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Study on the Removal of Methylene Blue Dye Using Chemically Treated Rice Husk

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Abstract: To remove methylene blue dye from wastewater, chemically modified rice husk has been used in the laboratory scale that comprises batch study leading to adsorption kinetics rate constants and maximum adsorption capacities. It has been observed that almost 95–99% of dye can be removed from the solution using treated rice husk. Langmuir adsorption isotherm, Freundlich isotherm model and Temkin model have been used to describe the distribution of dye between the liquid and solid phases in batch studies and it has been found that Langmuir isotherm represents the phenomenon better than other isotherm models. Due to low cost of rice husk this may be an effective material in the treatment of waste water containing dye and this material is biodegradable and eco-friendly.

Key words: Adsorption isotherm, adsorption kinetics, biosorption, rice husk, thermodynamic properties.

Introduction

Pollution by dye and its intermediates are worldwide problem nowadays. Dyes are used in different industries like textile, paper, cosmetics etc. to colour the products (Gong et al., 2005; Woon et al., 2008). Many of the synthetic dyes are carcinogenic in nature and create problems in life system. This dye interferes with the growth of bacteria and hinder photosynthesis in aquatic plants and environment.

The removal of dye from waste water can be done using different methods like ion exchange, reverse osmosis, chemical oxidation, electro-dialysis, adsorption using activated carbon or activated charcoal etc. (Brown et al., 1991; Cornelia et al., 2001; Kratochvil et al., 1998; Schiewer et al., 1996; Volesky et al., 1995; Volesky et al., 2001). But these treatment methods are costly and also suffer from incomplete removal besides being based on labour-intensive operation and high energy requirement. Disposal of the treated sludge is also a problem. The search for new and cost effective technologies involving the removal of dye has been oriented to biosorption based on dye binding capacities of different biological or agricultural materials (Chandrasekhar et al., 2006; Crini et al., 2008; Dogan et al., 2008; Hamdaoui et al., 2007; Han, 2006; Han et al., 2007).

The adsorption is the process where particles are removed from liquid phase through contact with solid adsorbent which has a special affinity for that particular solute (McCabe et al., 2005). When the solid adsorbent is a biological product the adsorption is referred to as biosorption. The main advantage of biosorption are low operating cost, easily available sources and minimization of volume of sludge to be disposed from the biosorbents. A number of natural and synthetic adsorbents have been studied by various researchers for the removal of dye.

Methylene blue is heterocyclic aromatic compound [$C_{16}H_{18}ClN_3S$]. It is solid, odourless powder which appears as blue solution when dissolved in water. It is used in a range of different fields such as printing cotton, dyeing, dyeing leather etc. (Dogan et al., 2008; Hamdaoui et al., 2007; Han, 2006, 2007). It is also used in dairy industry to determine the microbial load present in milk (Bapat et al., 2006). Excess use of these dye create different problems like hypertension, pre-cordial pain, dizziness, headache, fever, fecal discolouration, hemolytic anemia etc.

Rice husk is easily available agricultural waste material (Bharadwaj et al., 2004). It is the outer covering of paddy and accounts for 20–25% of its weight and is an agricultural byproduct whose major constituents are organic materials and hydrated silicon. It contains abundant fibre, and protein. Due to the groups such as carboxyl, hydroxyl and amidogen adsorption process is possible for rice husk. The organic materials present in rice husk are cellulose (55–60 wt% including cellulose and hemi-cellulose), lignin (22 wt%), crude protein (3%) etc.

The objective of the present study is to investigate biosorption properties of dye using chemically modified rice husk as biosorbent. For this, batch experiments are conducted. Attempt is also made to understand the kinetic rate constant of the reaction and thermodynamic parameters of the biosorption process. Error analysis was also carried out to test the accuracy of the kinetic equation.

Experiments

Preparation of Raw Biosorbents

Rice husk was obtained from an agro-industry of local area of Murshidabad district, West Bengal, India and washed properly with distilled water and dried at 333K in oven drier. It was subjected to 2.5% sodium hydroxide treatment and then the solution was autoclaved for about 15 minutes to separate the low molecular weight lignin compounds. After that the material was washed properly with double distilled water till the pH reached close to neutrality. The resulting solid particles were then separated from the solution using filtration process and dried at 333K. The particle size of treated rice husk was found to be less than 355 µm. Particle size analysis of the treated rice husk were carried out as per IS 2720 using standard sieves of different sizes. Scanning electron micrographs were studied using a scanning electron microscope, Model Hitachi S-3000N to understand the morphology of the original seashell. The particles were coated with gold using a Sputter Coater to give the conductivity of the samples. The scanning electron micrographs were then taken.

