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Adsorption of dye onto raw and surface modified tamarind seeds: isotherms, process design, kinetics and mechanism

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ABSTRACT

This paper describes the adsorption of basic dye, methylene blue (MB) dye, from aqueous solution using raw tamarind seeds (RTS) and surface modified tamarind seeds (SMTS). The adsorbents (RTS and SMTS) were characterized by using the Fourier Transform Infrared spectroscopy and Scanning Electron Microscopy analysis. The operating parameters such as pH, adsorbent dose, time, initial dye concentration, and temperature that influence the adsorption of MB dye onto adsorbents were investigated. The adsorption equilibrium data were tested by the Langmuir and Freundlich adsorption isotherm model. The results indicated that the adsorption of MB dye onto RTS and SMTS were best fit by the Langmuir and Freundlich model, respectively. The maximum monolayer adsorption capacity for the RTS and SMTS was found to be 16.611 and 34.483 mg/g, respectively. The best described adsorption isotherm model was used to design a single-stage batch reactor. Adsorption kinetics was well described by the pseudo-second-order kinetic model. Adsorption mechanism was explained with the intraparticle diffusion and Boyd kinetic model. The thermodynamic analysis revealed the exothermic and spontaneous nature of adsorption. The results indicated that the tamarind seeds have great potential to remove MB dye from aqueous solution.

Keywords: Adsorption; Isotherms; Kinetics; Methylene blue; Tamarind seeds; Thermodynamics

1. Introduction

The wastewater from the spent dye baths and dye rinsing unit shows unfixed dyes in it. Due to the low biodegradable nature of the dyes and also its color produces serious health problems to human beings and also other living organisms in the environment. Methylene blue (MB) dye is the most commonly used dye for dying cotton, wood, and silk. Some of the problems arises due to the entry of MB dye into the environment such as abdominal and chest pain, nausea, vomiting, diarrhea, gastritis, severe headache, profuse sweating, mental confusion, painful micturation, and methemoglobinemia. Hence, the treatment of wastewater which contains MB dye is highly important before it is going for safe discharge or reuse.

The various treatment methodologies such as biological degradation, photocatalytical degradation, electrochemical oxidation, oxidation with ozone/hydrogen peroxide, ion exchange, membrane filtration, and reverse osmosis have been adopted for the treatment of dye wastewater [1]. However, the above

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mentioned methods show some proved disadvantageous on the effective removal of dyes from the wastewater and also these methods are sometimes fails to satisfy the permissible limits prescribed by the Environmental Protection Agency. Considering all these facts, the adsorption method have proven that the most promising alternative method for the removal of dye from the wastewater. In many places, activated carbon is widely used an adsorbent for the treatment of water and wastewater but its application is limited because due to its cost. This gives an idea to search new low-cost alternative adsorbents. Some of the low-cost adsorbents utilized for the treatments of dye wastewater are orange peels [2], rice husk [3], neem leaf [4], cotton waste [5], cashew nut shell [6], luffa cylindrica fibers [7], yellow passion fruit [8], olive pomace [9], hazelnut shells [10], lemon peel [11], jute processing waste [12], cereal chaff [13], wheat straw [14], papaya seeds [15], peanut hull [16], garlic peel [17], tea waste [18], spent coffee grounds [19], hen feathers [20,21], bottom ash [22,23], de-oiled soya [22,24], coconut-husk [25], activated charcoal [26], wheat husk [26], etc.

In the current work, raw tamarind seeds (RTS) and surface modified tamarind seeds (SMTS) were utilized as an adsorbents for the removal of MB dye from its aqueous solution. The influence of various operating parameters such as solution pH, adsorbent dose, initial MB dye concentration, time, and temperature on the removal of MB dye was investigated. The adsorption equilibrium data were analyzed by adsorption isotherm models such as Langmuir and Freundlich adsorption isotherm equations. The amount of adsorbent required for the treatment of known volumes of effluents was estimated using a single-stage batch adsorber system. The adsorption kinetics of MB dye removal was analyzed by the kinetic models such as pseudo-first-order and pseudo-second-order kinetic equations. The adsorption kinetic data were applied to check the intraparticle diffusion and Boyd kinetic model, to know the adsorption mechanism for the removal of MB dye from its aqueous solution using adsorbents (RTS and SMTS). The thermodynamic studies were also carried out to evaluate the thermodynamic parameters such as standard free energy (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) and also to know the type of adsorption process (either exothermic or endothermic).

2. Experimental

2.1. Preparation of adsorbents

The tamarind seeds were collected from the domestic kitchen waste. The RTS powder was prepared by washing the collected seeds with double distilled water to remove the dust and drying them to remove moisture content. They are then crushed to make fine powder and are then sieved in the size range of 42 mesh particle size. This material was used as an adsorbent for further modification and adsorption studies, and it was abbreviated as RTS. The modified tamarind seeds powder was following the above steps for making the RTS powder and then soaking it in 98% H_2SO_4 for about 24 h. This is then washed to remove the excess acid with double distilled water and then allowed to dry completely at the temperature 80 °C. The above dried sample was grounded to a fine powder. The powder was sieved in the size range of 42 mesh particle size. The modified tamarind seed was abbreviated as SMTS and it was also used as an adsorbent for the removal of MB dye. Fourier Transform Infrared spectroscopy (FTIR) analysis was used to identify the different functional groups present in the RTS and SMTS. This FTIR analysis was carried out at the spectral range varying from 4,000 to 450 cm^{-1} (PE IR SPECTRUM ASCII PEDS 1.60 spectrometer). The surface morphology of the RTS and SMTS was analyzed by the Scanning Electron Microscopy (SEM) analysis at an accelerating voltage of 10.0 kV and with the working distance of 50.0 μm (Leo Gemini 1530 scanning electron microscope).

2.2. Preparation of MB dye solution

All the reagents were used of analytical reagent grade. MB dye powder purchased Merck, India, was used without any further purification. The chemical structure of MB dye is shown in Fig. 1. The initial pH of the solution was adjusted with NaOH or HCl solutions. A stock solution of 500 mg/L was prepared by dissolving the accurately weighed quantities of MB dye in 1 L of double distilled water. The desirable experimental concentration of MB dye solutions was prepared by diluting the stock solution with double distilled water. Before the unknown MB dye concentration measurement, a calibration curve was plotted by using the standard MB dye solutions with the known concentrations. The concentration of MB dye in the solution before and after adsorption was measured by using a UV–vis Spectrophotometer (Shimadzu, Japan) at an absorbance maximum wavelength of 664 nm. The solution pH was measured with a pH meter using a combined glass electrode (Model HI 9025C, Singapore).

