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Adsorption Characteristics of a Low-Cost Activated Carbon for the Reclamation of Colored Effluents Containing Malachite Green

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ABSTRACT: Adsorption characteristics of a low-cost activated carbon, rice husk activated carbon (RHAC), for the removal of malachite green (MG), a basic dye from aqueous solutions, have been investigated. Rice husk is peel-off from paddies and is a well-known agricultural waste material. Characterization of the activated carbon was carried out using different sophisticated methods. RHAC was characterized by Fourier transformation infrared spectrometry (FTIR), scanning electron microscopy (SEM), X-ray diffractometry (XRD), and thermogravimetric analysis (TGA). A nitrogen adsorption isotherm study revealed that the RHAC possessed micropores and mesopores. The porous properties of activated carbon were determined, and its surface area was found to be 180.50 m^2/g. The RHAC was used for the removal of MG from its aqueous solutions. The effect of initial concentration and contact time, temperature, and pH on the removal of MG was investigated. The removal of MG decreased from (94.91 to 93.75) % by increasing the initial dye concentration from (60 to 100) mg/L. A study of the effect of temperature revealed the process of removal of dye to be endothermic. Kinetic studies of the process of adsorption were also carried out. The experimental data were used to study the Langmuir and Frendulich adsorption isotherms.

1. INTRODUCTION

Because of the escalating world population, water pollution has been a topic of concern for the scientific community for many decades. The problem of water pollution is more severe in developing and underdeveloped nations as the resources to supply fresh drinking water are dwindling and thoroughly inadequate. Water is needed in all industrial applications, and the solution to this problem seems to be treatment of wastewater and its reuse. Osmosis, membrane separation, precipitation, adsorption, and chemical oxidation are common methods used for the treatment of wastewaters, but these methods are either expensive or pose other problems. Adsorption on activated carbon has been quite popular, and it has been frequently reported for treatment of effluents from the textile, chemical, leather, pharmaceutical, and food industries[1−6], but the high cost of activated carbon restricts its large scale application to developing nations. Activated carbons are mainly characterized by high surface area and developed pore structures.

Dyes like malachite green, methyl orange, acid red, and crystal violet are used regularly in textile, pulp and paper, leather, and paint manufacture and are discharged with effluents. These colors are generally nonbiodegradable and pose serious environmental problems. Malachite green (MG) has been known to cause diseases like eye burns, fast breathing, profuse sweating, and cancer of different parts of the body. Because of its harmful nature, MG should be removed from effluents prior to their discharge. Various raw materials have been used for the removal of pollutant species, but these alternative substances offer a poor efficiency of removal. A possible solution to this problem could be preparation of activated carbon from agricultural waste/raw materials. Use of these activated carbons for the removal of pollutant species from aqueous solutions and effluents may result in development of a low-cost technology for color removal. Activated carbons have also been synthesized from various locally available agricultural byproducts such as coconut coir, dried leaves, orange peel, sugar cane bagasse, banana peel, and tree bark.[7−12] Rice husk has little or no economic value, and its disposal is not only costly but may also cause other environmental problems.[13,14]

The present work has been devoted to prepare a low-cost activated carbon by using rice husk and then using the activated carbon for the removal of the selected dye, malachite green. The conditions of the synthesis of rice husk activated carbon (RHAC) have been optimized. The effect of important parameters, namely, contact time and initial concentration, adsorbent dose, and effect of temperature on the removal of MG by RHAC, has been reported. Kinetic and analytical studies for the removal of MG have also been conducted.

2. MATERIALS AND METHODS

All reagents used in the experiments were of analytical (AR) grade and were obtained from Merck, Mumbai, India. Stock solutions of the test reagents were prepared by dissolving the dye in distilled water. The dye, malachite green oxalate, C.I. Basic Green 4, C.I. Classification Number 42000, chemical formula, $C_{52}H_{54}N_4O_{12}$, molecular weight, 927.00, and λ_{max} 618 nm was also supplied by Merck India Ltd., Mumbai. Detailed information about the dye is given in Table 1.