Preparation of Methylene Blue Solutions

Stock solution of methylene blue (1000 ppm) was prepared using A.R grade methylene blue powder in distilled water (Hi-Media). Experimental methylene blue solutions were prepared by diluting the stock solutions using distilled water.

Determination of Methylene Blue Contents in the Solutions

Calibration curve was prepared by recording the absorbance values of various concentration of methylene blue dye at maximum absorbance of wavelength (663 nm). The free dye content of the solutions after biosorption in the effluent before and after treatment was determined spectrophotometrically (UV/VIS spectrophotometer, Model: Hitachi).

Influence of Agitation Speed

The biosorption capacity was determined at different agitation speeds ranging from 60 rpm to 400 rpm using a fixed amount (1 gm) treated rice husk and fixed amount methylene blue solution of 20 ppm at 308K temperature in the incubator shaker of Model Innova 42, New Brunswick Scientific, Canada. The initial and final concentrations of the solutions were measured using UV/VIS spectrophotometer and adsorption capacities of the adsorbent were calculated.

Influence of pH

Adsorption experiments for dye on rice husk were carried out through batch method. 0.1N hydrochloric acid and 0.1N sodium hydroxide was used for adjusting the initial pH of solution after addition of biosorbent. The pH measurements were made by using pH meter during all the experiments. One gm of treated rice husk was added to 100 ml of 20 ppm dye solution in each of the 250 ml Erlenmeyer flasks and pH was maintained using hydrochloric acid and sodium hydroxide. pH of the solution were: pH 2 to pH 7. These 250 ml flasks were stirred at a constant temperature (308K) in a digital incubator shaker at 200 rpm and samples were taken from the flasks at particular time interval and solution concentrations were analysed using UV/VIS spectrophotometer. All the experiment had been done thrice and the average results had been taken.

Adsorption Experiment

The biosorption capacity was determined at different dye concentrations ranging from 5 to 200 ppm and a fixed amount (1 gm) treated rice husk was used to calculate the biosorption constant by using different isotherms. 100 ml of different concentration of dye solution ranging from 5 mg L^{-1} to 200 mg L^{-1} were used and dried treated rice husk (1 gm) were added to Erlenmeyer flasks and agitated at 308K and 200 rpm for 2 hr. The initial and final concentrations of the solutions were measured using UV/VIS spectrophotometer and adsorption capacities of the adsorbent were calculated. After the equilibrium was attained by each system, the dye uptake capacity for each sample was calculated according to mass balance on the dye using (Anirudhan et al., 2008; Jaman et al., 2009):

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

where C_i is initial dye concentration, C_e is equilibrium dye concentration (mg L^{-1}), V is volume of the solution (L), m is the weight of the treated rice husk in gm. The extent of sorption in percentage was calculated using the equation:

$$Sorption(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

Langmuir adsorption isotherm and Freundlich adsorption isotherm models were used to analyse the experimental data.

For the Langmuir model the following equation was used (Jaman et al., 2009):

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad (3)$$

where q_e is the amount of dye adsorbed at equilibrium (mg L^{-1}), C_e is the concentration of dye in aqueous phase at equilibrium (mg L^{-1}). The Q^0 and b are the Langmuir constant related to adsorption capacity and the energy of adsorption.

For the Freundlich isotherm constants were calculated using the following equation (Jaman et al., 2009):

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad (4)$$

where q_e is the amount of dye adsorbed at equilibrium, K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

For the Temkin isotherm model the following equation was used (Jaman et al., 2009):

$$q_e = B_T \ln K_T + B_T \ln C_e \quad (5)$$

where q_e is the amount of dye adsorbed at equilibrium, C_e is the concentration of dye in aqueous phase at equilibrium (mg L^{-1}), and K_T and B_T are the constants.

Influence of Different Amount of Biosorbent on Biosorption

To achieve the optimized amount of biosorbent, different amount of biosorbent (from 0.2 gm to 3 gm of rice husk in 100 ml dye solution) were used with 100 ml of 20 ppm dye solution for 1 hr at 200 rpm speed and at 308K temperature.

Influence of Temperature and Kinetic Study

To achieve the optimized temperature and determine the reaction rate constant and activation energy, the sorption process was carried out at different temperatures ranging from 303K to 319K. 100 ml of dye solution was taken in Erlenmeyer flask and a fixed amount of rice husk was used and the mixture was agitated at 200 rpm for 1 hr. Kinetic rate constant was calculated at different temperatures. From the rate constant activation energy of the adsorption of dye was determined using Arrhenius equation (Jaman et al., 2009).

$$\ln k_2 = \ln A_0 - \frac{E_a}{RT} \quad (6)$$

E_a is the activation energy in KJ mol^{-1}, R is the gas constant (8.314 J mol^{-1} K^{-1}) and A_0 is the Arrhenius constant.

