

Research Article

Activated Sawdust-Based Adsorbent for the Removal of Basic Blue 3 and Methylene Green from Aqueous Media

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Dye pollution is a serious threat to aquatic environment and human health. Although activated carbon is an efficient adsorbent for dye reclamation from effluents, its expressive nature renders its use on large commercial scales. On the other hand, waste biomasses are not effectively used for any beneficial purposes. Sawdust is a waste biomass of wood mills, and due to its small particle sizes, it has the potential to be used as adsorbent. In spite of its uses for cooking purposes, it is sometimes used as adsorbent as such or converted into activated carbon. In raw form, it is not a good adsorbent; however, its adsorption capacity can be increased by applying chemical modifications. In the present study, sawdust of paper mulberry (*Broussonetia papyrifera*) was used as adsorbent for the removal of basic blue 3 and methylene green from water after chemical modification with NaOH and HCl in 1:1. The prepared adsorbent was characterized by SEM and FTIR, whereas the surface area was estimated through an already reported method in literature. Batch experiments were performed to determine the isothermal and kinetic parameters of the selected dyes adsorption on activated sawdust. The effect of adsorbent dosage and temperature on adsorption were also evaluated. The best fit of the kinetic data was achieved with pseudosecond-order model for which R^2 values were approximately equal to 1 whereas Langmuir model was most suitable model to explain the isothermal data. The optimum adsorbent dosage was 0.05 g for both of the selected dyes. Different thermodynamic parameters, such as enthalpy ($\Delta H = 18.5$ and 8.334 kJ/mol respectively for basic blue 3 and methylene green), entropy ($\Delta S^\circ = 62.41$ and 29.22 kJ/molK respectively for basic blue 3 and methylene green), and Gibbs free energy ($\Delta G^\circ = -83.6$, -410 , and -1658 kJ/mol (basic blue)/ -65 , -519 , and -1139 kJ/mol (methylene green), were estimated, and the process was found to be endothermic, spontaneous, and feasible. The increase in ΔG° with increase in temperature indicates that the adsorption process is favorable at high temperature. The prepared adsorbent could be effectively used in the reclamation of water loaded with other contaminants; however, further experiments are needed to increase the adsorption capacity of the adsorbent.

1. Introduction

Water body pollution comes from the domestic sewage and more importantly from the industrial effluents. Wastewater treatment is an important issue since water is the basic need of human, and its pollution is one of the most serious public health concerns. Besides drinking, in everyday life, clear water is also the need of other domestic uses. To fulfill the domestic demands of increasing population, rapid industrialization has been encountered from last few decades which have badly contaminated drinking water supplies everywhere in the world, and presently, it is almost difficult to get clear water for household and drinking purposes in many parts of the world. The industrial effluents are loaded with various poisonous substances, and their entry into water bodies is a serious issue rendering the water unfit for drinking purposes. Among the pollutants, synthetic organic dyes are considered as most serious threat that are not only toxic but also interfere photosynthesis of aquatic plants which in turn affects the oxygen supplies for the deep water dwellers. They are extensively used for coloring textile fibers, such as polyester and cotton [1]. Nearly 1×10^5 pigments/dyes are utilized in various industries with approximate use of about 7×10^5 tons per year all over the world [2]. A considerable part of these dyes are discharged into water bodies, and even in some cases, they give rise to other toxic substances on their exposure to sunlight or microorganisms and have thus become the major pollutant of the water bodies across the world. For scientists, it is a challenge to discover new ways to treat dye-loaded effluents of various industries, especially from the dye and fabric industries as well as from the food coloring, cosmetics, paper, and carpet industries [3]. Colored water cannot be used for agricultural purposes, and also, it affects the photosynthetic capability of plants by interference in the penetration of sunlight into deep waters as mentioned before [4, 5]. Polluted water badly affects human health and can cause health problems like diarrhea, dysfunction of kidney, liver, and the central nervous system [6, 7]. Many human diseases such as respiratory diseases, dermal, colon, and rectum cancer are also caused by polluted water [8]. Moreover, dye sewages also contain poisonous chemicals which disturb microbial growth and could be poisonous/carcinogenic to living organisms such as mammals [9]. There is need to find out efficient ways of treating dye-loaded effluents.

Numerous methods, such as flocculation, coagulation, adsorption, biodegradation, membrane removal, oxidation, ion-exchange, sedimentation, and selective bioadsorbents, are used for the removal of dyes from water. None of these methods are 100% efficient. Merits and demerits of every method have been reported in literature [10–12]. Most of the mentioned methods have some disadvantages like high operational cost and production of high amount of sludge, whereas in some cases, these methods have very less or no efficiency to remove the targeted dyes. Adsorption among them is the most efficient technique used to remove various organic and inorganic pollutants including dyes from wastewater due to availability of variety of adsorbents with wide range of particle sizes and low cost. This technique is also

superior as compared to other techniques due to its simple design and easy handling [13–17]. Various adsorbents have been reported in literature, used as dye adsorbents like activated clay, kaolinite, bentonite, hydrogels, modified alumina, organic metal framework, chemically activated carbon, metal oxide nanoparticles, molecularly imprinted polymer, monometallic nanoparticles, and bimetallic nanoparticles. Most of the mentioned adsorbents are comparatively expensive and less efficient for the removal of dyes; therefore, an alternative cheap adsorbents are needed. Generally, the regenerability, availability, and operational costs are the criteria taking into consideration while selecting a given adsorbent to be used for a given adsorbent. These days, the scientists are trying to convert low-priced agricultural waste material into efficient adsorbents. In some cases, they have converted them into activated carbons or even activated through treatment with different types of chemicals to get the efficient adsorbents [18]. Sawdust is a byproduct of the wood mills, where a variety of woods are cut down for different purposes which could be used as efficient low cost adsorbent if activated chemically [19, 20]. Its porous nature and small sized particles would offer a high surface area for the adsorption of dyes and other water pollutants.

The sawdust of mulberry plant has not been previously used as such or in activated form as adsorbent for any dye adsorption. Therefore, the current study was aimed at highlighting the adsorption capability of paper mulberry sawdust used as adsorbent for the removal of basic blue 3 (BB-3; Figure 1(a)) and methylene green (MG; Figure 1(b)) dyes being a cheap and abundant substance available everywhere, and it was expected that after activation, it will have outstanding adsorption characteristics. The activated sawdust was characterized by SEM and FTIR techniques as well. The work is a novel, as the chemically modified sawdust has not been used as adsorbent for the selected dyes before. Further enhancement of the adsorption capacity of the prepared adsorbent is needed practically in industries.

2. Materials and Methods

2.1. Experimental Setup. Basic blue 3 and methylene green dyes were used as the adsorbates that were adsorbed on the activated sawdust derived from paper mulberry wood. Both BB-3 and MG were purchased from Sigma Aldrich, Germany, and used as such without any further purification. Other chemicals used, such as HCl (99%), HNO₃ (99%), and NaOH (99%), were also purchased from Sigma Aldrich, Germany. The physiochemical properties of selected dyes are given in Table 1.

2.2. Instrumental Technique Applied. The prepared adsorbent was characterized by scanning electron microscopy (SEM, JSM5910, JEOL, Tokyo, Japan) and FTIR (Fourier transform infrared spectrophotometer). The instrument UV-vis spectrophotometer (UV-1800, Shimadzu Scientific Instruments Inc, Tokyo, Japan) was used to determine the concentration of dye solutions.

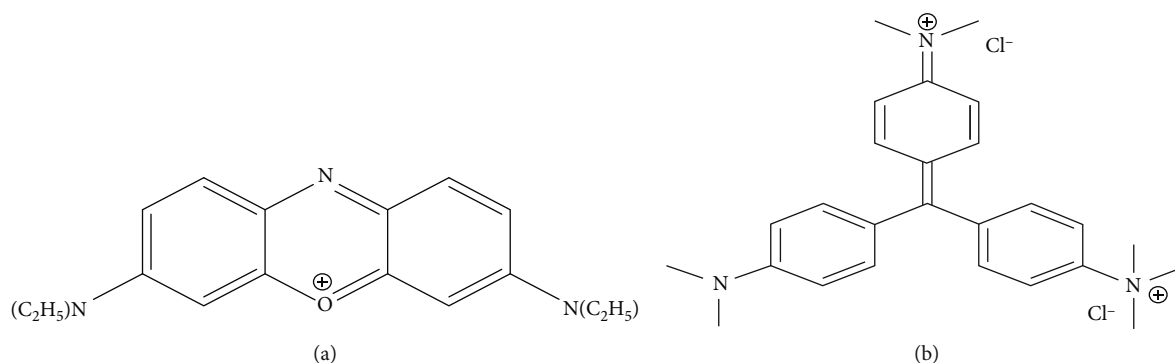


FIGURE 1: Chemical structures of (a) BB-3 and (b) MG.

