSB system was analyzed using linear forms of Freundlich, Langmuir, Temkin, and Jovanoic isotherm models. The calculated adsorption parameters and R^2 for both models are listed in Table 2. Based on the coefficient of determination (R^2) values, models followed the order: Freundlich ($R^2=0.959$) > Langmuir ($R^2=0.957$) > Temkin ($R^2=0.926$) > Jovanoic ($R^2=0.68$). However, best fit model was selected on the basis of error analysis (χ^2 test) along with high R^2 . χ^2 test is very important because a low/small χ^2 value means that the model prediction is very close/near to the observed/experimental value. Hence, on the basis of high R^2 along with low χ^2 value (Table 2), the order of models was Langmuir > Freundlich >> Temkin >>> Jovanoic. These results suggest that the Langmuir model with lowest χ^2 value and high R^2 is the best fit model to describe adsorption equilibrium [5,10]. Best fit of Langmuir isotherm also indicates monolayer nature of MB adsorption onto TSB. The Langmuir isotherm parameters, maximum adsorption capacity (b) and bonding energy constant (k) were estimated as 169.5 mg g^{-1} and 0.022 L mg^{-1} , respectively. Further, the R_L

Table 2. Adsorption isotherm model parameters for TSB-MB adsorption system.

Mathematical models	Parameters	Values
Freundlich isotherm	$K_F (\text{mg g}^{-1})$	6.449
	$1/n$	0.672
	R^2	0.959
	χ^2	7.094
Langmuir isotherm	$b (\text{mg g}^{-1})$	169.5
	$k (\text{L mg}^{-1})$	0.022
	R^2	0.957
	R_L	0.154
	χ^2	1.390
Temkin isotherm	A	8.599
	B	26.17
	R^2	0.926
	χ^2	54.20
Jovanoic isotherm	$q (\text{mg g}^{-1})$	14.79
	$K_1 (\text{L mg}^{-1})$	0.053
	R^2	0.680
	χ^2	78.80

value for MB adsorption on TSB was found to be positive and less than unity (0.154), indicating favorable ($0 < R_L < 1$) adsorption process [9]. A comparison of adsorption capacity of different adsorbents shows that TSB for MB was found substantially superior to that of many reported low-cost adsorbents (Table 3). The MB removal capacity of TSB is found substantially superior than many reported low-cost adsorbents. Therefore TSB emerges as a potential adsorbent to remove MB from aqueous solutions. The ΔG value for MB adsorption onto TSB was $-5.26 \text{ kJ mol}^{-1}$ at room temperature ($27 \pm 1 \text{ }^\circ\text{C}$), indicating a spontaneous and favorable process of MB adsorption onto TSB. Further, this ΔG value is within the range (0 to -20 kJ mol^{-1}) of free energy change for physisorption [9,22] and hence, MB adsorption onto TBS was by physisorption.

Design of Single-Stage Batch Adsorber from Isotherm Data

The dye adsorption isotherms have been widely used by researchers to design a single-stage batch adsorber [5,28]. A single stage batch adsorber was designed on the basis of the adsorption equilibrium data obtained (Figure 4a). The design objective is to reduce the initial concentration of MB from C_i (mg L^{-1}) to final concentration, C_f (mg L^{-1}) during treatment of effluent of volume, V (L) in the adsorber. The quantity of TSB added into the adsorber to treat MB contaminated water is W (g) and MB loading onto TSB changes from initial q_i to q_f (mg g^{-1}) during adsorption process. When fresh TSB is used, $q_i = 0$ (mg g^{-1}) and the mass balance equates the dye removed from the solution to that adsorbed by the TSB. The mass balance for MB in the single-stage adsorber system can be represented as:

$$V(C_i - C_f) = W(q_f - q_i) = Wq_f \quad (14)$$

At equilibrium $C_f \rightarrow C_e$ and $q_f \rightarrow q_e$, then Eq. 14 becomes Eq. 15:

$$V(C_i - C_e) = Wq_e \quad (15)$$

In this study, the Langmuir isotherm model gave a best fit to the adsorption equilibrium data. Therefore, Langmuir isotherm equation was substituted for q_e in the Eq. 15 to get the following Eq. 16:

$$\frac{W}{V} = \frac{(C_i - C_e)}{q_e} = \frac{(C_i - C_e)}{\left(\frac{kbC_e}{1 + kC_e}\right)} \quad (16)$$

The Eq. 16 was used to predict the quantity of TSB (kg) required to remove a certain percentage of MB from a batch volume of

Table 3. Comparison of MB adsorption capacities of different plant biomass-based adsorbents.