Thermodynamic Parameter

The thermodynamic parameters of the adsorption of dye were determined using the following basic equations:

$$K_c = \frac{C_a}{C_e} \quad (7)$$

$$\Delta G^0 = RT \ln K_c \quad (8)$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (9)$$

where K_C is the distribution coefficient for the adsorption, ΔH^0 is the change of enthalpy, ΔS^0 is the change of entropy, ΔG^0 is the change of Gibb's free energy, R is the gas constant, T is the absolute temperature, C_a is the dye adsorbed per unit mass of the adsorbent, and C_e is the equilibrium adsorbate concentration in aqueous phase.

Error Analysis

In order to compare the applicability of different models, a normalized standard deviation was calculated (Jaman et al., 2009).

$$\Delta q(\%) = 100 \times \sqrt{\frac{\Sigma[(q_{exp} - q_{cal})/q_{exp}]^2}{N-1}} \quad (10)$$

where N is the number of data points, and q_{exp} and q_{cal} (mg g^{-1}) are the experimental and the calculated values of the equilibrium biosorbate solid concentration in solid phase respectively.

Results and Discussions

Effect of Agitation Speed

From Figure 1 it is observed that as the agitation speed increases the adsorption capacity of rice husk increases from 60 rpm to 200 rpm but if the agitation speed is further increased beyond 200 rpm, the adsorption capacity decreases. The reason behind the phenomenon is that at higher agitation speed some amount of dye adsorbed by treated rice husk is desorbed. It is observed that the maximum percentage removal of dye is 99.21% at 308K temperature and 200 rpm and the equilibrium is reached within 30–60 min of the adsorption reaction.

Effect of Different Initial Concentration

The effects of initial concentration on the percentage removal of dye at different contact times are shown in Figure 2 and Table 2. From Figure 2 it is observed that as the initial concentration of dye increases, biosorption capacity of rice husk increases with the sorption percentage increasing first from 93% to about 98% then decreasing to about 96%. At higher dye concentration, the dye is adsorbed more than at low dye concentration as more binding sites of the biosorbent are free for interaction at low dye concentration.

Table 1: Adsorption capacity of treated rice husk at different initial concentration of Methylene Blue Dye solution

Initial concentration, mg/L	$Q_{exp,}$ *(mg/gm)*	$Q_{cal;,}$ *(mg/gm)*	*Δq%*	R^2	*Rate constant, gm.* $mg^{-1}min$	*h* $mg\ gm^{-1}\ min^{-1}$
5	0.468	0.457	1.588	0.99	6.289	1.317
10	0.964	0.957	0.526	1.00	8.196	7.514
20	1.94	1.96	0.625	1.00	12.98	49.86
30	2.94	2.94	0.24	1.00	8.68	75.026
50	4.88	4.96	1.29	0.99	0.76	18.697
100	9.85	9.94	0.413	1.00	0.316	31.22
200	19.86	22.12	12.57	0.976	0.015	7.19