2.3. Batch adsorption experiments

The batch adsorption experiments were carried out in a set of 100 mL conical flasks that contain a 100 mL

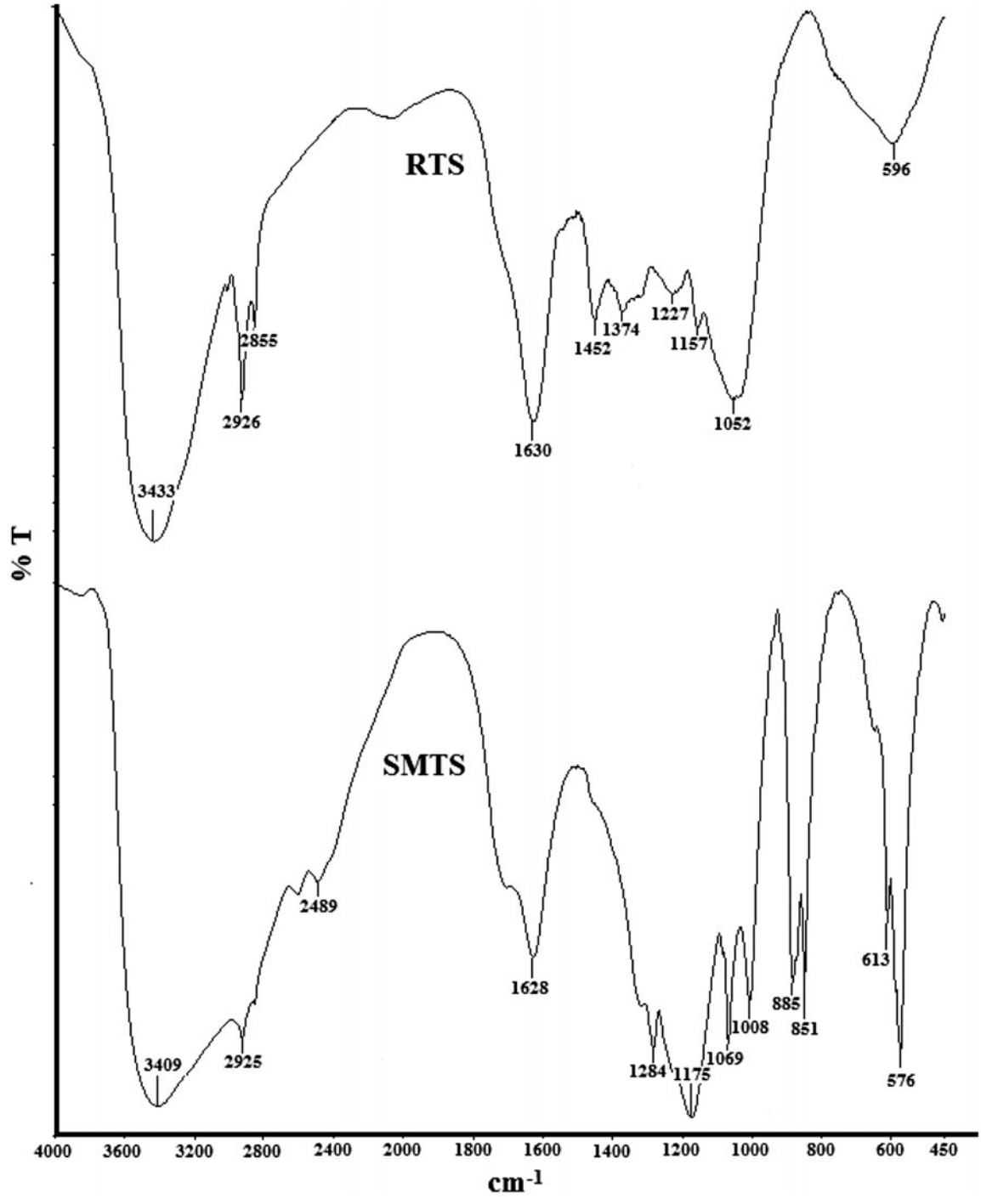

Fig. 1. FT-IR spectrum of RTS and SMTS.

of solution of fixed initial MB dye concentrations, to study the effect of operating parameters such as solution pH, adsorbent dose, contact time, initial MB dye concentration, and temperature for the removal of MB dye from the aqueous solution by using the adsorbents (RTS and SMTS). The conical flasks were kept in a rotary shaker at a constant speed of 80 rpm for a specified contact time (120 min for RTS and 60 min for SMTS). Once the system is attained equilibrium condition, the sample solutions were centrifuged and the supernatant were analyzed for the measurement of MB dye concentration by using the

UV–vis Spectrophotometer. The effect of initial MB dye concentration data was used to test the most commonly used adsorption isotherm models such as Langmuir and Freundlich adsorption isotherm models. The best fitted adsorption isotherm model for the adsorption equilibrium data is used to design a single-stage batch adsorber system. The experimental results obtained from effect of contact time studies were used to test the different kinetic models such as pseudo-first-order and pseudo-second-order kinetic equations. Adsorption mechanism is explained by the intraparticle diffusion and Boyd kinetic model equations. The data obtained from the effect of temperature on MB dye removal were used to check whether the adsorption of MB dye onto adsorbent is exothermic or endothermic and also it is used to find out the thermodynamic parameters such as Gibbs free energy, change in enthalpy, and change in entropy. The percentage removal of MB dye is calculated by using the following equation.

$$\% \text{ Removal of MB dye} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the initial and final concentration of MB dye in the solution (mg/L), respectively. The amount of MB dye adsorbed onto the adsorbent (q_t) was calculated by the following equation:

$$q_t = \frac{(C_i - C_t)\ V}{m} \quad (2)$$

where C_t is the concentration of MB dye in the solution at time t (mg/g), V is the volume of MB dye solution (liter), and m is the mass of the adsorbent (g). The amount of MB dye adsorbed onto the adsorbent at equilibrium, q_e (mg/g), was estimated by using the following equation:

$$q_e = \frac{(C_i - C_e)\ V}{m} \quad (3)$$

where C_e is the concentration of MB dye in the solution at equilibrium (mg/L).

3. Results and discussion

3.1. Characteristics of adsorbents

The FTIR spectrum is obtained to evaluate the chemical functional groups present in an adsorbent and which is shown in Fig. 1. The FTIR spectrum of RTS indicates the various chemical functional groups present in it. The broad band observed at 3,433 cm^{-1} is assigned to the O–H stretching vibration of water and the alcoholic groups. The water present in the adsorbent is also confirmed by the broad band observed at 1,630 cm^{-1}. The intense broad band observed at 1,052 cm^{-1} is assigned to the C–O stretching vibration of the alcoholic groups. The peaks observed at 2,926 and 2,855 cm^{-1} is due to the $–CH_2–$ vibrations of alkyl groups. Their presence is also evident by their $–CH_2–$ bending vibrations at 1,374 and 1,452 cm^{-1}. A shoulder close to 1,738 cm^{-1} is assigned to the C = O vibration of the esters/keto groups. The presence of the ester groups is partly evident by their –COO– vibration at 1,227 cm^{-1}. The results of the FTIR spectrum of the RTS show that it has a large proportion of alkyl groups, alcoholic groups, and smaller amount of ester/keto groups. The presence of a large amount of water indirectly establishes a lot of alcoholic groups. Thus, the FTIR spectrum of RTS reveals that there are several functional groups in RTS that can bind MB dye molecules. The FTIR spectrum of the SMTS is shown in Fig. 1. The peak due to the O–H stretching vibration in the higher energy region is not as intense as that of RTS. Hence, some of the alcoholic groups might be converted into ethers as a result of sulphuric acid treatment. Again, the water content is also reduced, which is evident by the decrease in the intensity of the peak due to its bending vibration at 1,628 cm^{-1}. High carbonization due to sulphuric acid treatment is also very clear by the decrease in the intensity of the peak due to the $–CH_2–$ stretching vibrations at 2,926 cm^{-1}. It is supported by the disappearance of the $–CH_2–$ bending vibrations, which occurred at 1,374 and 1,452 cm^{-1} as seen in FTIR spectrum of RTS. The peak at 1,738 cm^{-1} in the RTS is also retained in this FTIR spectrum of SMTS. Hence, the original ester/keto groups are established unaltered. The conversion of the alcoholic groups into ethers is clearly evident by the well-resolved –C–O–C– asymmetric vibrations at 1,175, 1,069, and 1,008 cm^{-1}. The corresponding bending vibrations are also clearly seen at 851 and 885 cm^{-1}. The results of FTIR spectrum of SMTS shows that the large proportion of the alcoholic groups of the RTS is converted into ether. The material is also made more carbonaceous. The formation of ethers results in the formulation of a matrix with a highly cross-linked network. The FTIR spectrum of the SMTS when compared to that of the RTS, shows that some of the associated functional groups in the SMTS have been modified. This confirms the high potential of the prepared SMTS adsorbent with respect to the removal of MB dye molecules from aqueous solutions.