TABLE 1: Physiochemical properties of the BB-3 and MG.

Chemical name	BB-3	MG
Molecular formula	$C_{20}H_{26}ClN_3O$	$C_{27}H_{35}BrClN_3 \cdot ZnCl_2$
Molecular weight	359.89 g/mol	653.24 g/mol
Classification	Cationic	Cationic
Physical description	Blue powder	Green powder
λ max	654 nm	653 nm
Solubility	Soluble in water	Soluble in water

2.3. Preparation of Activated Sawdust. Paper mulberry sawdust were collected from the local wood machine at Kalpani District Buner, KP, Pakistan, and was grounded well to fine powder. The grounded sawdust was passed through a sieve mesh (0.6 mm and particle size 0.1 mm) to obtain raw adsorbent of uniform sizes. For activation, 100 g of raw adsorbent was treated with solutions of HCl and NaOH in 1 : 1 ratio (to remove impurities). It was then rinsed with distilled water and finally dried at 90°C in an oven for 24 h. The dried sample was then cooled and stored in bottles till further use. The steps involved in adsorbent preparation are summarized in Figure 2 as follows:

2.4. Surface Area Measurement. About 1.35 g of the sawdust in 30 ml water was stirred at 25°C for 1 h. The resultant mixture was acidified to pH 3. Now NaCl (30 g) was added to the mixture, and its pH was adjusted to 4. Finally, the pH of the mixture was raised to 9 by addition of the 0.1 M NaOH, and its volume was noted. Equation (1) was used to estimate surface area:

$$A = 32V - 25, \quad (1)$$

where V is the volume of NaOH which raised the pH from 4 to 9.

2.5. Adsorption Experiments. To determine the kinetic parameters of adsorption, two concentrations 0.001 M and 0.002 M were contacted with 0.05 g of the prepared adsorbent and shaken for 8 h at room temperature on an automated shaker. The samples were withdrawn at various

internal of time, and the remaining concentration in the solution after adsorption was determined through spectrophotometer at wavelength 653 nm and 654 nm, respectively, for BB-3 and MG. Different kinetic models: pseudofirst-order and pseudosecond-order models and intraparticle diffusion model were applied to calculate the values of different kinetic parameters.

In order to find out different parameters of adsorption isotherm, 0.001, 0.002, 0.003, 0.004, 0.005, 0.006, and 0.007 M solutions were prepared from each of which 20 ml volume was contacted with 0.05 g of sawdust and shaken well for 30 min. Various isotherm models were applied to get best fit of isothermal adsorption data.

The effect adsorbent dosage was determined for both dyes where 0.001 M was contacted with different amounts of adsorbents ranging from 0.01 to 0.4 g and shaken for 30 min.

To evaluate the temperature effect on the process of adsorption, 0.05 g of sawdust was treated with 20 ml solution of dyes in reagent bottles and shaken well at 283, 293, and 303 K. The values of different parameters of thermodynamics such as enthalpy, entropy, and Gibbs free energy changes were calculated from Van't Hoff plot.

3. Results and Discussion

3.1. Characterization of the Sample

3.1.1. SEM Study. Scanning electron microscopy (SEM) technique was used to find out the characteristic features and visualize the surface morphology of activated sawdust. Various magnification images of the sample are shown in Figure 3. The figures clearly show that sawdust samples have irregular pores and cavities. Due to these pores and cavities, a rough interface has been formed which can easily adsorb dye molecules and other pollutants.

3.1.2. FTIR Analysis. Analysis of adsorbents by FTIR identifies the functional groups that are responsible for the adsorption of adsorbates which can be recognized from the presence of characteristic peak at certain wavenumbers. Figure 4 shows the FTIR spectra of activated sawdust. The peak at 3337 cm^{-1} gives information about the presence of

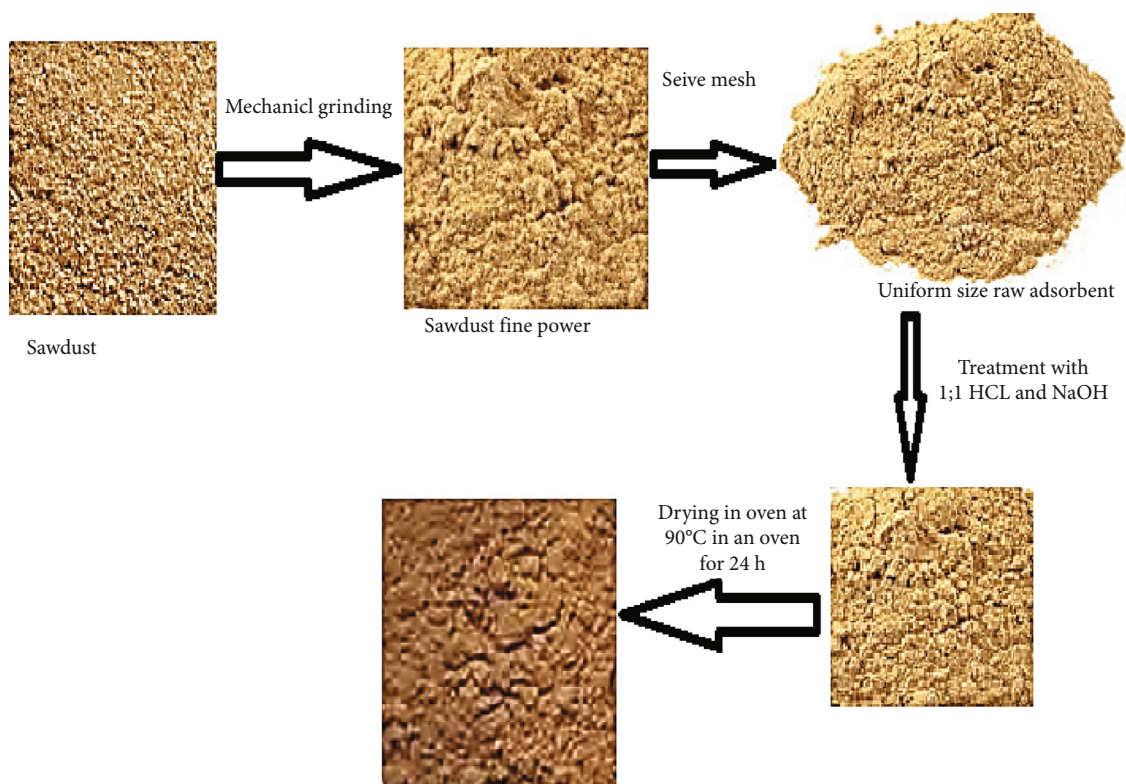


FIGURE 2: Processing of sawdust into a fine treated adsorbent.