2.1. Preparation of Adsorbent. The agricultural waste material, rice husk, used in the present investigations was collected from a nearby rice mill located in Varanasi, India. The rice husk was washed with distilled water several times to remove the dirt and dust and was subsequently dried in a hot air oven at 110 °C. Afterward, carbonization of the rice husk was carried out at 450 °C for 1 h in a tubular muffle furnace. A constant nitrogen (purity 99.99 %) flow of 150 mL/min was maintained

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Table 1. Detailed Information on Malachite Green

dye	malachite green
color index name	Basic Green 4 (BG 4)
color index number	42000
empirical formula	$C_{23}H_{25}N_2Cl$
molecular weight	365
dye content, (%)	90
λ_{max}, (nm)	618

throughout the process of carbonization. Primary carbon was obtained on carbonization, which was afterward mixed with zinc chloride. Zinc chloride acts as a catalyst in the process. The primary carbon was activated at 650 °C for 2 h under optimized conditions to obtain activated carbon. The activated carbon was thereafter cooled to room temperature in an inert atmosphere of nitrogen and washed with hot distilled water and 0.5 N hydrochloric acid until the pH of the material reached 7.0. The activated carbon was also 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.

2.2. Batch Adsorption Studies. Preliminary batch adsrption studies were conducted to determine the equilibrium time. Batch studies were performed by mixing 0.25 g of RHAC with 50 mL of solution of different initial concentrations of MG in 250 mL stoppered conical flasks. The dose of adsorbent was decided experimentally. All the adsorption experiments were conducted at 30 °C, at an agitation speed of 150 rpm on a thermostat shaking water bath. The progress of adsorption was noted, and equilibrium was achieved in 40 min. After equilibrium, the adsorbent was separated from the aqueous phase by centrifugation at 10000 rpm for 10 min using a centrifuge (Remi 24, India). The residual concentration of dye in the supernatant was determined by a UV−visible spectrophotometer (Spectronic 20, Bausch and Lomb, NY, USA) at 618 nm.

The percentage removal of the dye at equilibrium and the amount of dye transferred onto the surface of the adsorbent, q_e (mg/g) was calculated using the following relationships

$$\text{Percentage dye removal} = 100(C_o - C_e)/C_o \qquad (1)$$

Amount of adsorbed dye molecules per g of solid

$$q_e = (C_o - C_e)V/w \qquad (2)$$

where, C_o(mg/L) is the initial concentration of malachite green, C_e (mg/L) is the equilibrium concentration of dye, V is the volume of the solution (L), and w (g) is the mass of the adsorbent.

3. RESULTS AND DISCUSSION

3.1. Characterization of RHAC. The Brunauer−Emmett−Teller (BET) surface area of RHAC carbon was determined by using a surface area analyzer (ASAP 2020, Micromeritics, USA). The activated carbon sample was degassed for 12 h under vacuum at a temperature of 350 °C prior to analysis to remove impurities. The calculation of surface area, porosity, and pore volume were carried out by standard methods.[15] The adsorption characteristics of the activated carbon were determined from a nitrogen adsorption isotherm. The surface functional groups of rice husk activated carbon were detected by Fourier transform infrared spectrometry (FTIR-2000, Perkin-Elmer, USA) (figure not shown), and the spectra were recorded in the (4000 to 400) cm^{-1} range. The spectrum displayed the following bands: 2895.79 cm^{-1} (υ (C−H) (vibration in the aromatic group), 2291.80 cm^{-1} (C−H alkyl group vibration), 1583.50 cm^{-1} (υ (C=C) vibration in the aromatic group), 1102.15 cm^{-1}(υ (C=C) vibration in the aromatic group), and 800.16 cm^{-1} (γ (C−H) vibration in benzene derivatives).[16] The characteristics of RHAC are given in Table 2, indicating its surface area, pore volume, and pore diameter.

Table 2. Physical Characteristics of Rice Husk Activated Carbon

BET surface area (m^2/g)	180.50
micropore surface area, s_{mic} (m^2/g)	152.95
mesopore surface area, s_{mes} (m^2/g)	27.55
total pore volume, V_p (cm^3/g)	0.027
BET adsorption, average pore width (Å)	22.52
mean pore diameter, D (Å)	31.58