The SEM images of the RTS and SMTS are shown in Fig. 2. The SEM image of RTS shows that the

surface texture of the RTS was smooth, uneven, and undulating. The vesicles and spaces within this image show no pores within it. The RTS was treated with sulphuric acid, which created different pores on its surface. The SEM image of SMTS shows the irregular pores developed due to the effect of the sulphuric acid solution within the RTS, demonstrated by different sizes of the distributed pores. Based on this observation, it can be concluded that the SMTS has a more adequate morphology for MB dye molecules adsorption than the RTS.

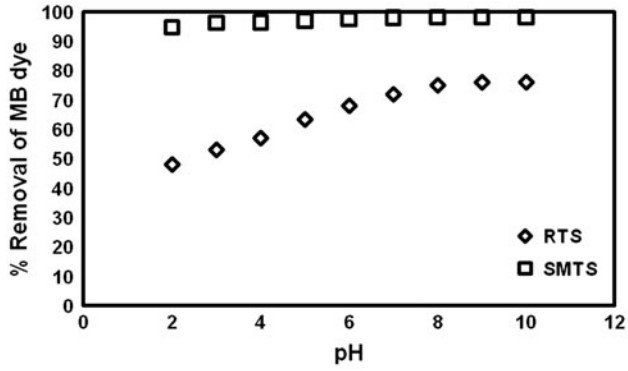

Fig. 3. Effect of pH on MB dye removal removal by RTS and SMTS (initial MB dye concentration = 50 mg/L, RTS dose = 0.6 g, SMTS dose = 0.3 g, time = 120 min for RTS and 60 min for SMTS, volume = 100 mL and temperature = 30 °C).

3.2. Effect of solution pH on the removal of MB dye

The solution pH is an important controlling parameter in the adsorption process. Because, the adsorption of hydronium ions and hydroxyl ions are somewhat easier than other ions present in the solution. This indicates that the adsorption of other ions present in the solution is affected by the solution pH. So, it is important to explain the effect of the solution pH (2.0–10.0) on the removal of MB dye from its aqueous solution (RTS and SMTS). The obtained experimental results are shown in Fig. 3. As seen from Fig. 3, the removal of MB dye is increases with an increase in the solution pH and beyond the pH of 8.0 it reaches almost a constant value. The maximum removal of MB dye is observed at pH of 8.0. At acidic pH, the surface of the adsorbent receives positive charges by absorbing the hydronium ions, which prevents the adsorption of MB dye molecules onto the adsorbent surface due to the electrostatic repulsion between the MB dye molecules and the positive charges of the adsorbent surface. Also, the competition between the hydronium ions and MB dye molecules is increased. As the solution pH is increased then the number of negatively charged adsorbent surface is also increased, which results in the increase in the removal of MB dye molecules due to the electrostatic attraction. But the SMTS-MB dye system have only slight changes in the percentage of MB dye removal when the pH was within the range of 2.0–10.0, which indicates that the electrostatic attraction/repulsion mechanism was not only the adsorption mechanism for the removal of MB dye in the present system. The percentage removal of MB dye molecules was also affected by the chemical reaction between the SMTS adsorbent and the MB dye molecules [27]. The original pH of the MB dye solution was nearer to 8.0 and there is no need to adjust the solution pH for further experimental studies.

3.3. Effect of adsorbent dose on the removal of MB dye

The effect of adsorbent dose (0.1–0.8 g) on the removal of MB dye was investigated by the use of different adsorbent doses between 0.1 and 0.8 g at a MB dye concentration of 50 mg/L and the result is shown in Fig. 4. From Fig. 4, it was observed that the removal of MB dye molecules increases with the

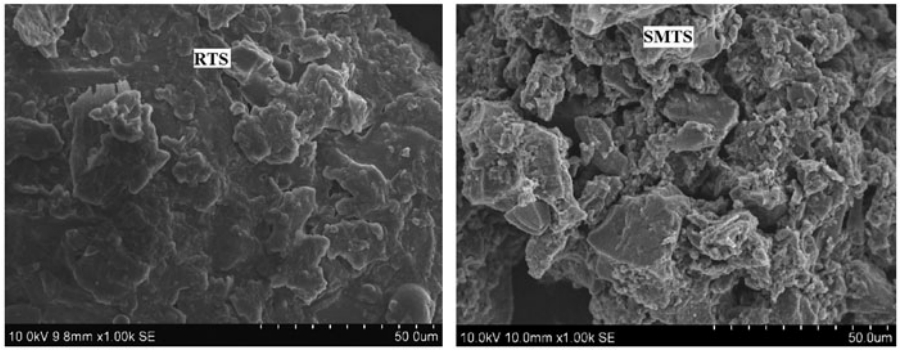

Fig. 2. SEM Image of RTS and SMTS.

increase in adsorbent dose and then reached a saturation value. This may be due to the increase active sites available for the adsorption of MB dye molecules with the increase in adsorbent dose. The maximum removal of MB dye was observed at an optimum dose of 0.6 g per 100 mL for RTS and 0.3 g per 100 mL for SMTS.

3.4. Effect of initial MB dye concentration on the removal of MB dye, adsorption isotherms, and a single-stage batch adsorber design

The effect of initial MB dye concentrations (25–125 mg/L) on the removal of MB dye by the adsorbent (RTS and SMTS) is shown in Fig. 5. From this figure, it can be seen that the removal of MB dye decreases with the increase in MB dye concentration. The maximum removal of MB dye was observed at a lower initial MB dye concentration, because, the ratio of the initial number of MB dye molecules to the available active sites of the adsorbent is low. And also the less removal of MB dye was observed at higher initial MB dye concentration, because, the ratio of the initial number of MB dye molecules to the available active sites of the adsorbent is high. The fixed quantity of adsorbent dose was utilized for the present study, so it can able to remove only a particular quantity of MB dye molecules from its aqueous solution.

Adsorption isotherm is the relationship between the amounts of MB dye molecules adsorbed per unit mass of adsorbent (q_e) and its concentration (C_e) in the equilibrium at constant temperature. The adsorption isotherms are important in determining the maximum monolayer adsorption capacity of MB dye molecules and also diagnose the nature of the adsorption of MB dye molecules onto the adsorbent (RTS and SMTS). The experimental data obtained from the effect of initial MB dye concentration was utilized for testing the different adsorption isotherm models such as Langmuir [28] and Freundlich [29] adsorption isotherm models (Fig. 6). The adsorption isotherm parameters and coefficient of determination values are tabulated in Table 1.