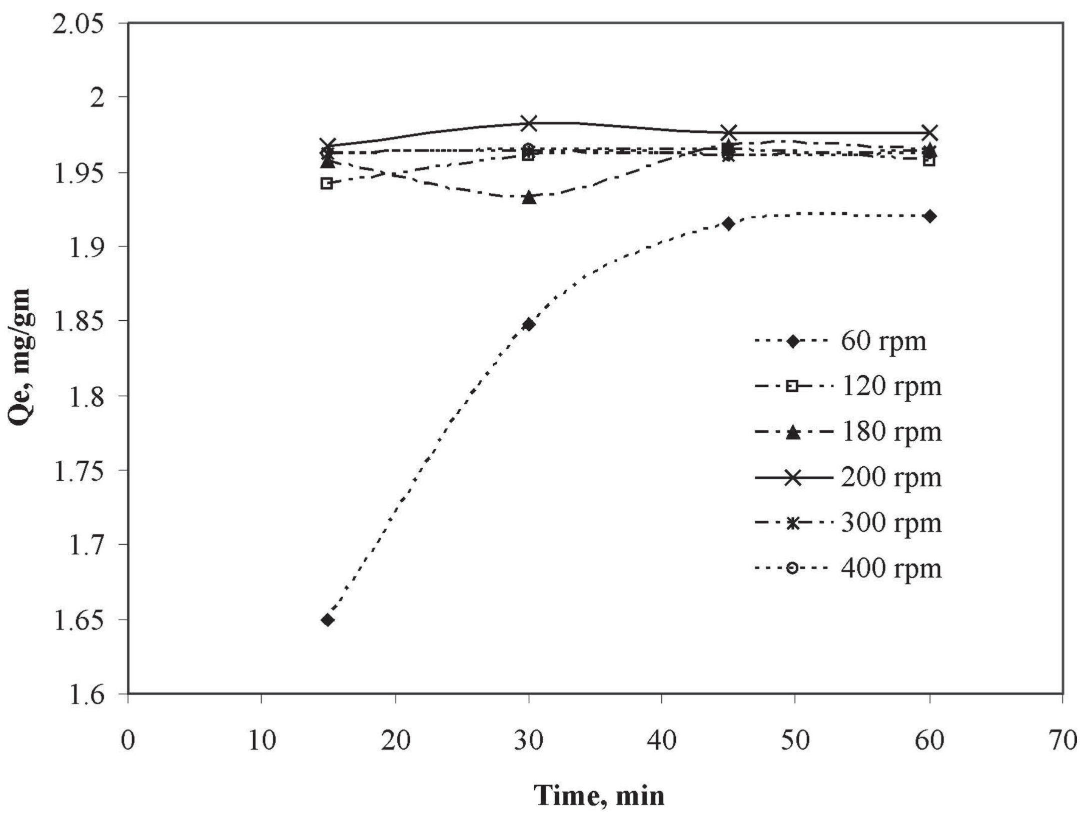

Figure 1: Effect of agitation speed on the adsorption capacity of dye using treated rice husk at different time at temperature 308K, adsorbent dose 1 gm, pH 7, and initial concentration of dye 20 mg/L.

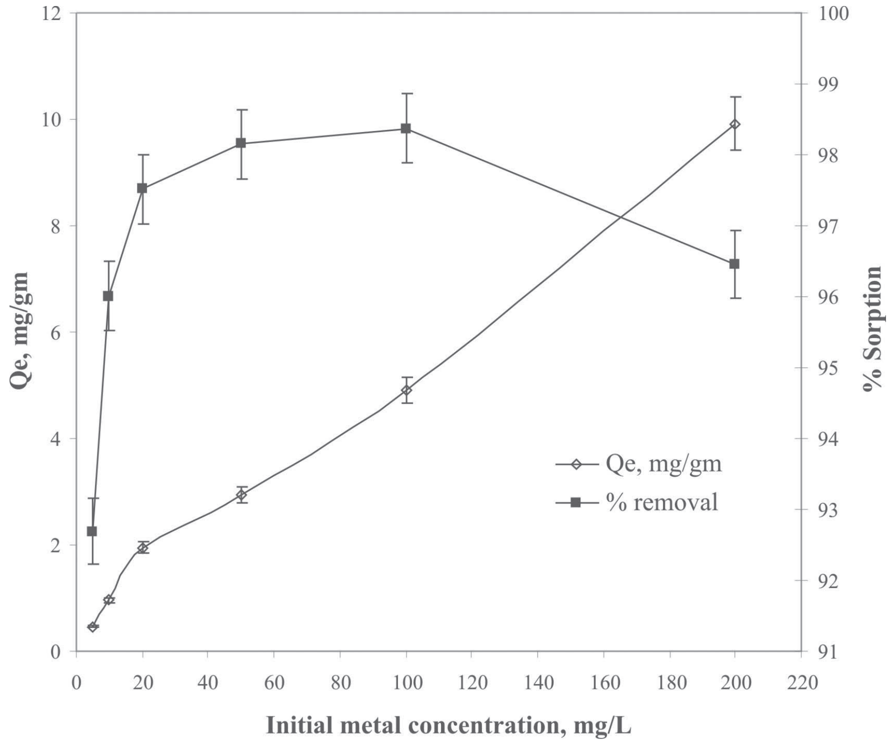

Figure 2: Effect of initial dye concentration on % sorption and adsorption capacity of treated rice husk at 308K temperature, adsorbent dose 1 gm, and pH 7.

