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Optimization of Parameters for Adsorption of Methylene Blue on a Low-Cost Activated Carbon

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We prepared activated carbon by pyrolyzing an agro-waste, rice husk, in the presence of $ZnCl_2$. The activated carbon displayed both microporous and mesoporous nature with a significant surface area of 180.50 $m^2 \cdot g^{-1}$. Fourier transform infrared (FTIR) spectrograms of the activated carbon were recorded to determine the number and positions of the functional groups available on its surface. The adsorption of methylene blue (MB) from its aqueous solutions by rice husk activated carbon (RHAC) was studied. The removal of dye increased from (82.75 to 93.20) % with decreasing initial concentration of MB from (100 to 60) $mg \cdot L^{-1}$. The time of equilibrium was found to be 100 min. Higher removal was obtained at higher dose of adsorbent, and the removal increased from (86.75 to 99.83) % with increasing adsorbent dose from (0.40 to 0.60) g. The removal of methylene blue increased from (93.20 to 99.16) % with increasing temperature from (30 to 50) °C at 60 $mg \cdot L^{-1}$ MB concentration, 150 rpm, and 100 μm particle size. Isotherm studies were conducted to know the capacity of the activated carbon. Langmuir and Freundlich isotherm equations were applied for the equilibrium data.

Introduction

Environmental pollution, in general, and water pollution, in particular, are of concern to the scientific community worldwide. Dyes are extensively used, especially in the textile, leather, pulp and paper, and cosmetic industries, and the discharge of effluents from these applications is a major source of color in water sources,[1-3] but, in particular, textile industries are responsible for the discharge of the largest amount of colored effluents in waters. The estimated annual production of commercially available dyes is approximately $7 \cdot 10^5$ tonnes, which includes more than 100 000 dyes. Although clear data on the share of methylene blue are not available, it is one of the highly applied dyes.[4] Dyes are generally nondegradable and constitute a problematic group of pollutants. Dyes are harmful to flora and fauna, and some of the dyes have been reported to be carcinogenic and mutagenic.[5] In addition to a number of adverse effects, colored waters are aesthetically unacceptable to people. Colored waters also inhibit solar radiation into the water sources and result in a reduced extent of photosynthesis. Flocculation, precipitation, ozonation, and adsorption are well-known treatment methods for the treatment of effluents and wastewaters,[6-8] but there is another problem associated with the colored effluents: because of a significant amount of organics in the dye molecules, most of the conventional treatment methods fail to remove them from effluents. Because of easy handling, simple operation, and low maintenance, adsorption has been recognized as one of the best methods for the removal of dyes from water and wastewaters.[9,10] Activated carbon is a prominent adsorbent for the removal of dyes from colored effluents.[11-14] The high cost of activated carbon is a parameter that restricts its large scale application to developed nations. To reduce the cost of treatment by activated carbon, several waste materials such as neem (a native tree) sawdust, waste apricot, and waste tires have been used for the preparation of activated carbon for removal of dyes. The present work has been an attempt to prepare activated carbon from an agricultural waste rice husk, which is plentiful in India.

Materials and Methods

Adsorbent. Rice is staple food of a sizable proportion of the world population with approximately 395 million tonnes production in 2003. In India, a large population consumes rice, and China and India account for more than half of the world rice production. Obviously, the production of a greater quantity of paddies results in the production of a larger amount of rice husk also. Rice husk has many applications, but its application in water pollution control is rather limited. This is the main reason for choosing rice husk for the present work. The rice husk used in the present investigation was procured locally. It was washed several times to remove any earthen impurities completely and then dried in a hot air oven at 110 °C. Carbonization was carried out in a quartz tube reactor placed in a tubular furnace at 450 °C for 1 h in the indigenous experimental setup.

A constant nitrogen (99.99 %) flow of 150 $mL \cdot min^{-1}$ was maintained throughout the process of carbonization. Activation of primary carbon was carried out at 650 °C for 2 h under optimized conditions. The carbon was cooled in an inert atmosphere in the presence of nitrogen at room temperature and washed with hot distilled water and 0.5 N hydrochloric acid until the pH of the sample reached 7.0. The carbon was dried in a hot air oven at 110 °C, ground, and sieved to obtain the desired particle size (150 μm) and stored in desiccators for further use.

Adsorbate. All reagents used were of analytical grade and were obtained from Merck, Mumbai, India. We prepared stock solutions of MB by dissolving an appropriate amount in double-distilled water. The chemical formula of the dye is $C_{16}H_{18}C$, $N_3S \cdot 3H_2O$, molecular weight 373.91 $g \cdot mol^{-1}$, and λ_{max} 663 nm. The C.I. number of the dye is 52015.