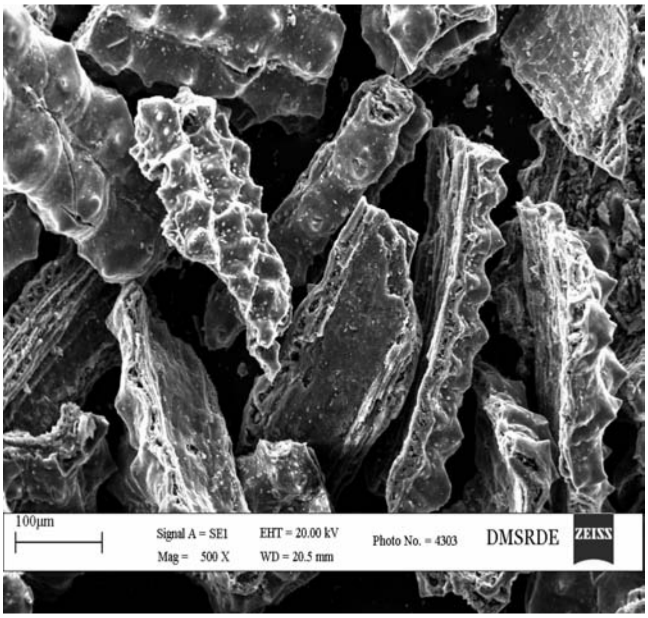

Figure 1. SEM of rice husk activated carbon.

3.2. Scanning Electron Micrograph of RHAC. The surface characteristics, especially surface morphology of the activated carbon, were analyzed using ZEISS, EVO 50, UK, and Quanta 200 FEG scanning electron microscopes. Samples were mounted on an aluminum stub and coated with a thin layer of gold. The micrograph of rice husk activated carbon is shown in Figure 1. This micrograph represents a higher magnification image and also a cracked and pitted surface morphology of rice husk activated carbon.[17] The surface is rough and seems to be suitable for the adsorption of different species from liquid and gaseous phases. Further, the micrporous and mesoporous surface area of RHAC are (152.95 and 27.55) m^2/g, respectively (Table 2), and it is apparent that adsorption of MG would be greater on the micropores in the adsorbent.

3.3. TGA−DTA Analysis. The TGA−DTA curves of the RHAC are shown in Figure 2. The thermogravimetric analysis is directly dependent on the decomposition temperature of various oxides and functional groups of the material. As shown in the TGA curve, there is a maximum weight loss (∼ 55 %) at

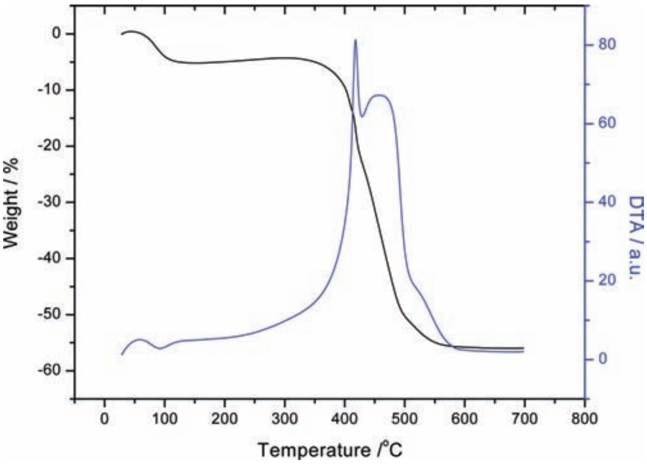

Figure 2. DTA−TGA curve of rice husk activated carbon.

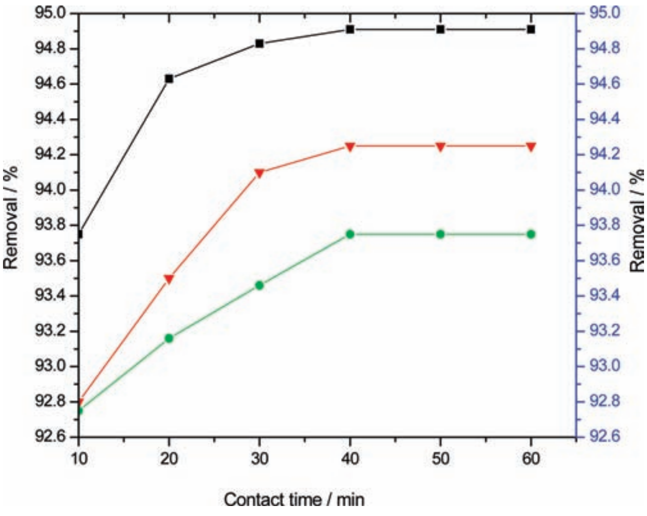

Figure 3. Effect of initial concentration on percent removal of malachite green on RHAC: □, 60 mg/L; ▲, 80 mg/L; and ●, 100 mg/L.