Table 2: Adsorption capacity of treated rice husk and kinetic rate constant at different temperature of adsorption

Temperature, K	$Q_{exp,}$ *(mg/gm)*	$Q_{cal;,}$ *(mg/gm)*	*Standard deviation*	R^2	*Rate constant, gm.* $mg^{-1}min$	*h* $mg\ gm^{-1}\ min^{-1}$
303	1.94896	1.9488	0.000113	0.997	6.57	24.95
308	1.957782	1.958	0.000154	0.998	11.976	45.913
310	1.976686	1.9786	0.001353	0.999	12.97	50.775
319	1.974795	1.9837	0.006297	0.9976	12.8998	50.76

Effect of pH

The effects of pH on the percentage removal of methylene blue are shown in Figure 3. With the increase of pH of the solution, an increase of adsorption has been observed. However for pH greater than 7, precipitation of dye has been observed to occur. So the experimental work has been done upto pH 7. As methylene blue is cationic dye, it is adsorbed onto the adsorbent surface at higher pH values. As a result, adsorption of dye achieved better removal of dye on increasing the solution pH.

Adsorption Isotherms

Experimental data have been fitted to Langmuir, Freundlich and Tempkin models. It is observed that Langmuir constants Q^0 is 1.957 mg gm^{-1} and b is 234.78 L mg^{-1} with a regression coefficient of 0.999 whereas in Freundlich model K_F is 1.935(mg g^{-1}) (L $mg^{-1})^n$ and n is 68.985 and regression coefficient is 0.983. For Temkin model, B_T is 0.0358, regression coefficient is 0.951. The experimental results indicate that dye ions adsorb on rice husk as a monolayer adsorption as the adsorption follows Langmuir adsorption. As the temperature increases adsorption capacity increases indicating that the process is endothermic in nature. The separation factor (R_L) can be calculated by using this equation:

$$R_L = \frac{1}{1+bC_0} \tag{12}$$

where C_0 is the initial concentration (mg L^{-1}) and b is the Langmuir constant. From Figure 4 the value of R_L is calculated as 0.0005 which is found to be less than 1 and greater than 0. From Table 2, it is observed that as the temperature increases, the adsorption capacity increases

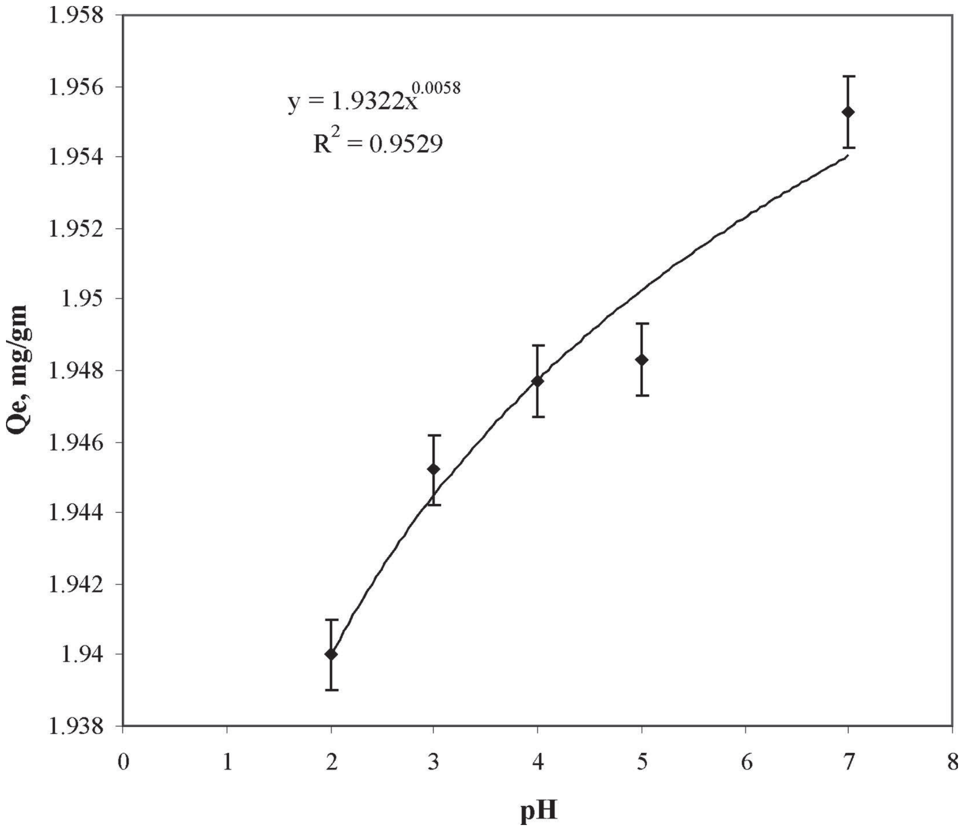

Figure 3: Effect of pH on adsorption capacity of treated rice husk at 308K temperature, adsorbent dose 1 gm, and initial concentration of dye 20 mg/L.

upto temperature 310K and after that adsorption capacity decreases because of the phenomenon of desorption at higher temperature.