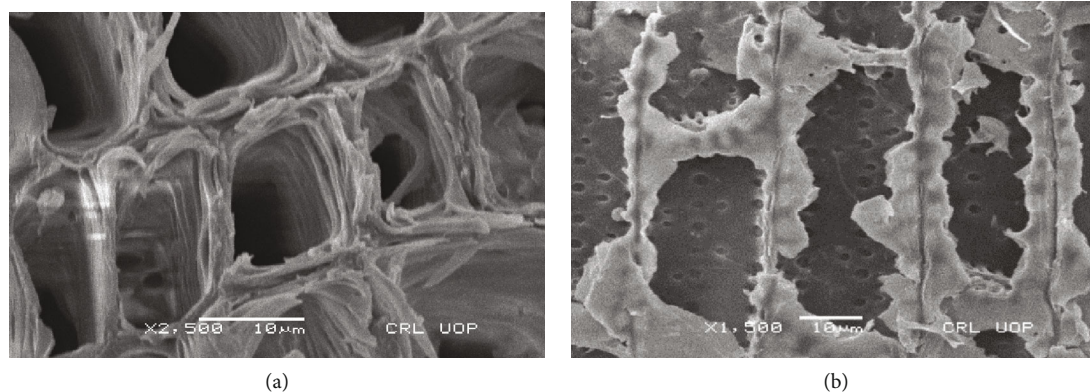


FIGURE 3: SEM images of sawdust at magnifications: (a) $\times 2500$ and (b) $\times 1500$.

hydroxide group (OH) that may belong to carboxylic acids, alcohols, or phenols present in the lignin, pectins, and cellulose of the sawdust sample. The peak at $2896\ \text{cm}^{-1}$ specifies stretching of the CH_3 group. The stretching vibration of carboxylic acid and ester C-O bonds was evident from the peak at $1732\ \text{cm}^{-1}$. The existence of amines and nitro groups was confirmed from peak at $1593\ \text{cm}^{-1}$. Peak at $1320\ \text{cm}^{-1}$ gives information about stretching vibrations of the $-\text{COOH}$ of pectin while peak at $1232\ \text{cm}^{-1}$ gives information about hemicellulose C-O stretching vibration. The existence of halogen groups (C-X) was confirmed from peaks at 1032 and $560\ \text{cm}^{-1}$ [10–12].

3.2. Surface Area of Sawdust. The surface area of the activated sawdust sample was calculated using formula (1) and was estimated to be $90\ \text{m}^2/\text{g}$.

3.3. Kinetic Studies

3.3.1. Effect of Contact Time on Adsorption. The rate and order of reaction were assessed by applying different kinetic models. Figures 5(a) and 5(b) demonstrate the contact time effect of adsorbates: BB-3 and MG on the sawdust surface, respectively. At the beginning of experiment, the adsorption rate increases very rapidly up to 30 min. After 30 min, there

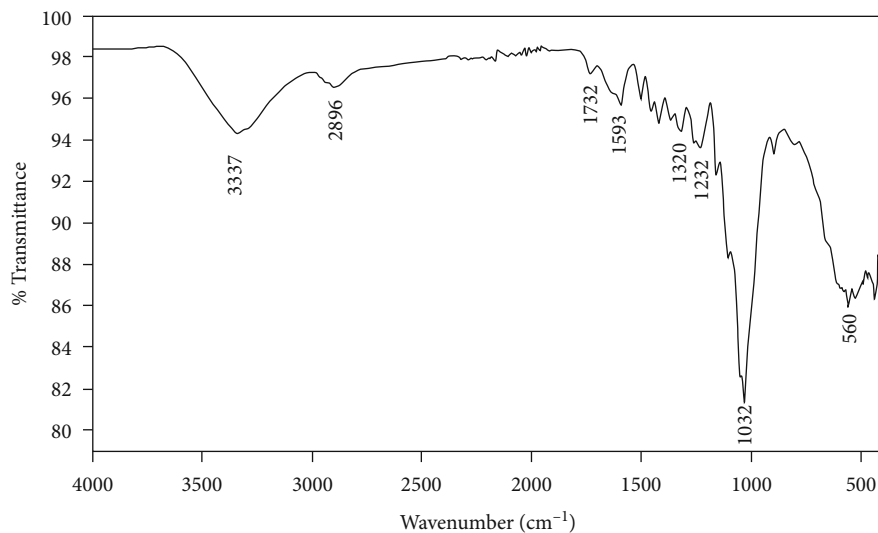


FIGURE 4: FTIR spectrum of activated sawdust.

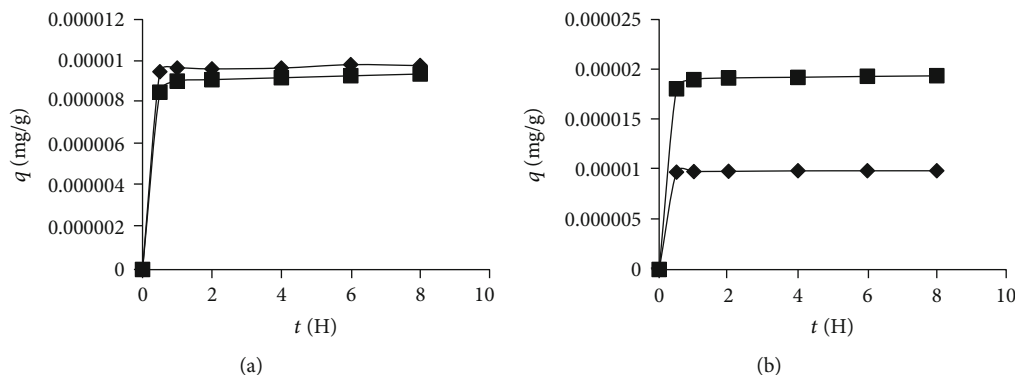


FIGURE 5: Equilibrium time plot for the adsorption of (a) BB-3 and (b) MG on sawdust.

was no further increase in the rate of adsorption because the whole surface of adsorbent was covered by the adsorbate molecules. Therefore, the time 30 min was considered as the equilibrium time.

3.3.2. Pseudo-1st-Order Rate Reaction. The pseudofirst-order equation was used to calculate the rate constant of reaction Equation (2):

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

where q_e is the adsorbate amount (mg g^{-1}) adsorbed by adsorbent at equilibrium time, q_t is the amount of adsorbate adsorbed at any time t in mg/g , and k_1 (min^{-1}) is the rate constant.

The value of constants k_1 and q_e can be calculated from the slope and intercept of the $\log (q_e - q_t)$ versus t graph [20] as given in Figure 6(a) for BB-3 and Figure 7(a) for MG.

3.3.3. Pseudo-2nd-Order Rate Equation. The mathematical form of this equation can be given as Equation (3):

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (3)$$

where k_2 (g/mg.min) is the pseudosecond-order rate constant, q_e corresponds to adsorbate amount adsorbed at equilibrium and q_t corresponds to the adsorbate amount adsorbed at any time t . The t/q_t versus “ t ” graph at different temperatures was plotted that gives straight lines having a slope of $(1/q_e)$ and intercept $(1/k_2 q_e^2)$ [21, 22] as given in Figures 6(b) and 7(b) for BB-3 and MG, respectively.

3.3.4. Intraparticle Diffusion Model. Intraparticle diffusion model was used to determine the rate limiting step and mechanism of the adsorption process.

Mathematically, the intraparticle diffusion model can be given by Equation (4):