Adsorbents	pH	Time	Adsorption capacity (mg g^{-1})	References
Coir pith carbon	6.9	100 min	5.9	[4]
Orange peel	7.2	24 h	18.6	[24]
Cotton stem ash	6.9	180 min	20.42	[23]
Salvadora stem ash	11.0	80 min	22.9	[25]
Sugarcane bagasse	–	24 h	30.7	[6]
Tobacco stem ash	6.9	180 min	35.7	[10]
Saw dust of cherry	–	180 min	39.8	[26]
Saw dust of walnut	–	180 min	59.2	[26]
Coconut bunch waste	6.5–7.5	315 min	70.9	[5]
Pine tree leaves biomass	9.2	100 min	126.9	[27]
<i>Eichhornia crassipes</i>	6.9	20 min	35.37	[8]
Tobacco stems biomass	6.9	120 min	169.5	Present study

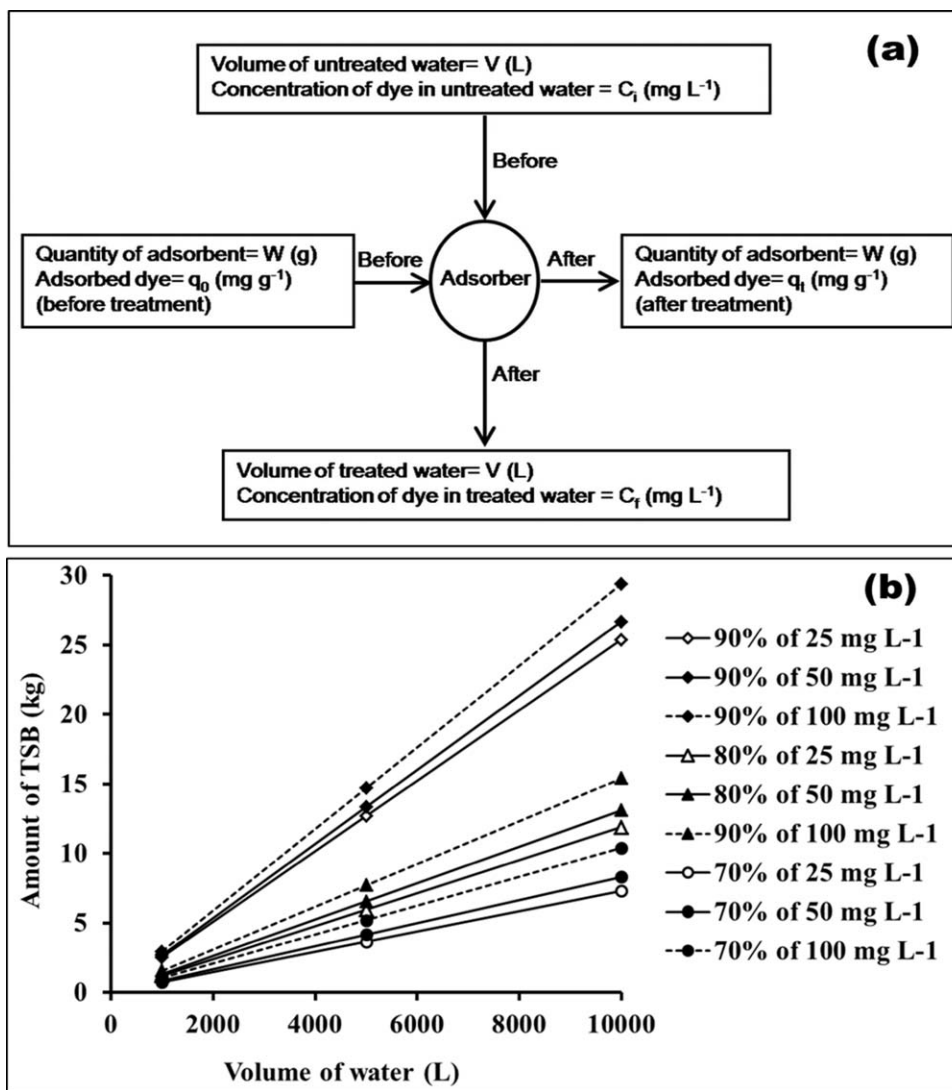


Figure 4. (a) Schematic design of single-stage batch adsorber for TSB-MB adsorption system and (b) amount of TSB required for treating MB contaminated (25-100 mg L⁻¹) water (1000-10,000 L) in the single-stage batch adsorber.

various capacity (1000-10000 L) at varying initial dye concentrations (25-100 mg L⁻¹). The TSB requirement increases with increasing levels of targeted percentage dye removal and initial dye concentration (Figure 4b). For example, to remove MB by 70, 80, or 90% from a batch volume of 1000 L with initial dye concentration of 25 mg L⁻¹, the quantity of TSB required is 0.73, 1.19, or 2.54 kg, respectively. Further, the TSB requirement for treating specified volume of dye solution at a given level of percentage dye removal increases with increasing initial dye concentration (Figure 4b). For example, to remove 90% dye from 1000 L of 25, 50, and 100 mg L⁻¹ dye-bearing water requires 2.54, 2.67, and 2.94 kg TSB, respectively.

CONCLUSION

This investigation demonstrates that TSB, an inexpensive and abundantly available agro-waste, is an excellent adsorbent for removal of MB dye in aqueous system. The dye removal percentage was higher at pH values above zero-point-charge of TSB and for adsorbent particle size < 0.5 mm. TSB with maximum adsorption capacity of 169.5 mg g⁻¹ is far superior to many other plant biomass based adsorbents reported in the literature. The MB removal by TSB is a spontaneous and favorable process ($\Delta G = -5.26$ kJ mol⁻¹) of physio-sorption.

Amount of TSB required to treat various volumes of effluent contaminated with MB was determined. Use of TSB as an adsorbent for sequestering cationic dyes from aqueous systems represents a novel application to the plant biomass that is otherwise considered a waste, and contributes to effective and low-cost remediation of dye bearing wastewater.

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