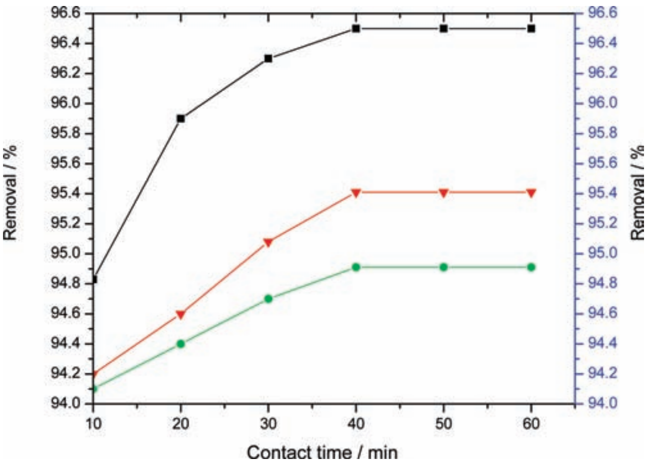

Figure 4. Effect of temperature on percent removal of malachite green on RHAC. Temperatures: □, 303 K; ●, 313 K; and ▲, 323 K.

450 °C, which was recorded under an oxidizing atmosphere. However, only an approximate 5 % weight loss was observed in the (50 to 100) °C range. In an oxidizing atmosphere, pyrolysis of RHAC takes place and shows maximum degradation in form of CO, CO_2, water vapor, and volatile matter in the gaseous form. An obvious weight loss between (50 to 600) °C is consistent with the analysis of the TGA curve.[18,19] In addition, the peak intensity of RHAC is found to rise once the temperature increases from (350 to 400) °C, while the peak intensity of RHAC has not obviously changed as temperature increases from (100 to 350) °C in the DTA curve.

3.5. Effect of Contact Time and Initial Concentration. The adsorption of malachite green by RHAC was substantially influenced by initial dye concentration. The variation in percentage removal of the dye with contact time at different initial concentrations ranging from (60 to 100) mg/L is shown in Figure 3. It is observed from the figure that the removal of MG acquired a maximum at the time of equilibrium, viz. 40 min, and becomes steady thereafter. It is clear from this figure that the rate of adsorption is very fast in the initial stages and after equilibrium; no significant change in the extent of adsorption is observed. For the initial concentration, the removal increased from (93.75 to 94.91) % by decreasing the initial concentration of malachite green from (100 to 60) mg/L. It is evident that although a significant variation in adsorption of MG is not observed, the extent of removal (%) is greater at lower initial concentrations, and the percent removal of dye decreases with an increase in initial concentration.

3.6. Effect of Temperature. Temperature is an important parameter for adsorption processes. It has significant influence on the adsorption of malachite green on RHAC also. The effect of temperature was investigated in the temperature range (30 to 50) °C. The experimental results show that the removal of MG increased from (94.91 to 96.50) % by increasing the temperature from (30 to 50) °C (Figure 4). Most adsorption processes are governed by exothermic processes, but the present system is governed by endothermic adsorption.[20]

Ravikumar et al.[21] reported that removal of Verofix Red (Reactive Red 3GL) and Lanasyam Brown Grl (Acid Brown 29) from aqueous solution was exothermic, and they found nearly a 100 % removal. Gupta and Suhas[22] also reported the process of removal of a number of dyes to be governed by exothermic processes. Navine[23] reported interesting data on the removal of reactive orange by adsorption on activated carbon prepared from bagasse. Contrary to these studies, the removal of Lanasyn Navy M-DNL by adsorption on activated carbon and on a neutral polymeric adsorbent, Macronet MN 200, was governed by an endothermic process.[24]

3.7. Effect of pH on Dye Uptake. The effect of pH on the adsorption of malachite green has been investigated, and the results indicated that the pH of the solution significantly influenced the adsorption of MG in the present studies. To study the influence of pH on the adsorption of MG on RHAC, the experiments were performed at a 60 mg/L initial dye concentration with 0.25 g adsorbent at 30 °C. The reaction mixture was agitated for 40 min, the equilibrium time. Figure 5 shows the variation of percent adsorption of MG at different values of solution pH. This figure shows that a lower removal of MG is obtained in the acidic range of pH. Lower adsorption of MG in the acidic pH range is probably due to the presence of excess H^+ ions competing with the cation groups on the dye for adsorption sites.[25,26] As the surface charge density decreases with an increase in the solution pH, the electrostatic repulsion between the positively charged dye (MG) and the surface of