$$q_t = k_{id} t^{1/2} + C \quad (4)$$

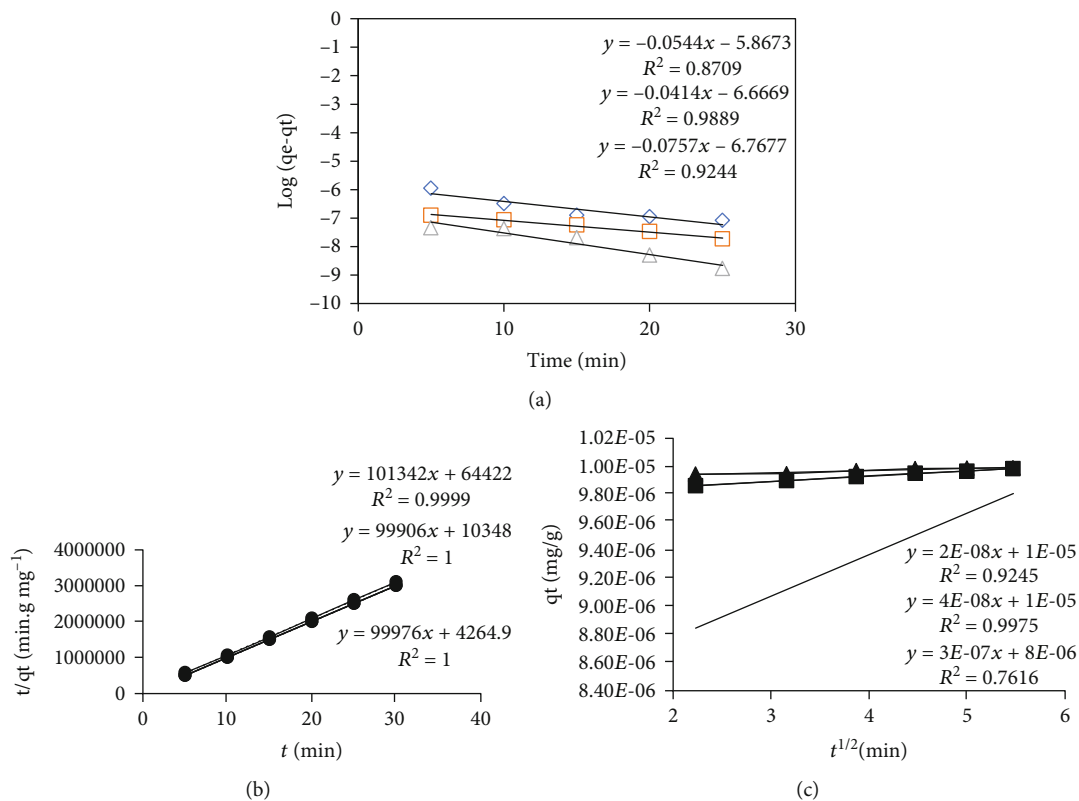


FIGURE 6: Kinetic models for BB-3 adsorption on prepared adsorbent: (a) pseudo-1st-order, (b) pseudo-2nd-order, and (c) intraparticle models of diffusion.

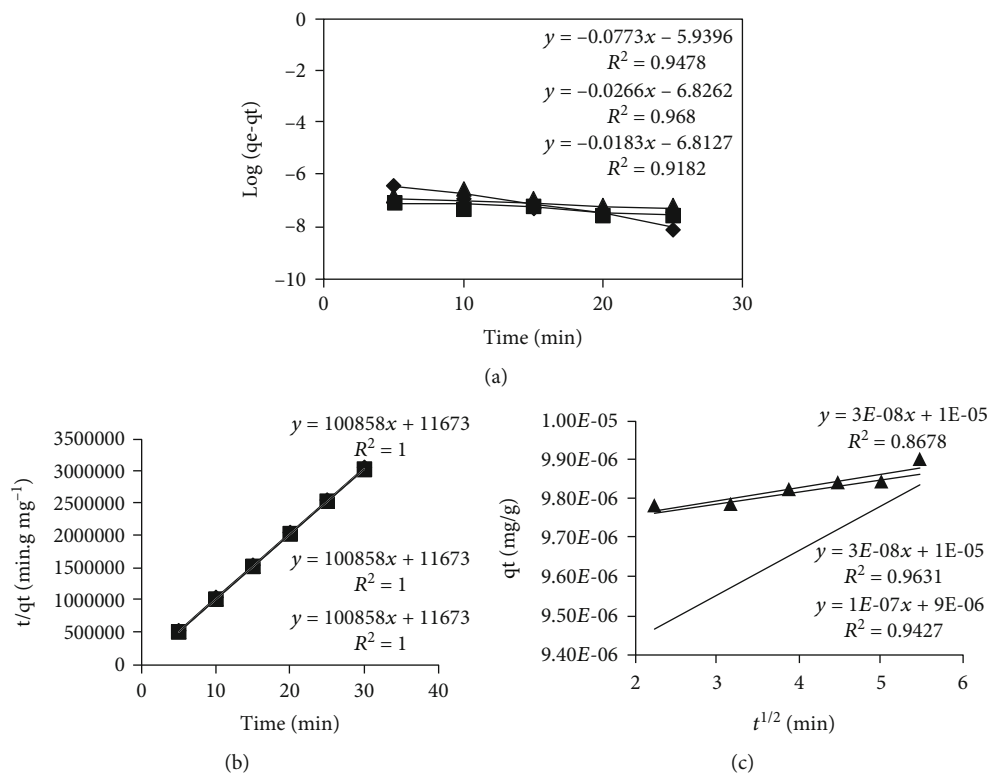


FIGURE 7: Kinetic models for MG adsorption on prepared adsorbent: (a) pseudo-1st-order, (b) pseudo-2nd-order, and (c) intraparticle diffusion models.

TABLE 2: Comparison of various parameters determined through different kinetic equations for MG and BB-3 dye adsorption on activated sawdust.

Kinetic model parameters		MG						BB-3		
		283 K	293 K	303 K	Adsorption temperatures		283 K	293 K	303 K	
Pseudofirst order	q_e (mol/g)	-0.07	-0.02	-0.01	-0.05	-0.04	-0.07			
	k_1 (g/mol.K ⁻¹)	-5.93	-6.82	6.81	-5.86	0.07	-6.76			
	R^2	0.94	0.96	0.91	0.87	-6.76	0.92			
Pseudosecond order	q_e (mol/g)	101148	100858	101109	101342	0.98	99976			
	k_2 (g/mol.K ⁻¹)	28332	11673	9761.7	64422	0.92	4264.9			
	R^2	1	1	1	0.99	99906	1			
Intraparticle diffusion	k_{id} (mg/g min)	1E-07	3E-08	3E-08	3E-07	99976	2E-08			
	Intercept	9E-06	1E-05	1E-05	8E-06	10348	1E-05			
	R^2	0.94	0.96	0.86	0.76	4264.9	0.99			

The R^2 value is closed to unity for pseudosecond order; therefore, pseudosecond order can better explain the results of kinetic studies.

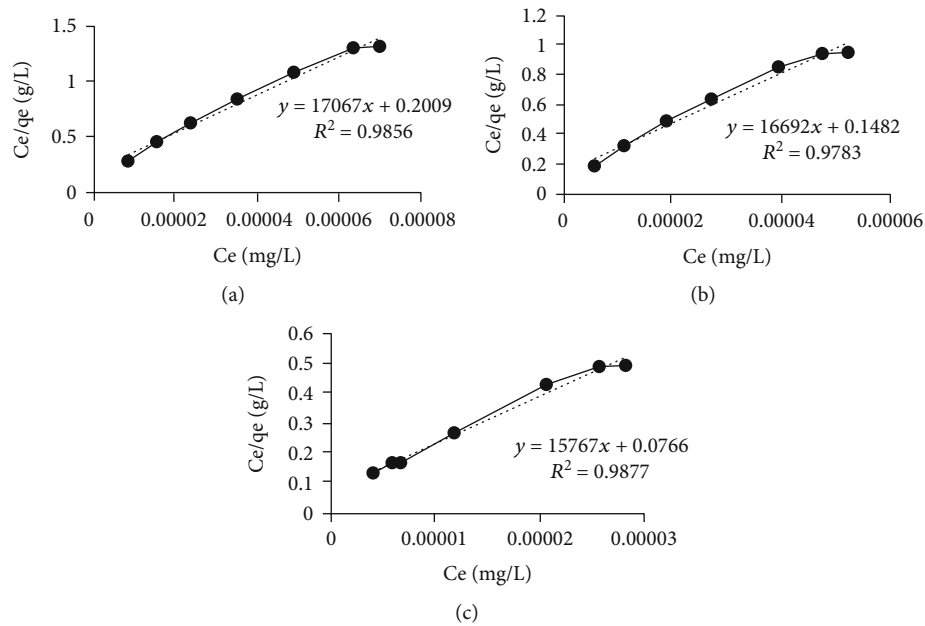


FIGURE 8: Langmuir isotherm model of adsorption on BB-3 on sawdust at (a) 283 K, (b) 293 K, and (c) 303 K.

Here, k_{id} represents the rate constant, and C is the graph intercept which represents the thickness of border sheet. A graph C_e vs. $t_{1/2}$ was plotted [23] as shown in Figures 6(c) and 7(c) for BB-3 and MG, respectively. From the given graph, the mechanism of adsorption can be investigated. Comparison data of various calculated parameters are given in Table 2. The lines in the graph do not pass through the origin indicating that intraparticle diffusion is not the only rate-limiting step in the process. There is an increase in the intercept values which means that the boundary layer effect has increased with rise in temperature.