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Table 1. Physical Characteristics of RHAC (Rice Husk Activated Carbon)

BET surface area ($m^2 \cdot g^{-1}$)	180.50
total pore volume, V_p ($\cdot 10^{-3}$ $cm^3 \cdot g^{-1}$)	2.70
micropore surface area, s_{mic} ($m^2 \cdot g^{-1}$)	152.95
mesopore surface area, s_{mes} ($m^2 \cdot g^{-1}$)	27.55
mean pore diameter, D (Å)	31.58

Methods

Adsorption Studies. We carried out adsorption experiments by agitating 0.50 g of rice husk activated carbon in 50 mL of dye solution of desired concentrations [(60 to 100) $mg \cdot L^{-1}$] in 250 mL stoppered conical flasks at 150 rpm and 30 °C in a thermostatted water bath shaker to reach equilibrium. The adsorbent was separated from the solution by centrifugation at 10 000 rpm for 10 min. Centrifugation of the content at 10 000 rpm provided complete separation of the aliquot. We estimated the concentration of residual dye in the supernatant spectrophotometrically by determining the absorbance of the solution at 663 nm (λ_{max}) using a UV−vis spectrophotometer (Spectronic 20, Bausch & Lomb). Langmuir and Freundlich adsorption isotherms were employed to study the adsorption capacity of the adsorbent. The percentage removal of methylene blue and equilibrium adsorption uptake in the solid phase, q_e ($mg \cdot g^{-1}$), was calculated using the following relationships.

Amount of adsorbed dye molecules per grams of solid:

$$q_e = (C_o - C_e)V/w \qquad (1)$$

where C_o is the initial concentration of methylene blue (milligrams per liter), C_e is the equilibrium concentration of dye (milligrams per liter), V is the volume of the solution (liters), and w is the mass of the RHAC (grams).

Result and Discussion

Characterization of the Adsorbent. The IR spectral absorption studies were carried out on an infrared spectrometer (Simadzu/8400S). A micromeritics ASAP 2020 surface area analyzer measured the surface area of the adsorbent. The absorbance of the samples was recorded by a UV−visible spectrophotometer (Spectronic 20, Bausch & Lomb) at 663 nm.

Textural characterization of the activated carbon was carried out, and the pore size distribution of the activated carbon was also determined. Physical characteristics of rice husk activated carbon have been shown in Table 1. The surface area of the activated carbon was determined by volumetric adsorption of nitrogen at 77 K, and the resultant isotherm is displayed in Figure 1a. Pore size distribution of the adsorbent has been given in Figure 1b.

The system provides data for the determination of the monolayer adsorbed amount, apparent specific surface area, and pore volume. The sample (activated carbon) was degassed for 12 h under vacuum at a temperature of 350 °C to remove impurities prior to analysis. The adsorption of nitrogen under different partial pressures of nitrogen was determined. The mesopores and micropores can be defined by the hystereses in loops during adsorption at relatively high relative pressures (P/P_o). The calculation of surface area, microporosity, mesoporosity, and pore volume were carried out by standard methods.[15] It was revealed that the RHAC had greater micropores (Table 1).

Changes in the chemical nature of the cellulosic material rice husk were expected to occur upon carbonization and activation. These possible modifications were studied by infrared spectroscopy and have been presented in Figures 2 and 3. Before
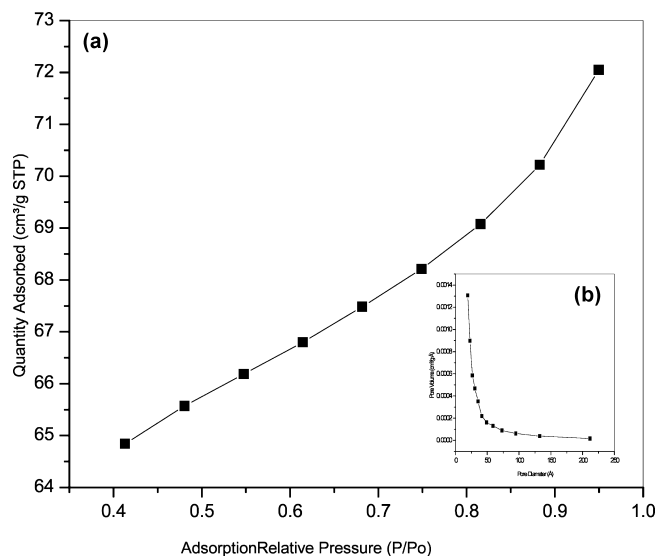