Influence of Amount of Biosorbent

The effect of different amount of adsorbent can be inferred from Figure 5. As the amount of adsorbent increases from 0.2 gm to 1 gm, the adsorption capacity decreases but the percentage removal of dye from solution increases. When the amount of adsorbent increases from 1 gm to 3 gm, the percentage removal of dye decreases. The reason behind the phenomenon may be speculated to be due to the interference between binding sites at higher concentrations or insufficiency of dye in solution with respect to available binding sites.

Influence of Temperature and Kinetic Study

As temperature of the solution changes from 303 to 319K, the amount of dye adsorbed using treated rice husk increases from 1.948 mg gm^{-1} to 1.987 mg gm^{-1} for 100 ml 20 ppm dye solution. This may be a result of increase in the mobility of dye ions with temperature. The pseudo-first order rate expression is generally described by the following equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (12)$$

where q_e is the amount of dye adsorbed at equilibrium per unit weight of adsorbent (mg g^{-1}), q_t is the amount of dye adsorbed at any time (mg g^{-1}) and k_1 is the rate constant (min^{-1}). Integrating and applying boundary conditions as $t = 0$ and $q_t = 0$ to $t = t$ and $q_t = q_t$, the final equation is:

$$\log(q_e - q_t) = \log q_e - k_1 \frac{t}{2.303} \quad (13)$$

The pseudo-second order kinetic model equation is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (14)$$

where k_2 is pseudo-second order rate constant of adsorption (gm. mg^{-1} min^{-1}) and q_e and q_t are the amounts of dye adsorbed (mg gm^{-1}) at equilibrium and at time t respectively. The initial adsorption rate, h (mg. gm^{-1} min^{-1}) as $t \to 0$ can be calculated as

$$h = k_2 q_e^2 \quad (15)$$

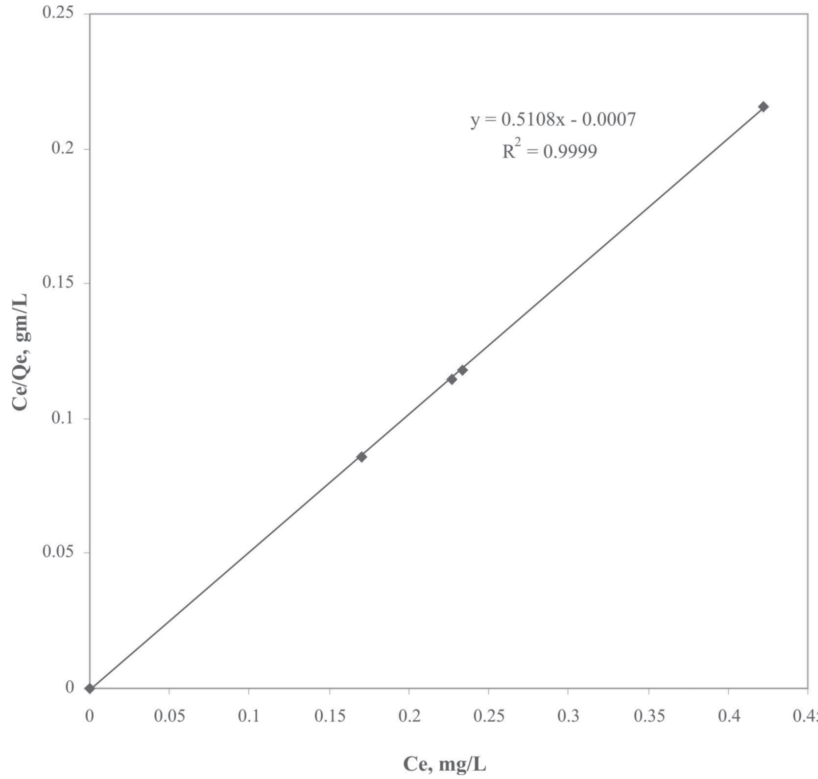

Figure 4: Langmuir adsorption isotherm plots for the adsorption of methylene blue dye solution at 308K, pH 7, adsorbent dose 1 gm, and initial concentration of dye 20 mg/L.