3.4. Isotherm Studies

3.4.1. *Langmuir Model.* Langmuir adsorption isotherm model can be applied to find out the maximum adsorption

capacity of adsorbents. The main assumption of this model can be applied to monolayer sorption on homogenous sites.

Its mathematical form is given by Equation (5):

$$\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{C_e}{q_m}, \quad (5)$$

where C_e is the concentration of adsorbate at equilibrium in solution, q_e is the adsorbed dye amount at equilibrium, k_L is the Langmuir constant related to the capacity of adsorption, and q_m is the maximum capacity of adsorption [24]. A plot C_e/q_e , against C_e , enables us to calculate the value of k_L and q_m from slope and intercept in (Figures 8 and 9). Their values along with the correlation coefficient R^2 are given in Table 3. The maximum capacity of adsorption q_m for

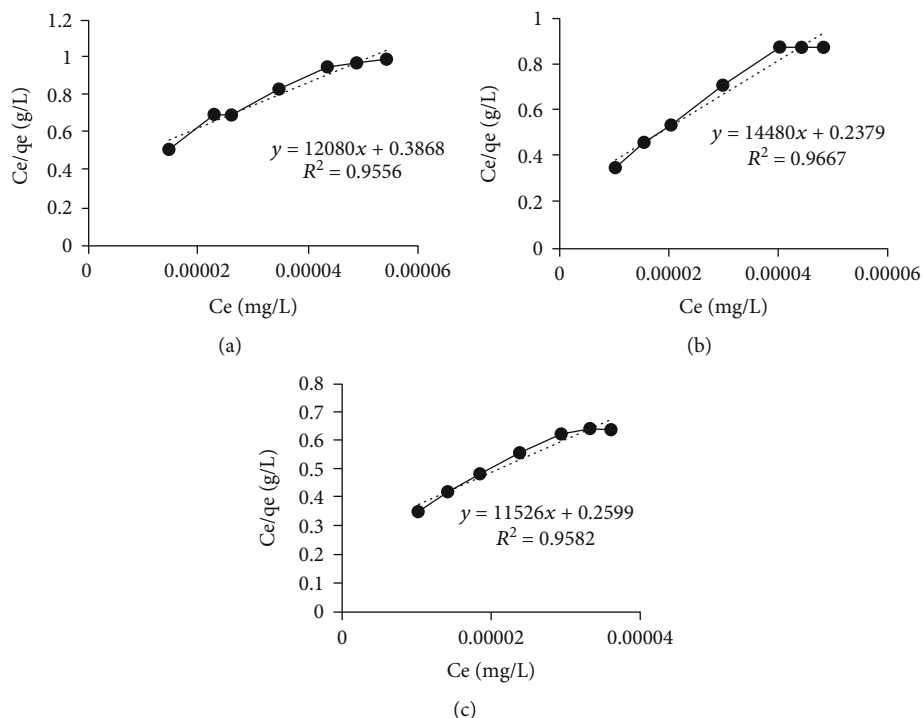


FIGURE 9: Langmuir isotherm model for the adsorption of MG on activated sawdust at (a) 283 K, (b) 293 K, and (c) 303 K.

TABLE 3: Isothermal parameters of MG and BB-3 adsorption on prepared adsorbent.

Isotherm models	Parameters	MG			BB-3		
		283 K	293 K	303 K	283 K	293 K	303 K
Langmuir	q_{\max} (mg/g)	$8.27E-05$	$6.90E-05$	$8.67E-05$	$5.85 E-05$	$5.99 E-05$	$6.34 E-05$
	k_1 (L/mol)	0.38	0.23	0.23	0.20	0.14	0.07
	R^2	0.95	0.96	0.96	0.98	0.97	0.98
Freundlich	Slope	0.48	0.38	0.50	0.26	0.26	0.29
	Kf (L/mol)	-5.04	-6.05	-4.66	-7.33	-7.28	-6.73
	R^2	0.97	0.97	0.99	0.98	0.97	0.95
Temkin	B_1	$2E-05$	$2E-05$	$2E-05$	$1E-05$	$1E-05$	$1E-05$
	k_T (L/mol)	0.0002	0.0002	0.0003	0.0002	0.0002	0.0002
	R^2	0.95	0.94	0.96	0.96	0.93	0.96

The R^2 value is closed to unity for Langmuir model; therefore, Langmuir model can better explain the results of isothermal studies.

adsorption of BB-3 on activated sawdust was found to be $5.8 \times E-5$, $6 \times E-5$, and $6.34 \times E-5$ mg/g whereas $8.2 \times E-5$, $6.9 \times E-5$, and $8.6 \times E-5$, respectively, at 283 K, 293 K, and 303 K for MG. Langmuir isotherm gives the correlation coefficient R^2 value near to 1 for both adsorbents; and hence, it is best model to explain the current adsorption process.

3.4.2. *Freundlich Isotherm Model of Adsorption.* The Freundlich adsorption isotherm model can be given as Equation (6):

$$\ln q_e = \ln Kf + \frac{1}{n} \ln C_e, \quad (6)$$

where C_e is the concentration of dye in solution at equilibrium state, q_e is the amount of dye adsorbed at equilibrium, K is the constant related to capacity of adsorption, and $1/n$ is the empirical constant. When $1/n = 0$, the process will be irreversible, and when $0 < 1/n < 1$, it will be favorable, and for $1/n > 1$, the process will be unfavorable [25].

A plot $\ln q_e$ against C_e enables us to calculate the values of the isothermal parameters from the slope and intercept (Figures 10 and 11). The values of $1/n$ were found: 0.2673, 0.2625, and 0.2929 for BB-3 adsorption on prepared adsorbent, and for the adsorption of MG, these values were 0.4898, 0.3833, and 0.5047, respectively, at 283, 293, and 303 K.

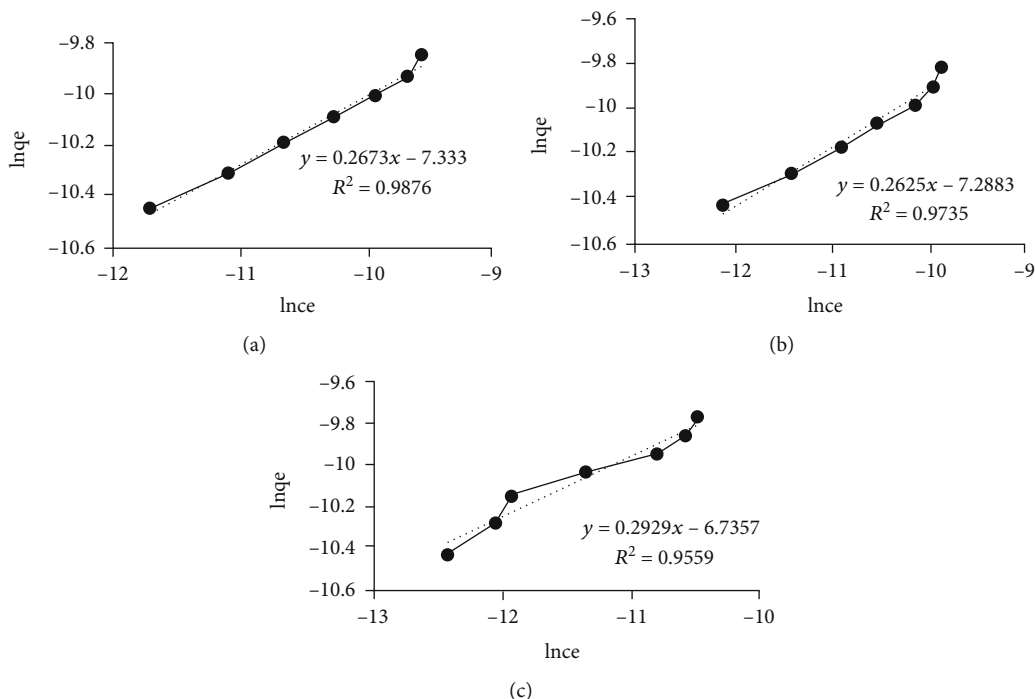


FIGURE 10: Freundlich isotherm model for the adsorption of BB-3 on AC sawdust at (a) 283 K, (b) 293 K, and (c) 303 K.