Figure 1. (a) Nitrogen adsorption isotherm at 77 K of rice husk activated carbon. (b) Pore size distribution of rice husk activated carbon.
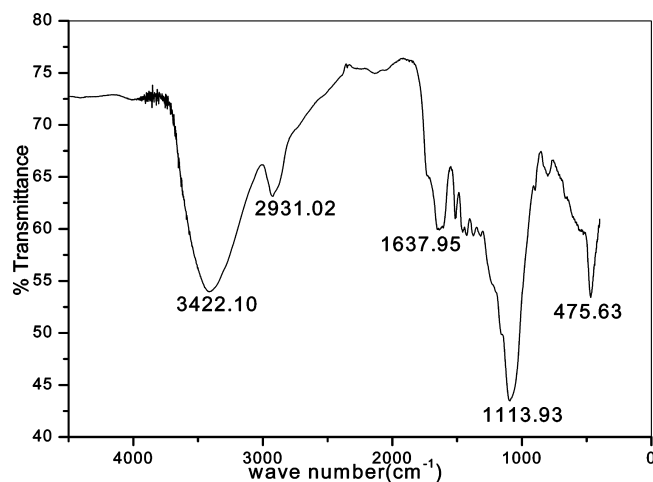

Figure 2. FTIR of the raw material (rice husk).

and after carbonization and activation, carbon and elimination of other elements in the form of water and other species, some changes were observed.[16] In the raw material, the peaks at 3422.10 correspond to −OH stretching, and those at 931.02 correspond to C=C−H stretching. The presence of an aromatic group in the rice husk is evidenced by the peak at 1637.95, whereas ν(C−O) is indicated by the peak at 1113.93, and the peak at 475.63 indicates a Si−O−Ca bend. The changes in the FTIR of RHAC (Figure 3) were evidence of the formation of structures containing multiple carbon−carbon bonds as well as the elimination of originally present oxygen and hydrogen atoms. The intense absorption band with a maximum of about 2916.60 cm^{-1} can be attributed to the stretching vibrations of C−H bonds in alkanes; carbon is bonded with hydrogen bonds. The band at 2291.69 cm^{-1} corresponds to vibration in alkanes and alkyl groups, whereas the band near 1583.39 cm^{-1} is attributed to the vibration in the aromatic group. At 1083.04 cm^{-1} is a less intense band related to the ν(C−O) stretching vibration of the bonds in esters, ether, or the phenol group. The weak absorption bands at 777.28 cm^{-1} correspond to γ(C−H) vibration in the benzene derivative. The absorbance peak at 458.13 cm^{-1} was due to the bending vibration of siloxane bonds.

Effect of Contact Time and Initial Concentration. The initial dye concentration has a pronounced effect on its removal from aqueous solutions. In the present studies, the removal of dye
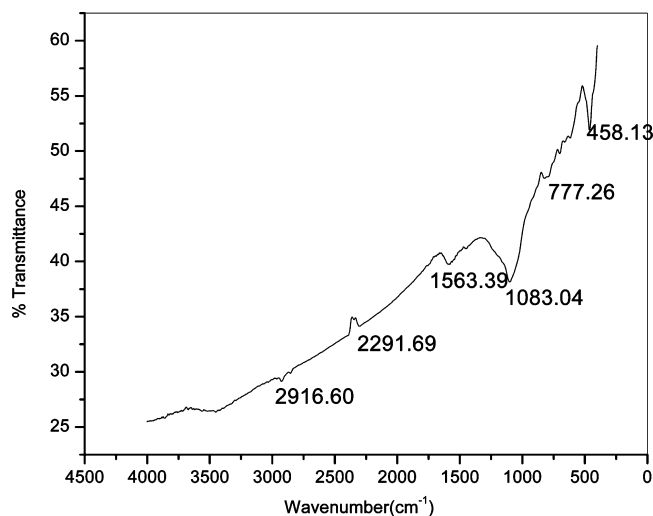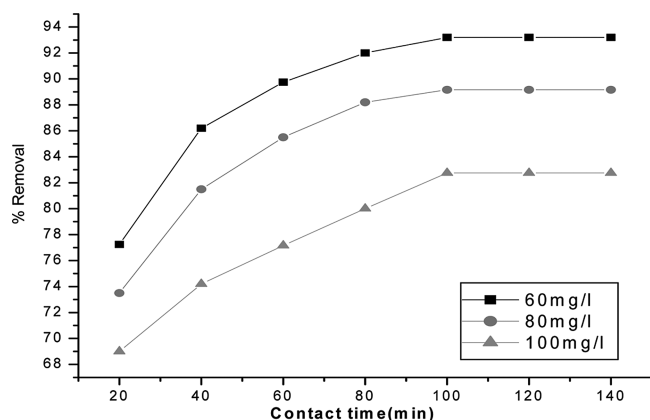
Figure 3. FTIR spectrum of RHAC.