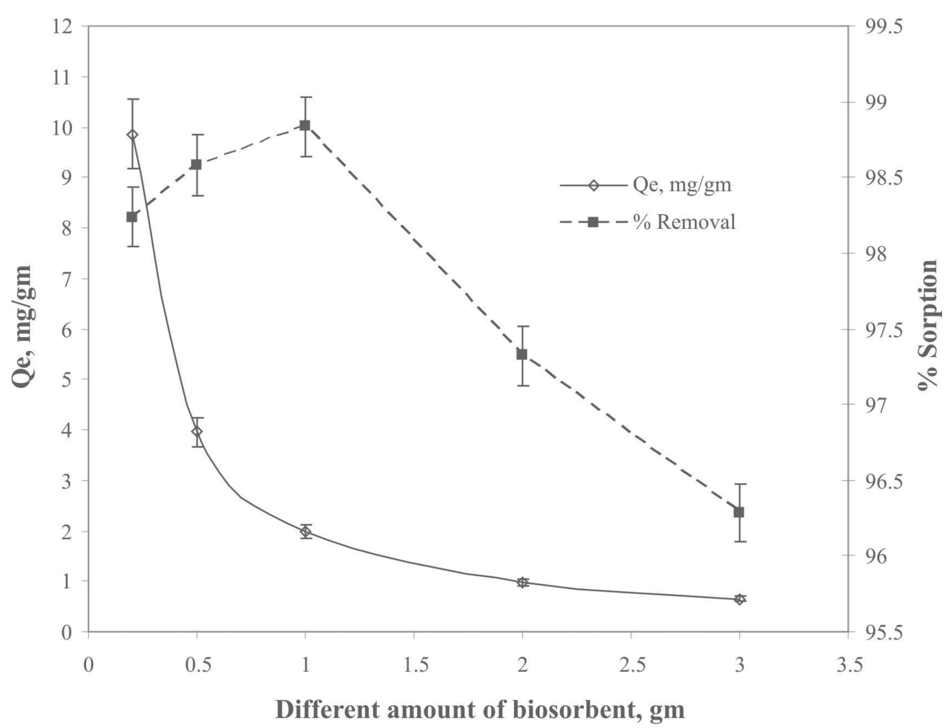

Figure 5: Effect of the different amount of biosorbent on adsorption capacity and % sorption of treated rice husk at 308K temperature, initial dye concentration 20 mg/L, and pH 7.

Calculations show for adsorption of dye using rice husk, pseudo-second order model better represents the phenomenon than first order model. The linear plots of $\frac{t}{q_t}$ versus t for different temperature and different initial concentration are shown in Figures 6a and 6b. It is observed from Table 2 that the rate constant increases as the temperature increases indicating that the adsorption of dye is endothermic process. At temperature of 308K, pH 7 the rate constant is 11.97 gm. mg^{-1} min^{-1} and initial adsorption rate is 45.91 mg. gm^{-1} min^{-1}. At 310K, the rate constant is 12.97 gm. mg^{-1} min^{-1} and adsorption capacity is 50.77 mg. gm^{-1} min^{-1}. But at 310K, in presence of bacteria contamination methylene blue dye can disappear as bacteria can consume methylene blue at this temperature (Bapat et al., 2006). So, the experimental work has been done at 308K temperature. From the pseudo-second order rate constant k_2, the activation energy E_a is calculated using Arrhenius equation. Activation energy for dye adsorption is calculated based on log k_2 versus $1/T$ as 12.905 KJ. $mole^{-1}$. Since the activation energy value is between 5 and 20 KJ $mole^{-1}$, physisorption is the predominant adsorption mechanism for dye reduction by rice husk. As activation energy is less than 40 KJ $mole^{-1}$, it follows that the reaction is diffusion controlled process which is a physical step in the adsorption process.

From surface morphology of rice husk it is observed that the surface texture of chemically treated rice husk and rice husk after adsorption is different (Figure 7a and 7b]. It is also observed that the surface texture of the treated adsorbents changes drastically after the loading of methylene blue dye on it.

Thermodynamic Parameters

The values of ΔH^0 and, ΔS^0 have been determined from the slopes and intercept of plot of (ln Kc) versus ($1/T$) (figure not shown). It is observed that ΔG^0 at all temperatures are negative. Their values are ranging from –3.685 KJ $mole^{-1}$ to –7.45 KJ $mole^{-1}$. It indicates that the dye adsorption reaction is spontaneous in nature and the process is a physical adsorption one. Enthalpy of the reaction is 74.846 KJ $mole^{-1}$, entropy of the reaction is 255 J $mole^{-1}$ K.

The background research works on removal of methylene blue dye are summarized in Table 3.