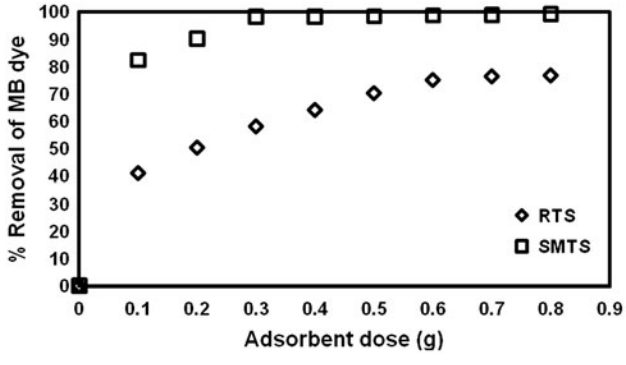

Fig. 4. Effect of adsorbent dose on MB dye removal (initial MB dye concentration = 50 mg/L, pH = 8.0, time = 120 min for RTS and 60 min for SMTS, volume = 100 mL and temperature = 30 °C).

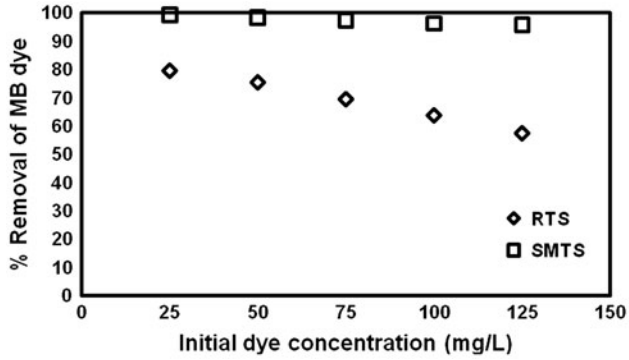

Fig. 5. Effect of initial MB dye concentration on MB dye removal (pH = 8.0, RTS dose = 0.6 g, SMTS dose = 0.3 g, time = 120 min for RTS and 60 min for SMTS, volume = 100 mL and temperature = 30 °C).

The most important assumption of the Langmuir adsorption isotherm model is that the adsorption of MB dye molecules occurs uniformly on the active sites of the adsorbent surface, and when a MB dye molecule is adsorbed onto the active sites of the adsorbent, after that it does not have any effects upon other incident molecules. The linear form of Langmuir adsorption isotherm model is given as follows:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L}\frac{1}{C_e} \tag{4}$$

where q_e is the equilibrium adsorption capacity (mg/g), C_e is the equilibrium concentration of MB dye molecule in the bulk solution (mg/L), q_m is the maximum monolayer adsorption capacity (mg/g), and K_L is the constant related to the free energy of adsorption (L/mg). As can be seen from the coefficient of determination values in Table 1, the Langmuir adsorption model is best suited model for the MB dye-RTS system. This shows that the monolayer adsorption of MB dye molecule is observed onto the RTS surface. The maximum monolayer adsorption capacity from the Langmuir adsorption isotherm model was found to be 16.611 mg/g for RTS and 34.483 mg/g for SMTS. The important characteristics of the Langmuir adsorption isotherm model is also expressed in terms of separation factor (R_L) [30]. The values of R_L were estimated using the following equation:

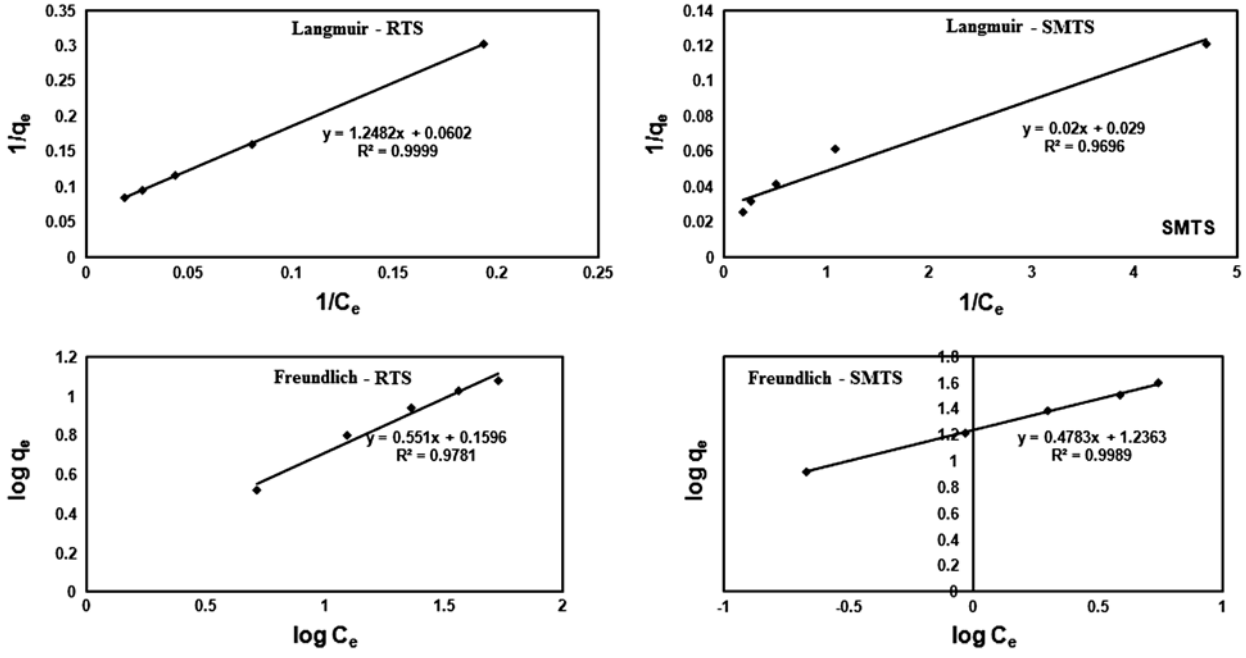

Fig. 6. The linear adsorption isotherms for MB dye removal.

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

where C_o is the initial concentration of MB dye molecules (mg/L) and K_L is the constant related to the free energy of adsorption (L/mg). This R_L value gives important news about the nature of adsorption. The R_L value says that the type of Langmuir adsorption isotherm model is to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). The R_L value was found to be 0.4535–0.1423 (RTS-MB dye system) and 0.0268–0.00549 (SMTS-MB dye system) for the initial MB dye concentration of 25–125 mg/L. The observed R_L values are in the range of 0–1, which indicates that the adsorption of MB dye molecules onto the adsorbent is a favorable adsorption [31].

The adsorption equilibrium data were also fitted to the Freundlich adsorption isotherm model. The main assumption of this isotherm is that the exponential distribution of adsorption active sites and energies and the interaction between the adsorbed molecules onto the adsorbent surface. The linear form of Freundlich adsorption isotherm model is given as follows:

$$\log\ q_e = \log\ K_f + \frac{1}{n}\ \log\ C_e \quad (6)$$

where q_e is the equilibrium adsorption capacity (mg/g), C_e is the equilibrium concentration of MB dye molecules in the bulk solution (mg/L), K_F ((mg/g)(L/mg)$^{(1/n)}$) is Freundlich equilibrium constant, and n (g/L) is the exponent in the Freundlich equation. It is observed from the coefficient of determination values in Table 1, the Freundlich adsorption isotherm model is a best suitable isotherm model for the MB dye-SMTS system. This shows that the multilayer adsorption of MB dye molecule is observed onto the SMTS surface. The value of "n" shows the degree of non-linearity between the MB dye concentration and adsorption as follows: when $n = 1$, adsorption is linear; $n < 1$, adsorption is a chemical process; and $n > 1$, adsorption is a physical process. The values of n observed between 1 and 10 for MB dye-RTS and MB dye-SMTS systems. This indicates that the adsorption of MB dye molecules onto the adsorbent takes place through a physical process [32].