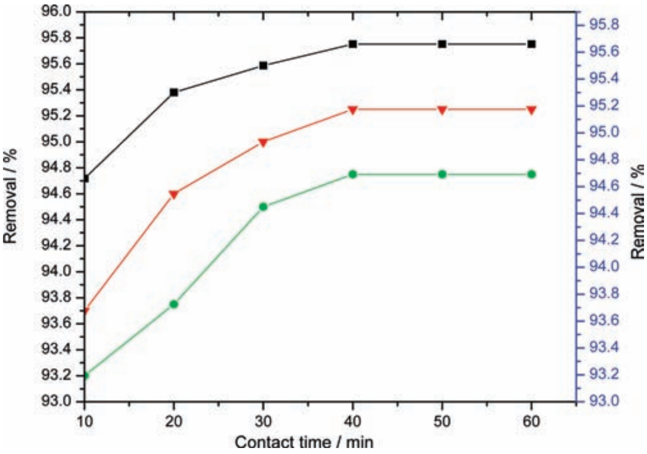

Figure 5. Effect of pH on percent removal of malachite green on RHAC. pH values: ●, 4.0; ▲, 6.0, and ☐, 8.0.

the RHAC is lowered, which may result in an increase in the rate of adsorption. At higher solution pH, the surface of RHAC might have become negatively charged, which enhances the positively charged dye cations through electrostatic forces of attraction and hence resulted in a higher removal in the alkaline pH range.

3.8. Kinetic Studies. In order to test the suitability of the adsorbent for the removal of MG, the data were analyzed using both the pseudo first-order and second-order rate equations. A detailed discussion is presented as follows.

3.8.1. Pseudo First-Order Kinetic Model. The kinetics of adsorption of malachite green on RHAC were studied with respect to different initial concentrations. For evaluating the adsorption kinetics of MG by RHAC, a number of models were examined, but the pseudo first-order and second-order kinetic models were found to be suitable for the experimental data. The pseudo first-order kinetic model can be represented as[27]

$$\log(q_e - q) = \log q_e - (K_1/2.303)\cdot t \qquad (3)$$

where q_e and q (both in mg/g) are the amounts of malachite green adsorbed at equilibrium and at any time, t, respectively, and K_1 (min^{-1}) is the rate constant of adsorption. The straight line plots of "log ($q_e - q$) vs t" (Figure 6) confirm that the process of removal is governed by pseudo first-order kinetics. Further, the straight line plots of Figure 7 indicate the suitability of the proposed pseudo first-order kinetic model for the adsorption of MG by RHAC. The values of the rate constant of adsorption were determined from the slopes of Figure 6 and are given in Table 3. The values of the rate constant of adsorption were found to increase with temperature, indicating involvement of an endothermic process for the removal of MG in the present studies.

3.8.2. Second-Order Kinetic Model. The kinetic data for the removal of MG onto RHAC was also fitted by a second-order kinetic model. The model is expressed by the following equation[28]

$$t/q = 1/k_2 q_e^{\,2} + t/q_e \qquad (4)$$

where q_e (mg/g) is the equilibrium adsorption capacity. The deviation of the straight lines from the origin (Figure 7) may be due to differences in the rates of mass transfer in the initial and final stages of sorption. Further, such deviation of the straight lines from the origin indicates that pore diffusion is not the sole rate-controlling step and the second-order rate constants k_2 (mg/g/min) can be determined from the slope and intercept of a plot of "t/q vs t" (Figure 7). The parameters k_2 and q_e determined from the model are presented in Table 3, along with the corresponding coefficients of determination. The calculated and experimental values of q_e are given in Table 3.

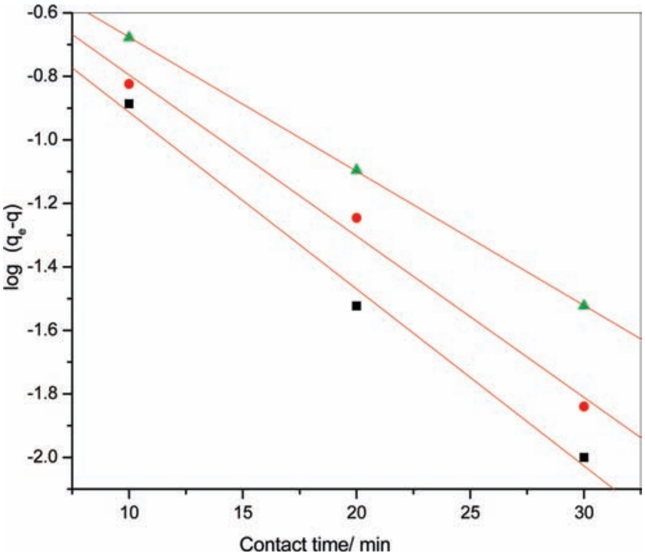

Figure 6. Lagergren's plot for kinetic modeling of the adsorption process of removal of malachite green on RHAC: ☐, 303 K; ●, 313 K; and ▲, 323 K