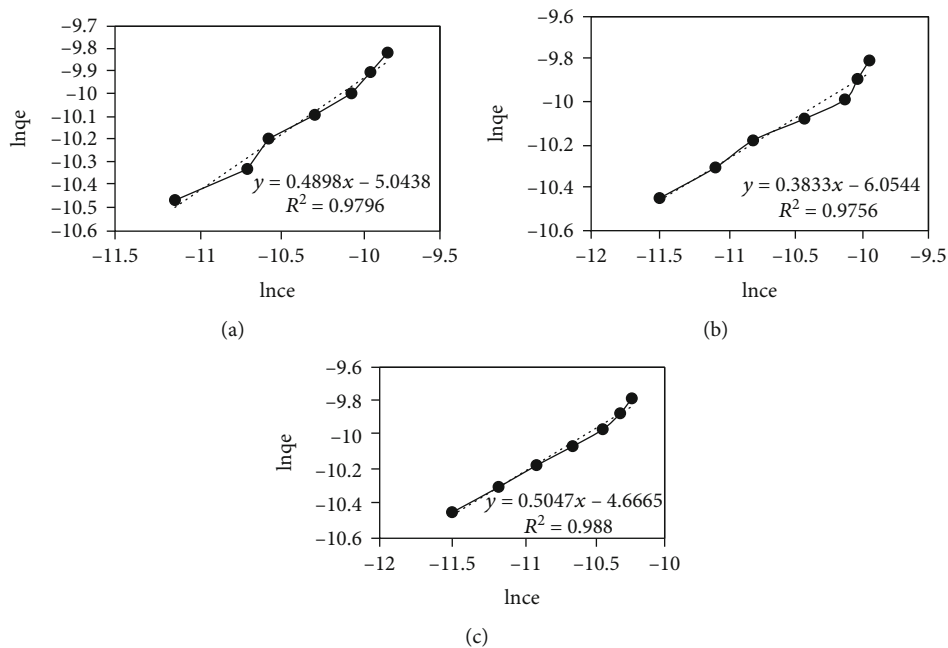


FIGURE 11: Freundlich isotherm model for the adsorption of MG on activated sawdust at (a) 283 K, (b) 293 K, and (c) 303 K.

3.4.3. *Temkin Isotherm Model.* Temkin isotherm model can be given as Equation (7) [26–28].

$$q_e = B_1 \ln k_T + B \ln C_e, \tag{7}$$

where B_1 is the Temkin constant associated with heat of adsorption and k_T is the isotherm constant, and its value

can be obtained from the graph plotted between q_e and $\ln C_e$ as shown in Figures 12 and 13 for BB-3 and MG, respectively. The estimated constant values are shown in Table 3.

3.4.4. *Effect of Adsorbent Dosage.* Figures 14(a) and 14(b) show the effect of adsorbent dosage on adsorption of BB-3 and MG. The removal efficiency increases linearly with rise of adsorbent dose up to 0.05 g. So, 0.05 g of adsorbent dosage

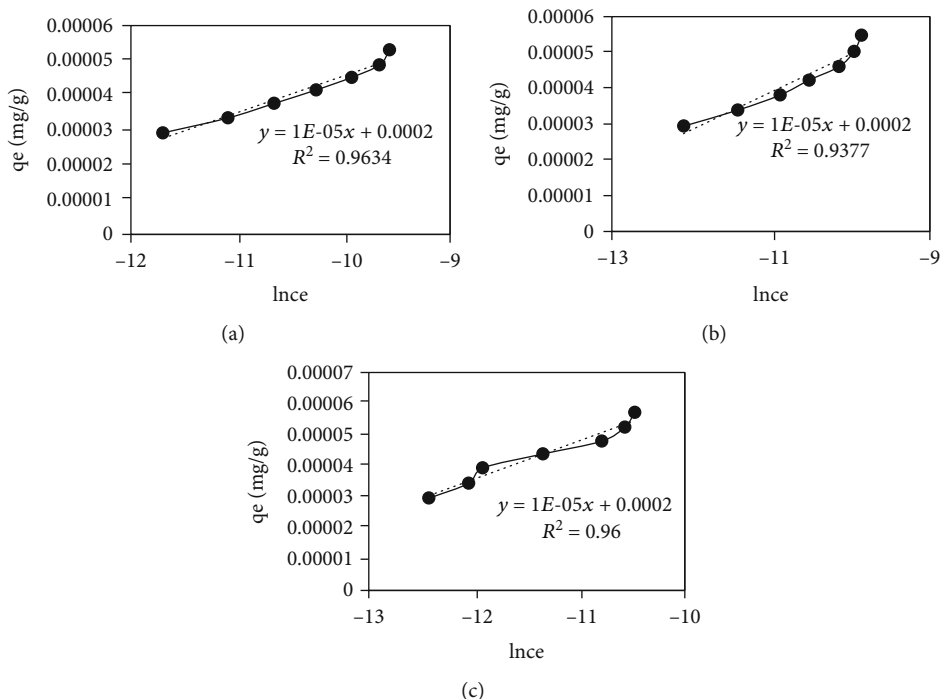


FIGURE 12: Temkin isotherm model of adsorption for BB-3 on activated sawdust at (a) 283 K, (b) 293 K, and (c) 303 K.

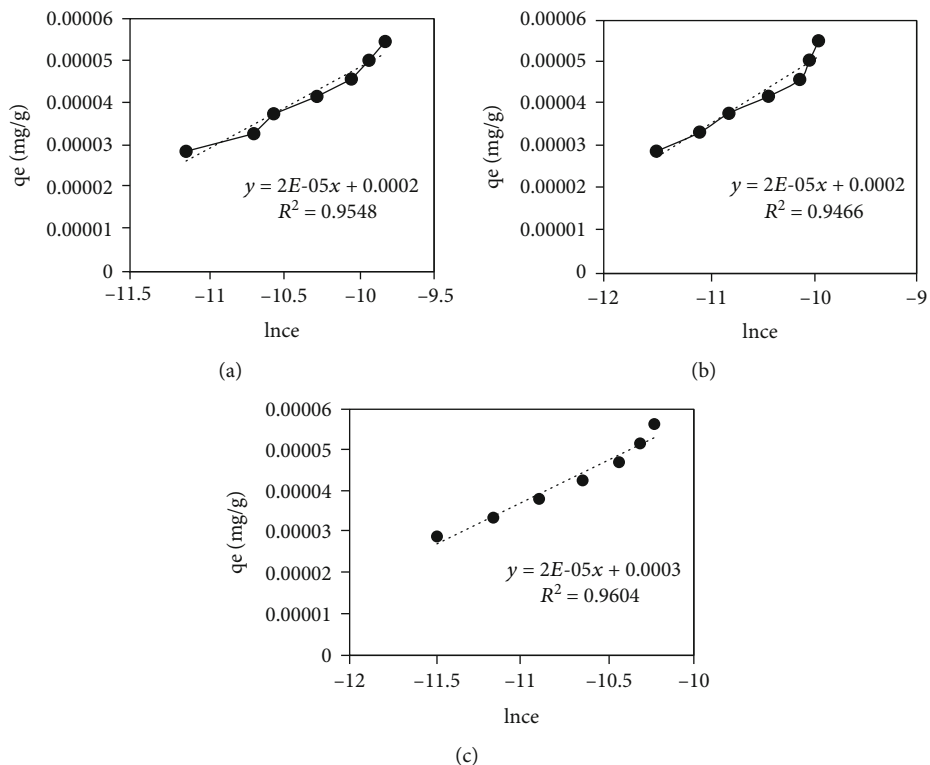


FIGURE 13: Temkin isotherm model of adsorption for MG on activated sawdust at (a) 283 K, (b) 293 K, and (c) 303 K.

was taken as optimum dosage which was used in subsequent studies.

sawdust were estimated using Equations (8) and (9), respectively, given below:

3.5. *Thermodynamic Study.* Various thermodynamics parameters of BB-3 and MG dye adsorption on activated

$$\ln Kc = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}, \tag{8}$$

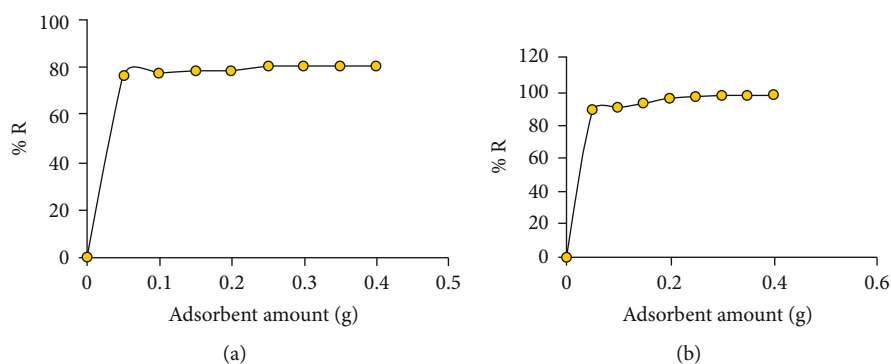


FIGURE 14: Effect of adsorbent dosage on removal efficiency of selected dyes on activated sawdust (a) BB-3 and (b) MG.