In order to predict the adsorber size and efficiency in the removal of MB dye molecules by the adsorbent

Table 1
The adsorption isotherm parameters for the removal of MB dye

Isotherm model	Parameters	Values		R^2	
		RTS	SMTS	RTS	SMTS
Langmuir	q_m (mg/g)	16.611	34.483	0.9999	0.9696
	K_L (L/mg)	0.0482	1.45		
Freundlich	K_F ((mg/g)(L/mg)$^{(1/n)}$))	1.444	17.231	0.9781	0.9989
	n (g/L)	1.815	2.091		

(RTS and SMTS), an empirical procedure based on the adsorption equilibrium data has been designed [33]. A schematic diagram of a single-stage batch adsorber is shown in Fig. 7. The main objective of the proposed design is to reduce the initial MB dye concentration from C_0 (mg/L) to final concentration C_e (mg/L) of MB dye solution volume V (L). The amount of adsorbent is M (g) and the MB dye loading changes from q_o (mg/g) to q_e (mg/g). The material balance for a single-stage batch adsorber system was made at equilibrium condition (i.e. the best fitted adsorption isotherm model such as Langmuir adsorption isotherm model for MB dye-RTS system and Freundlich adsorption isotherm model for MB dye-SMTS system were used).

$$V\ (C_0 - C_e) = M(q_e - q_o) = Mq_e \tag{7}$$

The above Eq. (7) may be rewritten as:

$$M = \frac{(C_0 - C_e)}{q_e} V \tag{8}$$

The above Eq. (8) was used to estimate the amount of adsorbent required to treat the known volume (1–10 L) of the MB dye solution (Fig. 7).

3.5. Effect of contact time on the removal of MB dye, adsorption kinetics, and mechanism

The effect of contact time (0–150 min) on the removal of MB dye by the adsorbent (RTS and SMTS) is shown in Fig. 8. From this figure, it was observed that the percentage removal of MB dye increases with increase in contact time and it reaches equilibrium time at 120 min for MB dye-RTS system and 60 min for MB dye-SMTS system. At less contact time, the

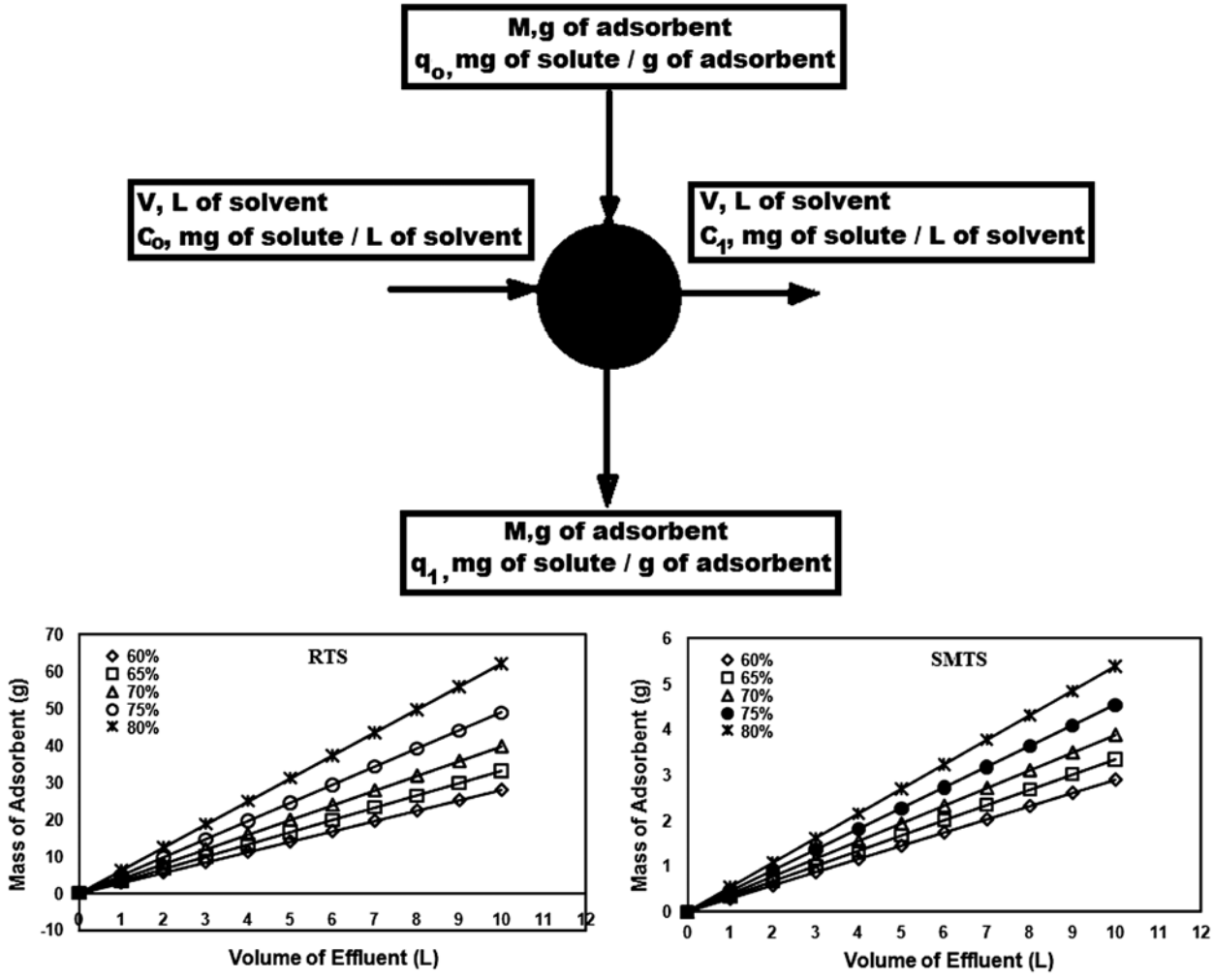

Fig. 7. A single stage batch adsorber design.

residential time provided for the adsorption of MB dye onto the adsorbent is less, so, the percentage removal of MB dye is less. If the residential time provided for the adsorption of MB dye onto the adsorbent is high then the percentage removal of MB dye observed at maximum.

To estimate the kinetic parameters which governs the adsorption kinetics of MB dye molecules onto the adsorbent (RTS and SMTS), the adsorption kinetics data acquired empirically were fitted to the pseudo-first-order [34] and pseudo-second-order [35] kinetic models (Fig. 9). The linear form of pseudo-first-order kinetic model is given by the following equation:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (9)$$

where q_e is the adsorption capacity at equilibrium (mg/g), q_t is the adsorption capacity at time t (mg/g), and k_1 is the pseudo-first-order kinetic rate constant (min^{-1}). The linear form of pseudo-second-order kinetic model is given by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

where q_e is the adsorption capacity at equilibrium (mg/g), q_t is the adsorption capacity at time t (mg/g), h is the initial adsorption rate ($mg\,g^{-1}\,min^{-1}$), and k_2 is the pseudo-second-order kinetic rate constant ($g\,mg^{-1}\,min^{-1}$). The estimated parameters such as q_e, h, k_1 and k_2, and R^2 values were listed in Table 2 for both MB dye-RTS and MB dye-SMTS systems. The comparison was made between the experimental equilibrium adsorption capacity (q_e, exp) values and the calculated adsorption capacity (q_e, cal) values, which shows that the calculated adsorption capacity (q_e, cal) values were very close to the experimental equilibrium adsorption capacity (q_e, exp) values for the pseudo-second-order kinetic model than the pseudo-first-order kinetic model. Moreover, the coefficients of determination (R^2) values for the pseudo-second-order kinetic model were higher than that of the pseudo-first-order kinetic model and it is more than 0.98. Therefore, it can be concluded that the adsorption of MB dye onto the adsorbent (RTS and SMTS) follows the pseudo-second-order kinetic model, and assumes that the chemisorption is the rate controlling step [35].