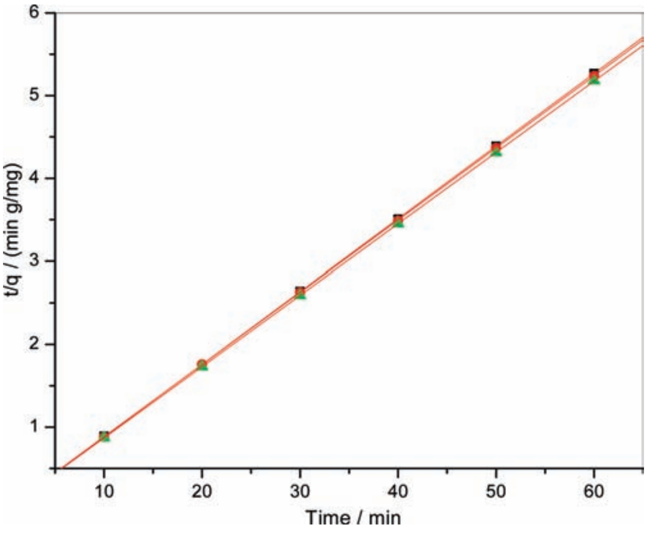

Figure 7. Plot of second-order kinetic modeling of the adsorption process of removal of malachite green on RHAC. Temperatures: ☐, 303 K; ●, 313 K; and ▲, 323 K.

Since neither the pseudo first-order nor the second-order model can identify the diffusion mechanism, the kinetic results were further analyzed by the intraparticle diffusion model to elucidate the diffusion mechanism[29]

$$q_t = K_{id} t^{1/2} + C \qquad (5)$$

where C is the intercept and K_{id} is the intraparticle diffusion rate constant (mg/(g min$^{1/2}$)), which can be evaluated from the slope of the linear plot of "q_t vs $t^{1/2}$". According to this model, a plot of 'q_t vs $t^{1/2}$' (Figure 8) should be linear if intraparticle

Table 3. Values of Rate Constants of Pseudo First-Order ($\times 10^{-2}$ min^{-1}) and Pseudo Second-Order ($\times 10^{-3}$ gmg^{-1}min^{-1}) Reaction and Intraparticle Diffusion at Different Temperatures for the Removal of MG by Adsorption on RHAC

temperature	K_1		k_2		K_{id}	
(K)	($\times 10^{-2}$ min^{-1})	R^2	(gmg^{-1} min^{-1})	R^2	(10^{-6} mgg^{-1} min$^{-1/2}$)	R^2
303	4.22	1.0	0.13	1.0	4.32	0.9666
313	5.08	0.9905	0.12	1.0	4.41	0.9363
323	5.57	0.9932	0.66	1.0	6.64	0.8961

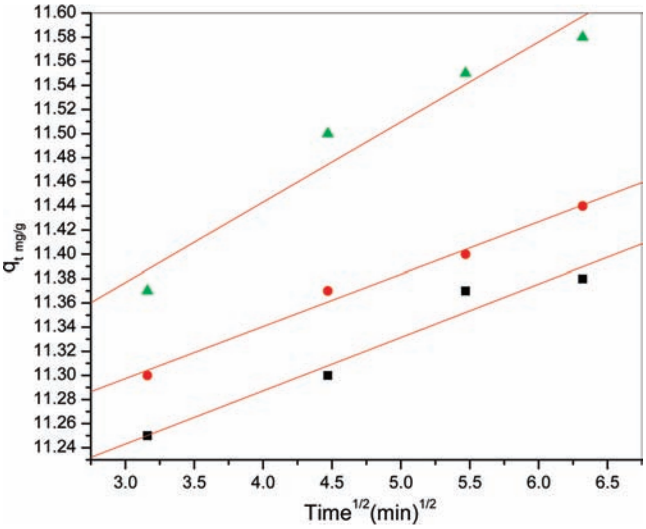

Figure 8. Plot of intraparticle diffusion of the adsorption process of removal of malachite green on RHAC. Temperatures: □, 303 K; ●, 313 K; and ▲, 323 K.