Figure 4. Effect of initial concentration on removal of methylene blue on RHAC.

increased from (82.75 to 93.20) % with decreasing initial concentration of MB from (100 to 60) mg·L^{-1}. It is clear from Figure 4 that the graphs are single and smooth, indicating monolayer coverage of the adsorbent surface by the dye molecules. Furthermore, the removal is rapid in the initial stages, decreases slowly, and acquires a maxima at the time of equilibrium, which is 100 min for the present system. A similar trend of removal of dyes has also been reported by other workers.[17−19]

Effect of Adsorbent Dose. The effect of different doses of RHAC on the removal of MB was carried out, and the results have been presented in Figure 5. We conducted the experiments by taking different adsorbent doses from (0.40 to 0.60) g in 50 mL of dye solution. Other parameters, namely, pH, rpm, contact time, and temperature, were kept constant. The removal increased from (86.75 to 99.83) % with increasing adsorbent dose from (0.40 to 0.60) g. As expected, higher removal of dye was obtained at increased adsorbent dose. The higher removal at increased dose may be attributed to larger availability of active sites for the same number of adsorbate molecules.[20,21]

Kinetic Studies. First- and second-order kinetic models were attempted for the experimental data, but the data fit well in the first-order kinetic model. The kinetic data for the removal of MB by adsorption on RHAC were fitted in Lagergren's model[22,23]

$$\log(q_e - q) = \log q_e - (K_{ad}/2.303)t \qquad (2)$$

where q_e and q (both in milligrams per gram) are the amounts of dye adsorbed at any time and at equilibrium, respectively,

and K_{ad} (min^{-1}) is the rate constant of adsorption. The straight line plots of $\log(q_e - q)$ versus t (Figure 6) confirm that the process of removal is governed by first-order kinetics. The linear plots also demonstrate the applicability of Lagergren's model for this study. The values of K_{ad} were determined by the slopes of the graphs of Figure 6, and the value of K_{ad} was found to be $1.41 \cdot 10^{-2}$ min^{-1} at 60 mg·L^{-1} concentration of MB at 30 °C.

Effect of Temperature. Temperature effects the process of removal significantly. The effect of temperature on the removal of MB by adsorption on RHAC was investigated in the temperature range from (30 to 50) °C. The experimental results show that in the present investigation, the removal of methylene blue increased from (93.20 to 99.16) % with increasing temperature from (30 to 50) °C (Figure 7). Most of the adsorption processes are governed by exothermic processes, but the present studies show the process of removal to be endothermic.

Equilibrium Modeling. Several mathematical models have been applied for describing equilibrium studies for the removal of dyes and colors by adsorption on solid surfaces. The selection of an isotherm equation depends on the nature and type of the system. Out of several isotherm equations, the Langmuir isotherm equations have been reported most frequently. The Langmuir model assumes that the uptake of MB occurs on a homogeneous surface through a monolayer adsorption. The Langmuir equation is expressed by the following expression[24,25]
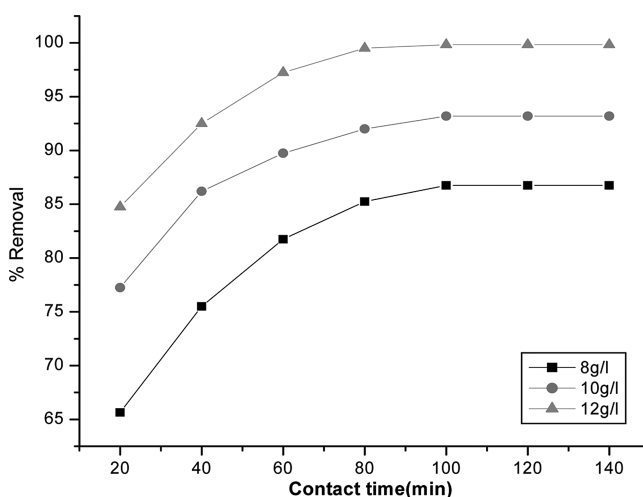