The rate determining step in the adsorption process is the most important step to understand the adsorption mechanism for the removal of MB dye by the adsorbent (RTS and SMTS). The MB dye molecules transfer in the solid-liquid non-catalytic heterogeneous adsorption process is usually characterized by either fluid film diffusion (external diffusion) or intraparticle diffusion (internal diffusion) or both (external diffusion and external diffusion). The following three consecutive steps were involved in the adsorption of adsorbate molecules onto the adsorbent surface (Fig. 10).

(1) The movement of the adsorbate molecules from the bulk solution to the external surface of the adsorbent through the fluid film (Film diffusion or external diffusion).
(2) Adsorbate molecules move towards the interior part of the pore of the adsorbent particles (Intraparticle diffusion or internal diffusion).
(3) Adsorption of the adsorbate molecules on the interior surface of the pores and capillary spaces of adsorbent (Adsorption).

The adsorption kinetic data were analyzed by an Weber and Morris intraparticle diffusion model [36] and Boyd kinetic model [37] to elucidate the diffusion mechanism (i.e. external and internal diffusion) in the adsorption of MB dye molecules onto the adsorbent (Fig. 10).

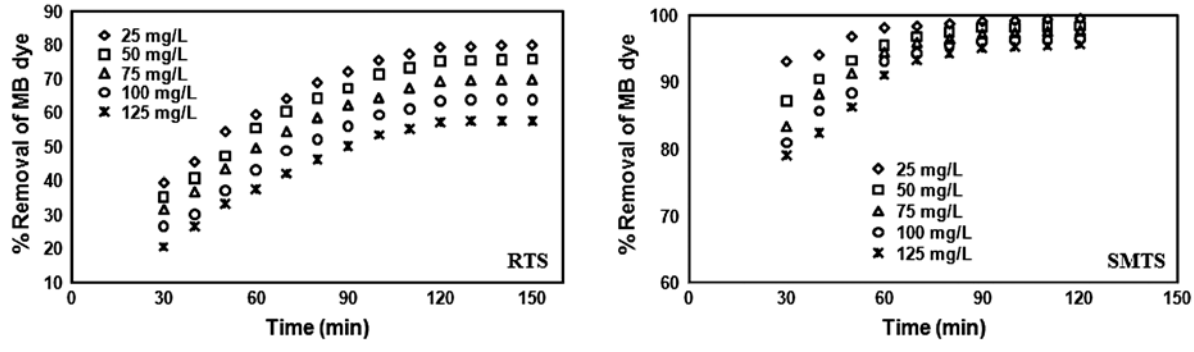

Fig. 8. Effect of contact time on MB dye removal (initial MB dye concentration = 25–125 mg/L, pH = 8.0, RTS dose = 0.6 g, SMTS dose = 0.3 g, volume = 100 mL and temperature = 30 °C).

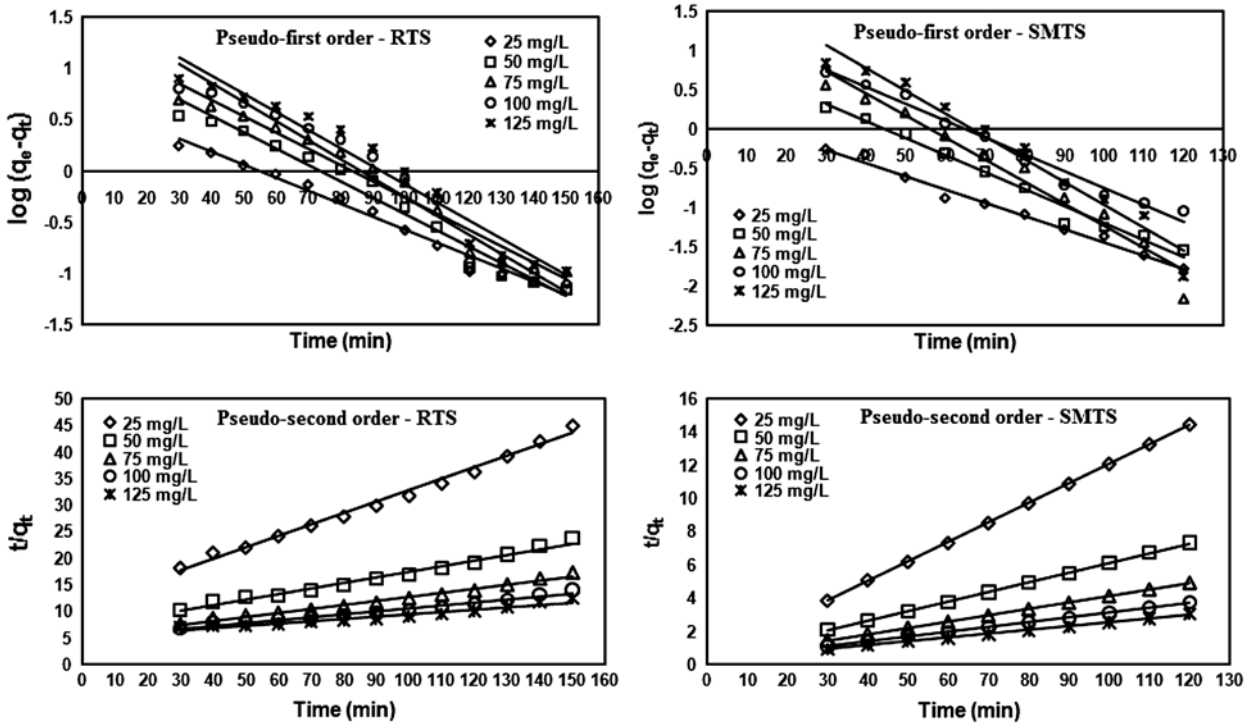

Fig. 9. Kinetic models.

The intraparticle diffusion model is given by the following equation:

$$q_t = k_p t^{1/2} + C \quad (11)$$

where q_t is the adsorption capacity at time t (mg/g), k_p is the intraparticle diffusion rate constant, (mg/gmin$^{1/2}$), "t" is the time (min), and C is the intercept. The values of k_p, C and, R^2 were listed in Table 3. From the Fig. 10 of intraparticle diffusion model for both MB dye-RTS and MB dye-SMTS systems, it was observed that the line does not passes through the origin, which indicates the intraparticle diffusion is not only the sole rate determining step in the adsorption of MB dye onto the adsorbent, but also be the rate determining step of adsorption or film