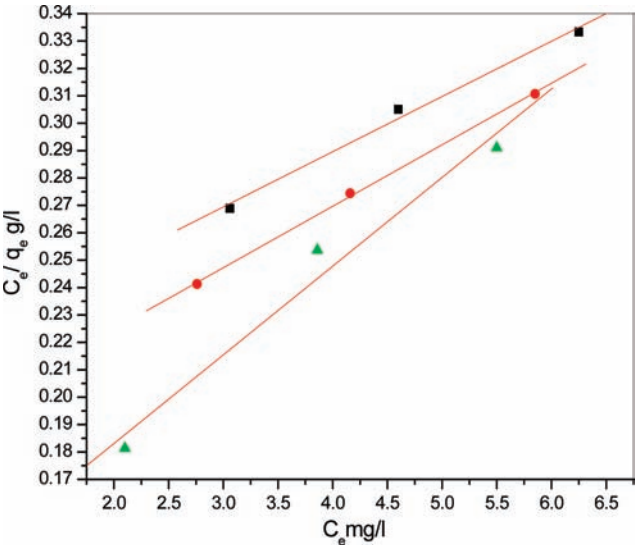

Figure 9. Langmuir plot for the removal of MG by adsorption on RHAC. Temperatures: □, 303 K; ●, 313 K; and ▲, 323 K.

diffusion is involved in the adsorption process, and if these lines pass through the origin, then intraparticle diffusion is the rate-controlling step. A perusal of Figure 8 indicates very interesting results that at 30 °C the uptake is controlled by pore diffusion, whereas at the other two values of temperature, pore diffusion is not the only rate controlling step for the present system.

Though both the kinetic models fit the experimental data, it is clear from Table 3 that at the three temperatures, the value of R^2 (1.0) suggests that second-order kinetic model fits the data better.

3.9. Analytical Study. An analytical study provides the basic requirements for the design of adsorption systems for the removal of soluble pollutant species, and in the present study, an analytical study was performed by fitting the experimental data to well-known isotherm equations. Selection of an isotherm equation depends on the nature and type of the system. The adsorption capacity of activated carbon prepared from rice husk was determined by fitting the experimental data to the Langmuir and Frendulich isotherm equations.

3.10. Langmuir Isotherm. The Langmuir model assumes that uptake of malachite green occurs on a homogeneous surface by monolayer adsorption. The Langmuir equation is expressed by the following expression[30]

$$C_e/q_e = 1/(Q^\circ \cdot \mathrm{b}) + C_e/Q^\circ \qquad (6)$$

where C_e (mg/L) is the equilibrium concentration of the solute, q_e is amount of solute adsorbed at equilibrium (mg/g), and Q° (mg/g) and b (L/mg) are constants related to the adsorption capacity and energy of adsorption, respectively. A plot of C_e/q_e vs C_e (Figure 9) gives a straight line. The values of Q° and b were determined by the slopes and intercepts of Figure 10 and are given in Table 4.

3.11. Freundlich Isotherm. Adsorption data for the adsorption of MG on RHAC was fitted to the linear form of the Freundlich isotherm[31]

$$\log x/m = \log K_f + 1/n \log C_s \qquad (7)$$

where x/m is the amount adsorbed per unit mass of the adsorbate, C_s the equilibrium concentration, and $1/n$ (L/g) and K_f (L/g) are the Frendulich constants. The constant K_f is related to the degree of adsorption, and n provides a tentative estimation of the intensity of the adsorption. The values of these parameters were determined from the straight line plots of "log x/m vs C_s" (Figure 10) and are given in Table 4. It may be noted that the values of K_f and n increase with an increase in temperature for the present system, indicating that adsorption of MG on RHAC is favorable at higher temperature[32] and the process of removal is endothermic. When the value of n is 1, the adsorption is a linear isotherm. When the value of $n < 1$ or $n > 1$, this implies that the adsorption process is related to a chemical or favorable physical process, respectively. The value of n in all the cases are > 1, indicating a favorable adsorption process for removal of malachite green (Table 4). A perusal of the R^2 values shows (Table 4) that the kinetic data for the present system fits better the Freundlich isotherm (coefficient of determination $R^2 > 0.99$), as compared with Langmuir's model. The monolayer adsorption capacity according to this model was 9.83 mg/g at 30 °C.