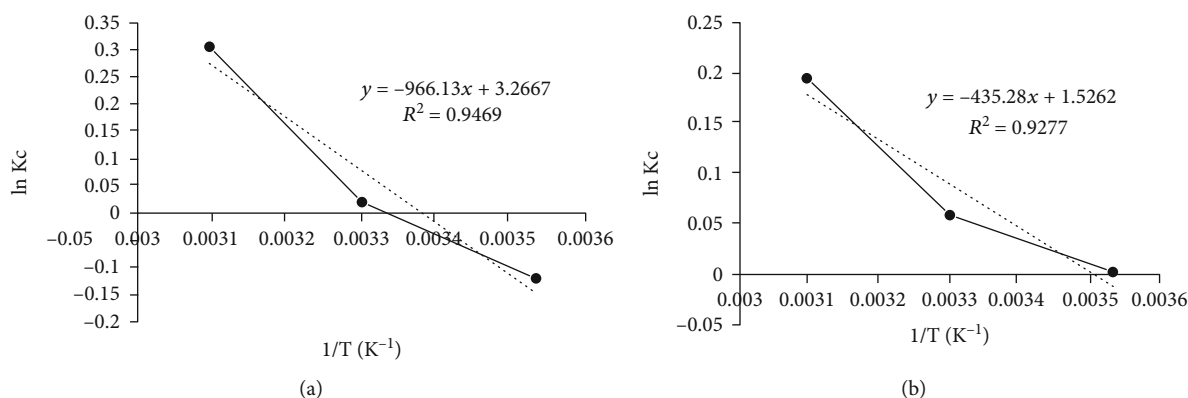


FIGURE 15: Plot of $1/T$ vs. $\log Kc$ for adsorption of (a) BB-3 and (b) MG on activated sawdust.

TABLE 4: Different parameters of thermodynamics for adsorption of BB-3 and MG onto activated sawdust.

Sample	ΔH° (kJ/mol)	ΔS° (kJ/molK)	ΔG° (kJ/mol)		
			283 K	293 K	303 K
Basic blue 3 -1658	18.5	62.41		-83.6	-410
Methylene green -1139	8.334	29.22		-65.0	-519

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ, \quad (9)$$

whereas in Equations (8) and (9), ΔG° , ΔH° , ΔS° , and Kc are the changes in Gibbs free energy, enthalpy, entropy, and ratio of equilibrium adsorption/equilibrium concentration, respectively. R is universal gas constant, and T is the absolute temperature. A plot $\ln Kc$ vs. $1/T$ enables us to calculate the values of ΔH° and ΔS° from slope and intercept (Figure 15). The values of these parameters are given in Table 4.

The negative value of Gibbs free energy change (ΔG°) indicates that the adsorption process is feasible and spontaneous in nature. The increase in ΔG° values with increase in temperatures indicates that the process is favorable at high temperature [29]. The increased randomness at the interfaces of dye/adsorbent is evident from positive value of the entropy change whereas the endothermic nature of the process is clear from positive value other enthalpy change [30].

3.6. Regeneration of Used Adsorbent. In order to check the regenerability of the prepared adsorbent, the used sample was washed with different reagents such as ethanol and NaOH. After washing, the same adsorbent sample was used for six cycles. In spite of low adsorption capacity, still its initial value only drops to 70% showing that the prepared adsorbent could be effectively used for several cycles.

3.7. Comparison of Adsorption Extents of Current Adsorbent to Remove BB-3 and MG Dyes with Previous Reported Adsorbents. Sawdust has rarely been used as an adsorbent. Mostly activated carbon is prepared from it which has been used for the removal of different types of dyes from aqueous solutions previously. Comparison of current adsorbent adsorption potential with previously used adsorbents described in literature is shown in Table 5 [31–34]. From data in the table, it is evident that its adsorption capacity is

TABLE 5: Comparison of the previous works and for the present study with reported data on dye treatment.

Dyes	Adsorbent	q_{\max} (mg/g)	References
Basic Red 46 and Reactive Red 196	Sawdust-based adsorbent	13.94 and 13.39	[31]
Methylene blue	Rattan sawdust	294.14	[32]
Acid Yellow 29	Activated Ailanthus altissima sawdust	13	[33]
Basic blue 3 and methylene green	Acidic sawdust acacia	6.19 and 230.76	[34]
Basic blue 3 and methylene green	Activated paper mulberry sawdust	6.34×10^{-5} and 8.67×10^{-5}	Present study

very low as compared to other adsorbents. To improve the adsorbent for practical uses, further experiments are needed.

Both the dyes BB-3 and MG are not significantly removed by the activated sawdust. The current adsorbent has low cost over other highly expensive adsorbents such as activated carbon but its removal efficiency is pretty low as compared to other costly adsorbents. Further enhancement in the adsorption capacity is needed.

4. Conclusions

The study was aimed at effective use sawdust as adsorbent after necessary chemical treatment, in reclamation of industrial effluents loaded with selected dyes (BB-3 and MG). The best fit of kinetic data was obtained with pseudosecond-order model for isothermal data with Langmuir model. The feasible and spontaneous in nature of the adsorption process is evident from negative value of Gibbs free energy change (ΔG°) whereas the increase in ΔG° values with increase in temperatures indicated the favorability of the process at elevated temperature. The endothermic nature of the process is clear from the positive value of ΔH° . Although we were trying to get an efficient adsorbent, the low adsorption capacity value of the prepared adsorbent indicates that it is not a good adsorbent for the selected dye adsorption in the present form. Further, modification and experiments are needed to enhance its adsorption capacity towards dyes.

Data Availability

All required data is present in this file.

Conflicts of Interest

The authors declare no conflict of interest.