Table 2
Kinetics values estimated for the removal of MB dye

Conc. of MB dye solution (mg/L)	Pseudo-first order equation			Pseudo-second order equation				
	k_1 (min^{-1})	q_e, cal (mg/g)	R^2	k_2 (g mg^{-1} min^{-1})	q_e, cal (mg/g)	h (mg g^{-1} min^{-1})	q_e, exp (mg/g)	R^2
Kinetic model—RTS								
25	0.0290	4.8574	0.9819	0.00664	3.6533	0.0886	3.412	0.9913
50	0.0366	14.7741	0.9709	0.00264	7.4250	0.1458	6.385	0.9835
75	0.0364	21.1300	0.9643	0.00180	10.3155	0.1915	8.824	0.9844
100	0.0426	39.6735	0.9483	0.00086	15.1159	0.1976	10.725	0.9812
125	0.0405	42.2766	0.9576	0.00056	18.7273	0.1962	12.124	0.9822
Kinetic model—SMTS								
25	0.0389	1.7522	0.9872	0.04199	8.5034	3.0367	8.312	0.9999
50	0.0497	9.1538	0.9823	0.01136	17.1821	3.3557	16.421	0.9998
75	0.0647	36.9403	0.9644	0.00584	25.9067	3.9200	24.422	0.9996
100	0.0652	55.2713	0.9797	0.00373	34.4827	4.4345	32.231	0.9992
125	0.0670	88.0846	0.9666	0.00247	43.2901	4.6318	39.841	0.9990

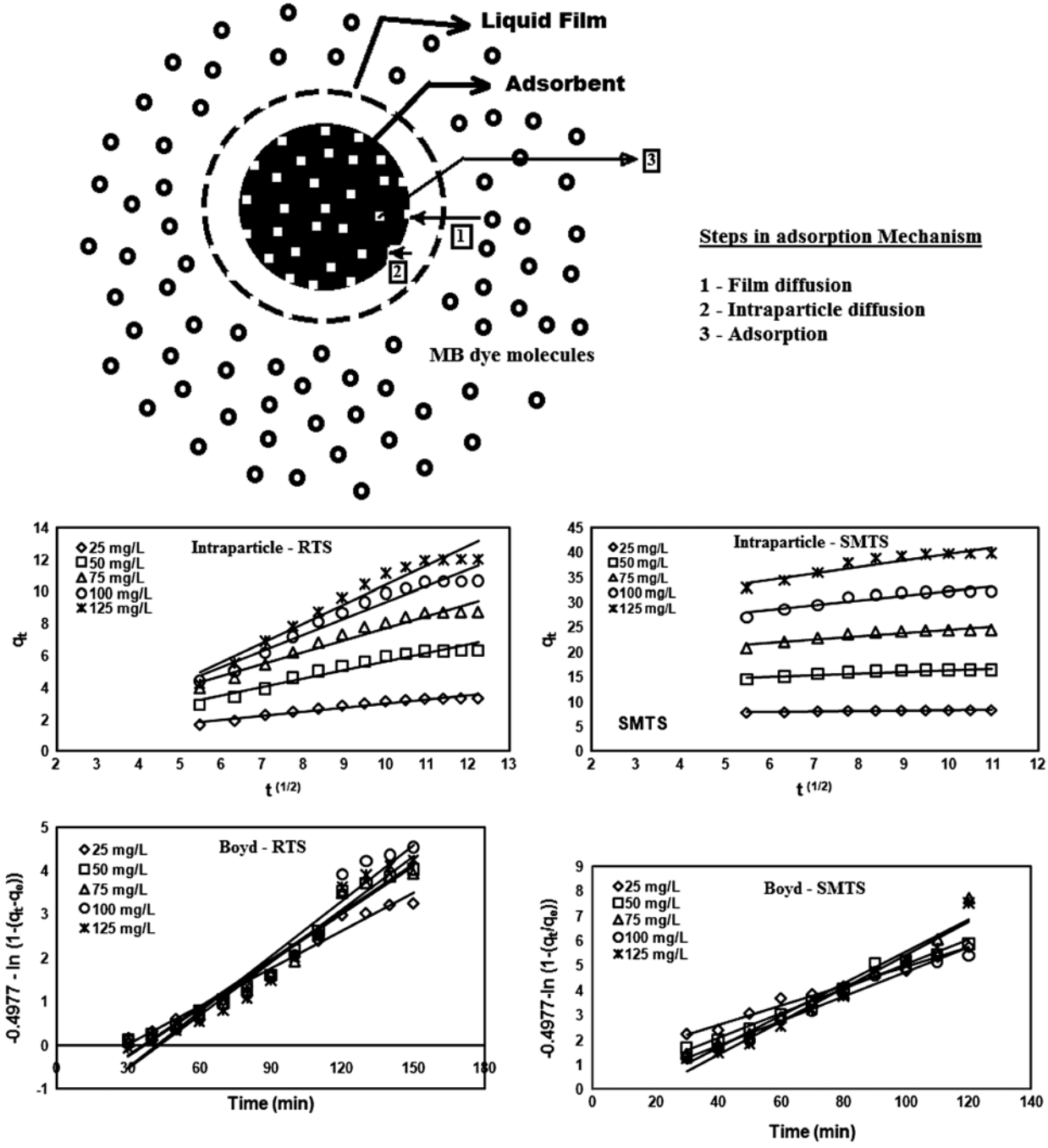

Fig. 10. Adsorption mechanism.

diffusion or all may be operating simultaneously. This deviation from the origin may be due to the difference in the rate of mass transfer in the initial and final stages of adsorption of MB dye onto the adsorbent. The actual slowest step in the adsorption of MB dye onto the adsorbent (RTS and SMTS) process was identified and discussed by the Boyd kinetic model [37]. The Boyd kinetic equation is given by the following equation:

$$F = \frac{q_t}{q_e} = 1 - \frac{6}{\pi^2}\exp(-Bt) \quad (12)$$

The above Eq. (12) may be rearranged into the following form of the equation:

$$Bt = -0.4977 - \ln(1 - F) \quad (13)$$

Table 3
Intraparticle diffusion rate parameter and effective diffusivity calculation for the removal of MB dye

Conc. of MB dye solution (mg/L)	Intraparticle diffusion model			Boyd kinetic model		
	k_p (mg/g.min$^{1/2}$)	C	R^2	B	D_i (x 10^{-12} m^2/s)	R^2
Adsorption mechanism - RTS						
25	0.2581	0.418	0.9422	0.0289	1.5288	0.9819
50	0.5316	0.3148	0.9427	0.0367	1.9414	0.9709
75	0.7520	0.2105	0.9508	0.0365	1.9309	0.9643
100	0.9151	0.1421	0.9508	0.0426	2.2535	0.9483
125	1.0061	0.0101	0.9532	0.0405	2.1425	0.9576
Adsorption mechanism - SMTS						
25	0.0959	7.3272	0.8463	0.0388	2.0525	0.9872
50	0.3297	13.095	0.8655	0.0498	2.6344	0.9823
75	0.6156	18.255	0.8526	0.0647	3.4226	0.9644
100	0.9244	22.922	0.8585	0.0496	2.6238	0.9797
125	1.3038	26.753	0.8802	0.0671	3.5496	0.9666

where q_e is the adsorption capacity at equilibrium (mg/g), q_t is the adsorption capacity at time t (mg/g), F is the fraction of MB dye molecules adsorbed at time t, and Bt is a mathematical function of F. From the Fig. 10 of Boyd kinetic model, it can be seen that the line does not passes through the origin, which indicates that the intraparticle diffusion is not only the sole rate determining step in the adsorption of MB dye onto the adsorbent, but also be the rate determining step of film diffusion.