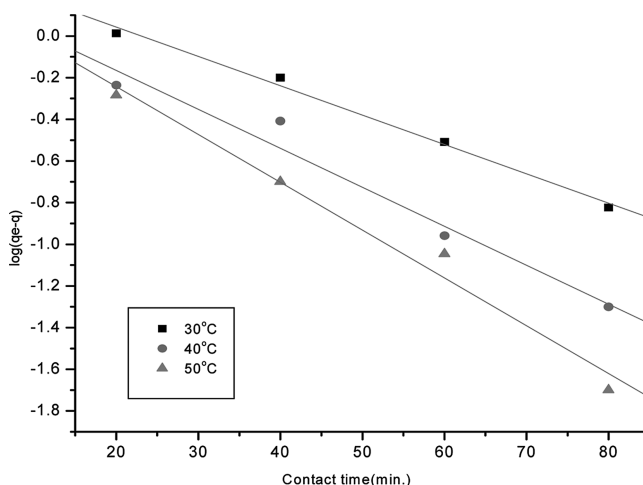**Figure 5.** Effect of adsorbent dose on the percent removal of methylene blue on RHAC.

Figure 6. Lagergren's plot for kinetic modeling of the adsorption process of methylene blue on RHAC.
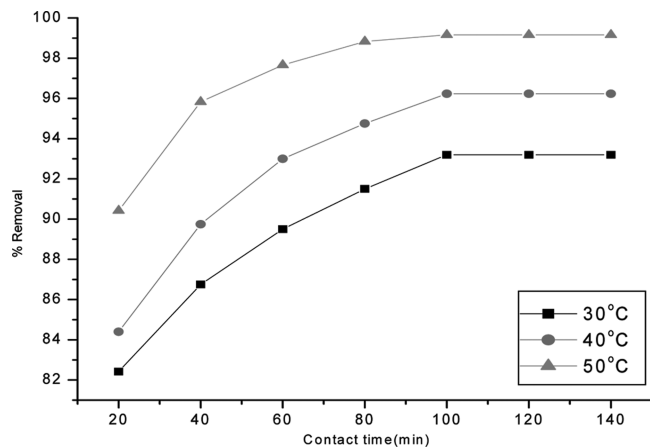
Figure 7. Effect of temperature on the percent removal of methylene blue on RHAC.
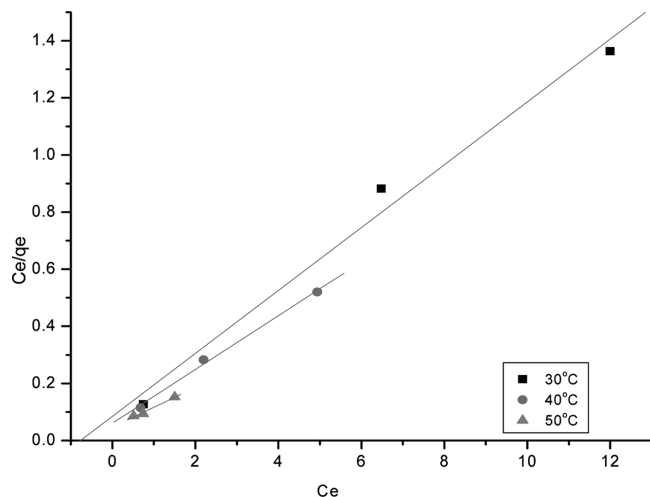

Figure 8. Langmuir's isotherm plot for the adsorption of MB on RHAC.

Table 2. Isotherm Parameters for the Removal of MB on RHAC

isotherms		parameters		
		Q^o	b	
Langmuir	temperature (K)	mg·g^{-1}	L·mg^{-1}	R^2
	303	9.83	1.29	0.984
	313	10.62	1.55	0.9904
	323	14.34	1.49	0.8343
		K_f	$1/n$	
Freundlich		L·g^{-1}	(L·g^{-1})	R^2
	303	0.21	0.78	0.9972
	313	0.22	0.811	0.9923
	323	0.44	0.925	0.9937

$$C_e/q_e = 1/Q^o b + C_e/Q^o \qquad (3)$$

where C_e (milligrams per liter) is the equilibrium concentration of the solute, q_e is amount adsorbed at equilibrium (milligrams per gram), and Q^o (milligrams per gram) and b (liters per milligram) are constants related to the adsorption capacity and energy of adsorption, respectively. A plot of C_e/q_e versus C_e (Figure 8) gives a straight line. The values of Q^o and b were determined from the slopes and intercepts of Figure 8 and are given in Table 2.