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References

- [1] M. Ikram, M. Zahoor, and G. E. S. Batiha, "Biodegradation and decolorization of textile dyes by bacterial strains: A biological approach for wastewater treatment," *Zeitschrift für Physikalische Chemie*, vol. 235, no. 10, pp. 1381–1393, 2021.
- [2] B. Dash, "Competitive Adsorption of Dyes (Congo Red, Methylene Blue, Malachite Green) on Activated Carbon," Department of Chemical Engineering National Institute of Technology, Rourkela Orissa, 2010.
- [3] A. Janet, R. Kumaresan, and S. U. Maheswari, "Adsorption of anionic and cationic dyes onto granular activated carbon," *Middle-East Journal of Scientific Research*, vol. 23, no. 2, pp. 308–317, 2015.
- [4] V. S. Mane, I. D. Mall, and V. C. Srivastava, "Use of bagasse fly ash as an adsorbent for the removal of brilliant green dye from aqueous solution," *Dyes and Pigments*, vol. 73, no. 3, pp. 269–278, 2007.
- [5] M. R. Fathi, A. Asfaram, and A. Farhangi, "Removal of Direct Red 23 from aqueous solution using corn stalks: Isotherms, kinetics and thermodynamic studies," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 135, pp. 364–372, 2015.
- [6] M. Valix, W. H. Cheung, and G. Mckay, "Role of the textural and surface chemical properties of activated carbon in the adsorption of acid blue dye," *Langmuir*, vol. 22, no. 10, pp. 4574–4582, 2006.
- [7] T. Robinson, G. McMullan, R. Marchant, and P. Nigam, "Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative," *Bioresource Technology*, vol. 77, no. 3, pp. 247–255, 2001.
- [8] A. Ullah, M. Zahoor, W. U. Din et al., "Removal of methylene blue from aqueous solution using black tea wastes: used as efficient adsorbent," *Adsorption Science & Technology*, vol. 2022, pp. 1–9, 2022.
- [9] W. T. Tsai, C. Y. Chang, M. C. Lin, S. F. Chien, H. F. Sun, and M. F. Hsieh, "Adsorption of acid dye onto activated carbons prepared from agricultural waste bagasse by $ZnCl_2$ activation," *Chemosphere*, vol. 45, no. 1, pp. 51–58, 2001.
- [10] A. Ullah, M. Zahoor, S. Alam, R. Ullah, A. S. Alqahtani, and H. M. Mahmood, "Separation of levofloxacin from industry effluents using novel magnetic nanocomposite and membranes hybrid processes," *BioMed Research International*, vol. 2019, 13 pages, 2019.
- [11] S. Jabeen, S. Alam, L. A. Shah et al., "Removal of safranin-T and toluidine from water through gum Arabic/acrylamide hydrogel," *Adsorption Science & Technology*, vol. 2022, pp. 1–17, 2022.
- [12] M. U. R. Khattak, M. Z. Muhammad, B. Muhammad, F. A. Khan, R. Ullah, and N. M. AbdeI-Salam, "Removal of heavy metals from drinking water by magnetic carbon nanostructures prepared from biomass," *Journal of Nanomaterials*, vol. 2017, 10 pages, 2017.
- [13] A. Gallo-Cordova, J. J. Castro, E. L. Winkler et al., "Improving degradation of real wastewaters with self-heating magnetic

- nanocatalysts,” *Journal of Cleaner Production*, vol. 308, pp. 127–385, 2021.
- [14] M. A. Islam, D. W. Morton, B. B. Johnson, B. K. Pramanik, B. Mainali, and M. J. Angove, “Opportunities and constraints of using the innovative adsorbents for the removal of cobalt(II) from wastewater: a review,” *Environmental Nanotechnology, Monitoring & Management*, vol. 10, pp. 435–456, 2018.
- [15] A. R. Teixeira, E. C. Lima, A. D. Benetti et al., “Preparation of hybrids of wood sawdust with 3-aminopropyl-triethoxysilane. Application as an adsorbent to remove Reactive Blue 4 dye from wastewater effluents,” *Journal of the Taiwan Institute of Chemical Engineers*, vol. 125, pp. 141–152, 2021.
- [16] D. O. Salomon, L. Yamil, J. GeorGIN et al., “Utilization of Pacara Earpod tree (*Enterolobium contortisilquum*) and Ironwood (*Caesalpinia leiostachya*) seeds as low-cost biosorbents for removal of basic fuchsin,” *Environmental Science and Pollution Research*, vol. 27, no. 26, pp. 33307–33320, 2020.
- [17] K. Y. Foo and B. H. Hameed, “Insights into the modeling of adsorption isotherm systems,” *Chemical Engineering Journal*, vol. 156, no. 1, pp. 2–10, 2010.
- [18] E. V. Veliev, T. Ozturk, S. Veli, and A. G. Fatullayev, “Application of diffusion model for adsorption of azo reactive dye on pumice,” *Polish Journal of Environmental Studies*, vol. 15, pp. 347–353, 2006.
- [19] B. S. Zadeh, H. Esmaeili, R. Foroutan, S. M. Mousavi, and S. A. Hashemi, “Removal of Cd²⁺ from aqueous solution using eucalyptus sawdust as a bio-adsorbent: kinetic and equilibrium studies,” *Journal of Environmental Treatment Techniques*, vol. 8, pp. 112–118, 2020.
- [20] N. U. Rahman, I. Ullah, S. Alam et al., “Activated ailanthus Altissima sawdust as adsorbent for removal of acid yellow 29 from wastewater: Kinetics approach,” *Water*, vol. 13, no. 15, p. 2136, 2021.
- [21] A. M. Aljeboree, S. J. Baqir, and A. F. Alkaim, “Experimental studies of thermodynamics parameters: as a model adsorption and removal of textile,” *Journal of Physics: Conference Series*, vol. 1664, no. 1, 2020.
- [22] A. Asfaram, M. Ghaedi, S. Hajati, M. Rezaeinejad, A. Goudarzi, and M. K. Purkait, “Rapid removal of Auramine-O and Methylene blue by ZnS:Cu nanoparticles loaded on activated carbon: A response surface methodology approach,” *Journal of the Taiwan Institute of Chemical Engineers*, vol. 53, pp. 80–91, 2015.
- [23] A. A. Giwa, M. A. Oladipo, and K. A. A. Salam, “Adsorption of Rhodamine B from single, binary and ternary dye systems using sawdust of *Parkia biglobosa* as adsorbent: isotherm kinetic and thermodynamics studies,” *Journal of Chemical and Pharmaceutical Research*, vol. 7, pp. 454–475, 2015.
- [24] V. S. Munagapati and D. S. Kim, “Equilibrium isotherms, kinetics, and thermodynamics studies for Congo red adsorption using calcium alginate beads impregnated with nano-goethite,” *Ecotoxicology and Environmental Safety*, vol. 141, pp. 226–234, 2017.
- [25] A. A. Giwa, A. A. Olajire, M. A. Oladipo, M. O. Bello, and I. A. Bello, “Adsorption of ternary metals system onto the sawdust of locust bean tree (*Parkia biglobosa*): equilibrium, kinetics and thermodynamics studies,” *International Journal of Scientific and Engineering Research*, vol. 4, pp. 1275–1296, 2013.
- [26] A. A. Olajire, A. A. Giwa, and I. A. Bello, “Competitive adsorption of dye species from aqueous solution onto melon husk in single and ternary dye systems,” *International journal of Environmental Science and Technology*, vol. 12, no. 3, pp. 939–950, 2015.
- [27] M. Zahoor, M. Wahab, S. M. Salman, A. Sohail, E. A. Ali, and R. Ullah, “Removal of doxycycline from water using Dalbergia sissoo waste biomass based activated carbon and magnetic oxide/activated bioinorganic nanocomposite in batch adsorption and adsorption/membrane hybrid processes,” *Bioinorganic Chemistry and Applications*, vol. 2022, 17 pages, 2022.
- [28] N. V. Farinella, G. D. Matos, and M. A. Z. Arruda, “Grape bagasse as a potential biosorbent of metals in effluent treatments,” *Bioresource Technology*, vol. 98, no. 10, pp. 1940–1946, 2007.
- [29] M. Bagane and S. Guiza, “Removal of a dye from textile effluents by adsorption,” *Annales de Chimie Science des Matériaux*, vol. 25, no. 8, pp. 615–625, 2000.
- [30] M. Doltabadi, H. Alidadi, and M. Davoudi, “Comparative study of cationic and anionic dye removal from aqueous solutions using sawdust-based adsorbent,” *Environmental Progress & Sustainable Energy*, vol. 35, no. 4, pp. 1078–1090, 2016.
- [31] B. H. Hameed, A. L. Ahmad, and K. N. A. Latiff, “Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust,” *Dyes and Pigments*, vol. 75, no. 1, pp. 143–149, 2007.
- [32] S. Larous and A. H. Meniai, “The use of sawdust as by product adsorbent of organic pollutant from wastewater: adsorption of phenol,” *Energy Procedia*, vol. 18, pp. 905–914, 2012.
- [33] H. Tounsadi, Y. Metarfi, N. Barka, M. Taleb, and Z. Rais, “Removal of textile dyes by chemically treated sawdust of acacia: kinetic and equilibrium studies,” *Journal of Chemistry*, vol. 2020, pp. 1–12, 2020.
- [34] M. Kumar and R. Tamilarasan, “Modeling studies for the removal of methylene blue from aqueous solution using *Acacia fumosa* seed shell activated carbon,” *Journal of Environmental Chemical Engineering*, vol. 1, no. 4, pp. 1108–1116, 2013.