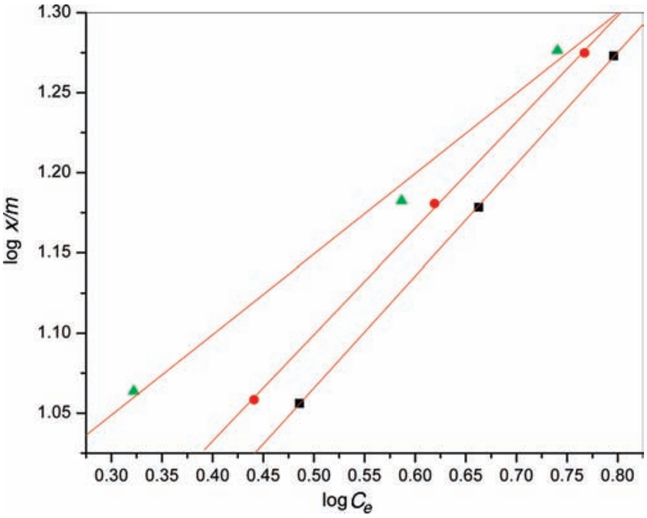

Figure 10. Freundlich adsorption isotherm for the removal of malachite green on RHAC. Temperatures: □, 303 K; ●, 313 K; and ▲, 323 K.

Table 4. Values of Constants of Langmuir and Freundlich Isotherms for Adsorption of Malachite Green on RHAC

isotherms		parameters		
Langmuir	temperature (K)	$Q°$ (mg/g)	b (l/mg)	R^2
	303	30.90	0.096	0.999
	313	44.58	0.124	0.995
	323	49.62	0.273	0.9674
Freundlich		K_f (l/g)	$1/n$ (l/g)	R^2
	303	3.01	1.86	0.9946
	313	3.74	2.11	0.9944
	323	3.99	3.14	0.9955

Table 5. Thermodynamic Parameters for Removal of Malachite Green on RHAC

temperature (K)	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJmol^{-1} K^{-1})
303	−3.32	8.58	28.91
313	−3.71	23.59	87.03
323	−4.56		

3.12. Thermodynamic Study. Experiments were conducted at three different temperatures (30, 40 and 50) °C. The thermodynamic parameters, namely, change in standard enthalpy ($\Delta H°$), standard entropy ($\Delta S°$), and standard Gibbs energy ($\Delta G°$) for the present system, were determined using following expressions[33]

$$K_c = C_{ae}/C_e \qquad (8)$$

$$\Delta G^o = -RT \ln K \qquad (9)$$

$$\Delta H^o = R(T_2 T_1/T_2 - T_1) \cdot \ln(K_2/K_1) \qquad (10)$$

$$\Delta S^o = (\Delta H^o - \Delta G^o)/T \qquad (11)$$

where R (8.314 kJ/mol K) is the universal gas constant, and T (K) is the absolute temperature. C_e is the equilibrium concentration of malachite green in the solution (mg/L), and C_{ae} (mg/L) is the amount adsorbed on the surface of the adsorbent at equilibrium. The values of K_c increased by increasing the temperature, which indicates an endothermic nature of the process of removal. K, K_1, and K_2 are the equilibrium constants at temperatures T, T_1, and T_2, respectively. The values of K increased by increasing the temperature, which further indicates the endothermic nature of the process of removal. The values of these parameters are given in Table 5. The negative values of the Gibbs energy ($\Delta G°$) change are an indication of the spontaneous nature of the adsorption process. The values of $\Delta G°$ changed from (−3.32 to −4.56) kJ mol^{-1}. The positive values of the standard enthalpy change ($\Delta H°$) for the intervals of temperature were further indication of the endothermic nature of the adsorption process, and the positive values of $\Delta S°$ for the corresponding temperature intervals suggest the probability of favorable adsorption.

4. CONCLUSIONS

Rice husk is a common material and is available in large quantities in most parts of the world. It has quite a few applications, and its use for the removal of malachite green is another application. The activated carbon derived from rice husk (RHAC) has shown promising results. The RHAC has been characterized for pore size distribution and availability of various functional groups onto its surface. The surface morphology of the surface of the adsorbent was confirmed by SEM.

Up to (94.91 and 93.75) % color removal could be achieved in 40 min contact time from aqueous solutions at initial concentrations of (60 to 100) mg/L range. The process of removal followed first-order as well as pseudo second-order kinetic equations. The data followed both the Frendulich and Langmuir isotherm models. RHAC displayed a significant adsorption capacity. Thermodynamic parameters were determined, and the process of removal of MG by adsorption on RHAC was found to be spontaneous.

The experimental data can serve as baseline data for designing treatment plants for the treatment of dyehouse wastewaters.

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