For Langmuir isotherm, the essential characteristics can be expressed in terms of a dimensionless equilibrium parameter (R_L)[23]
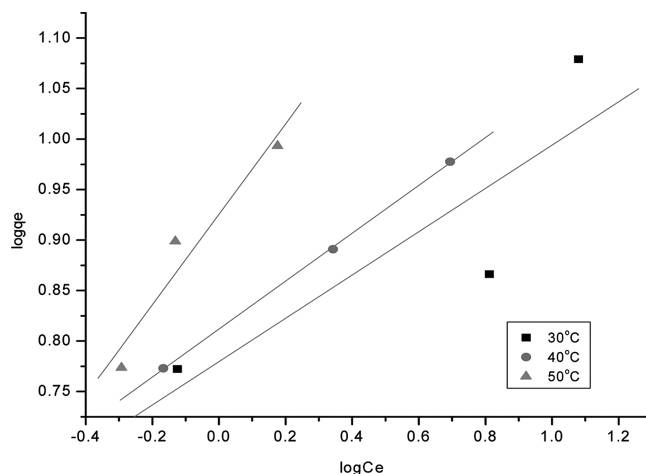

Figure 9. Plot of Freundlich adsorption isotherms of MB on RHAC.

Table 3. Comparison of Adsorption Capacities of Different Adsorbents for the Removal of Methylene Blue

adsorbent	q_m mg·g^{-1}	refs
coconut coir	15.59	Sharma et al., 2009[12]
yellow passion fruit	44.70	Pavan et al., 2008[26]
hazelnut shell	41.30	Ferrero, 2008[27]
lemon peel	29.0	Kumar and Porkodi, 2006[28]
orange peel	20.50	Annadurai et al., 2002[29]
orange peel	5.87	Kavitha and Namasivayam, 2007[30]
marine seaweed	5.23	Cengiz and Cavas, 2008[31]
sawdust	4.89	Pekkuz et al., 2008[32]
rice husk	9.83	this study

$$R_L = 1/(1 + KC_o) \qquad (4)$$

where K is the Langmuir constant (liters per gram) and C_o is the initial dye concentration (milligrams per liter). The value of R_L indicates the type of the isotherm to be either unfavorable, linear, or favorable. If $R_L > 1$, then it follows an unfavorable adsorption, a value of 1.0 for R_L indicates linear, a value of R_L less than 1.0 indicates favorable, and a value of R_L equal to zero suggests irreversible adsorption.

Adsorption data for the dyes on RHAC were also fitted in the linear form of the Freundlich isotherm

$$\log x/m = \log K_f + 1/n \log C_S \qquad (5)$$

where x/m is the amount adsorbed per unit mass of the adsorbate, C_s is the equilibrium concentration, and $1/n$ and K_f are the constants. The constant K_f is related to the degree of adsorption, and n provides the tentative estimation of the intensity of the adsorption. The values of n were determined from the straight line plots of $\log x/m$ versus C_s (Figure 9). K_f and n were calculated from the slopes and intercepts of the straight line plots and are given in Table 2. It may be noted that the value of K_f and n increases with an increase in temperature for the dye on activated carbon, indicating that adsorption is favorable at higher temperature.

Comparison of the Adsorption Capacity of RHAC. Adsorption capacity of the adsorbent, RHAC, was compared with that of the capacities of other nonconventional low-cost adsorbents. It can be seen from Table 3 that the adsorption capacity of RHAC is significant and comparable to that of other adsorbents used for the removal of methylene blue.[12,26−32] Yellow passion fruit,[26] however, displayed the maximum value (44.70 mg·g^{-1}), and saw dust[32] was reported to possess a capacity of 4.89 mg·g^{-1} for the removal of MB. The results show the applicability of RHAC for the removal of MB from aqueous solutions.

Conclusions

In the present study, activated carbon was both microporous and mesoporous with the BET surface area of 180.50 $m^2 \cdot g^{-1}$, which is quite significant. The activation was carried out by $ZnCl_2$ as an activating agent. The adsorption experiments indicate that the activated carbon of rice husk has good adsorption capacity for basic dye from aqueous solutions. The isotherm studies indicate good capacity for the removal of dye by RHAC. Rice husk, an agricultural waste material, can be effectively used for the preparation of activated carbon. The generated data can be used as baseline data for designing treatment plants for the treatment of dye containing effluents.

Acknowledgment

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