3.6. Effect of temperature on the removal of MB dye and thermodynamic study

The effect of temperature (30–60°C) on the removal of MB dye by the adsorbent (RTS and SMTS) is shown in Fig. 11. From Fig. 11, it was observed that the percentage removal of MB dye decreases with the increase in the temperature. This may be due to the reduction in the surface activity of the adsorbent and which indicates the adsorption of MB dye onto the adsorbent follows exothermic process. The maximum removal of MB dye was observed at the temperature of 30°C. The effect of temperature data was utilized for the estimation of thermodynamic parameters such as Gibbs free energy (ΔG°), change in enthalpy (ΔH°), and change in entropy (ΔS°) for both MB dye-RTS and MB dye-SMTS systems from the following basic equations of thermodynamics (Fig. 12) and the values are listed in Table 4.

$$\Delta G^\circ = -RT \ln\left(\frac{C_{Ae}}{C_e}\right) \tag{14}$$

$$\log\left(\frac{C_{Ae}}{C_e}\right) = \frac{\Delta S^\circ}{2.303\,R} - \frac{\Delta H^\circ}{2.303\,RT} \tag{15}$$

where C_{Ae} is the amount of MB dye molecules adsorbed onto the adsorbent per liter of solution at

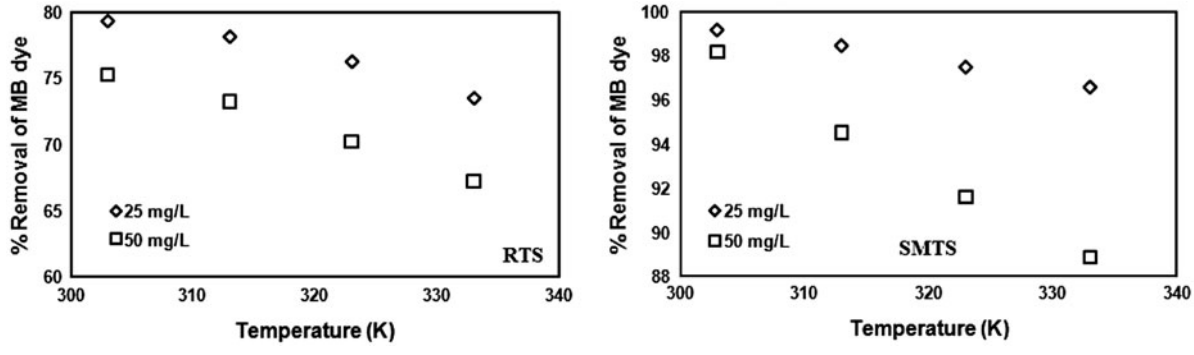

Fig. 11. Effect of temperature on MB dye removal (initial MB dye concentration = 25–50 mg/L, pH = 8.0, RTS dose = 0.6 g, SMTS dose = 0.3 g, time = 120 min for RTS and 60 min for SMTS and volume = 100 mL).

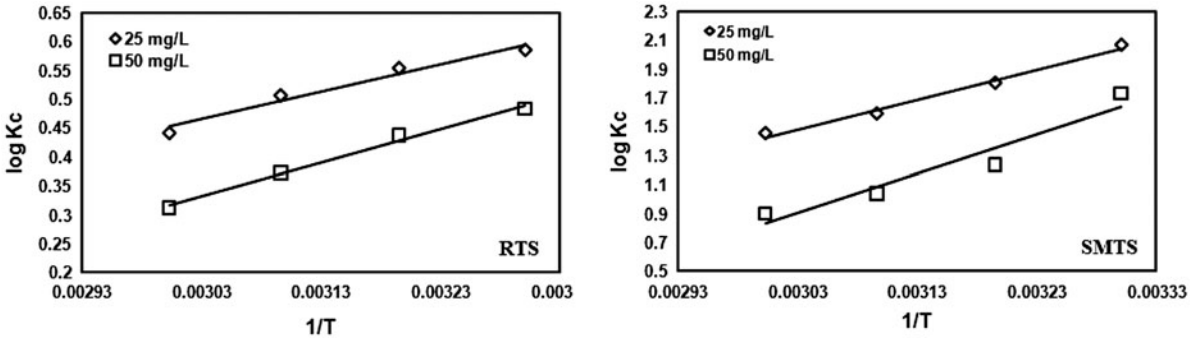

Fig. 12. Thermodynamic study.

Table 4
Thermodynamic parameters for the removal of MB dye

Conc. of MB dye solution (mg/L)	ΔH° (kJ/mol)	ΔS° (J/mol/K)	ΔG° (kJ/mol)			
			30°C	40°C	50°C	60°C
Thermodynamic study—RTS						
25	−9.131	−18.760	−3.391	−3.316	−3.132	−2.817
50	−11.097	−27.252	−2.801	−2.620	−2.306	−1.992
Thermodynamic study—SMTS						
25	−39.838	−92.349	−11.989	−10.801	−9.828	−9.261
50	−52.136	−140.666	−10.032	−7.406	−6.423	−5.755

equilibrium (mg/L), C_e is the concentration of MB dye molecules in the solution at equilibrium (mg/L), R is the gas constant (8.314 J/mol/K), and T is the temperature (K). The negative value of ΔG° indicates the feasibility of the adsorption of MB dye onto the adsorbent process. The ΔG° value is more negative with decrease in temperature, which suggests that the lower temperature makes the adsorption of MB dye onto the adsorbent is easier. The negative value of ΔS° suggests that the adsorption of MB dye onto the adsorbent is enthalpy driven. The negative value of ΔH° indicates that the adsorption of MB dye onto the adsorbent is exothermic in nature.

4. Conclusions

In order to determine the potential use of native and SMTS as an efficient adsorbent for the treatment of synthetic MB dye wastewater, a number of batch adsorption experiments were carried out. The FTIR study showed the presence of different chemical functional groups present in the RTS and SMTS which are responsible for the adsorption of MB dye onto the adsorbents. Adsorption of MB dye onto the adsorbents may be influenced by the variety of operating parameters such as solution pH, adsorbent dose, contact time, initial MB dye concentration, and temperature. Adsorption equilibrium data were analyzed using linear form of Langmuir and Freundlich adsorption isotherm models. The Langmuir adsorption isotherm model is a best suitable adsorption isotherm model for the experimental data obtained from the adsorption of MB dye onto the RTS and the Freundlich adsorption isotherm model is a most preferred isotherm model for the MB dye-SMTS system. The maximum monolayer adsorption capacity for the RTS and SMTS were estimated from the Langmuir adsorption isotherm model was 16.611 and 34.483 mg/g, respectively. A single-stage batch adsorption system was designed based on the Langmuir and Freundlich adsorption isotherm model for RTS-MB dye system and SMTS-MB dye system, respectively. The kinetics of MB dye adsorption was very well described by the pseudo-second-order kinetic model with the higher coefficient of determination values for all MB dye concentrations studied. The results obtained from the adsorption mechanism shows that the adsorption of MB dyes onto adsorbents were controlled by both film and particle diffusion. The negative value of ΔG° shows that the adsorption of MB dyes onto the RTS and SMTS is a spontaneous process. The ΔS° was found to have negative values for the adsorption of MB dye onto adsorbents, which shows a decrease in the randomness at solid-liquid surface during the adsorption of MB dye onto the adsorbent surfaces. And also a negative value of ΔH° shows the adsorption of MB dye onto the adsorbent surface is exothermic, which is identified from the decrease in the percentage removal of MB dye with the increase in the temperature. Based on the above results obtained, it can be concluded that the RTS and SMTS is a most suitable adsorbent for the removal of MB dye from the aqueous solution in terms of low cost, natural, and abundant availability.

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