Conclusion

Experimental results show that in batch experiments almost 95–99% dye can be removed from the wastewater. The rice husk has the potential biosorption capacity to remove dye from concentrated dye solution. Furthermore, the results show that the adsorption equilibrium data fitted very well to the Langmuir adsorption at different temperature and pseudo-second order kinetic model provides the best correlation of the experimental data whereas pseudo-first order model does not fit the

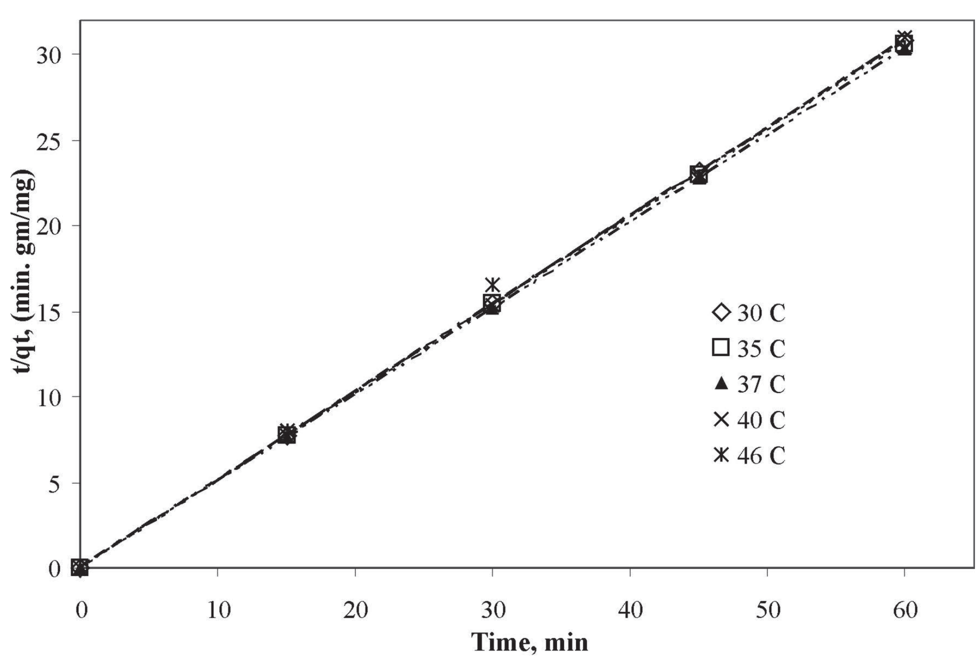

Figure 6a: Pseudo-second order kinetics at different temperature. Adsorbent dose 1 gm, pH 7, and initial concentration of dye 20 mg/L.

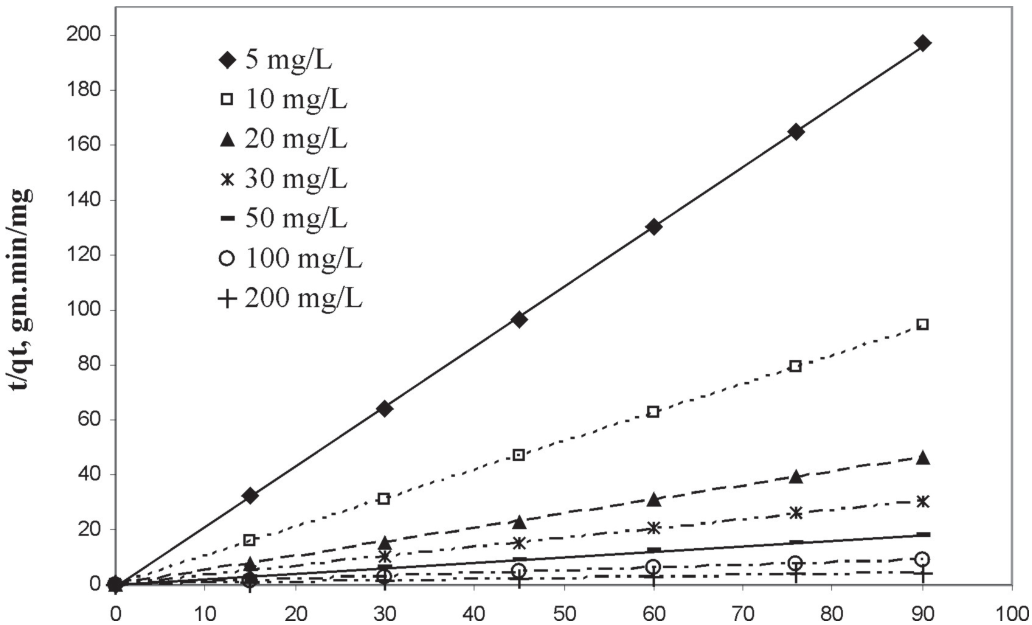

Figure 6b: Pseudo-second order kinetics at different initial concentration. Temperature 308K, adsorbent dose 1 gm, and pH 7.

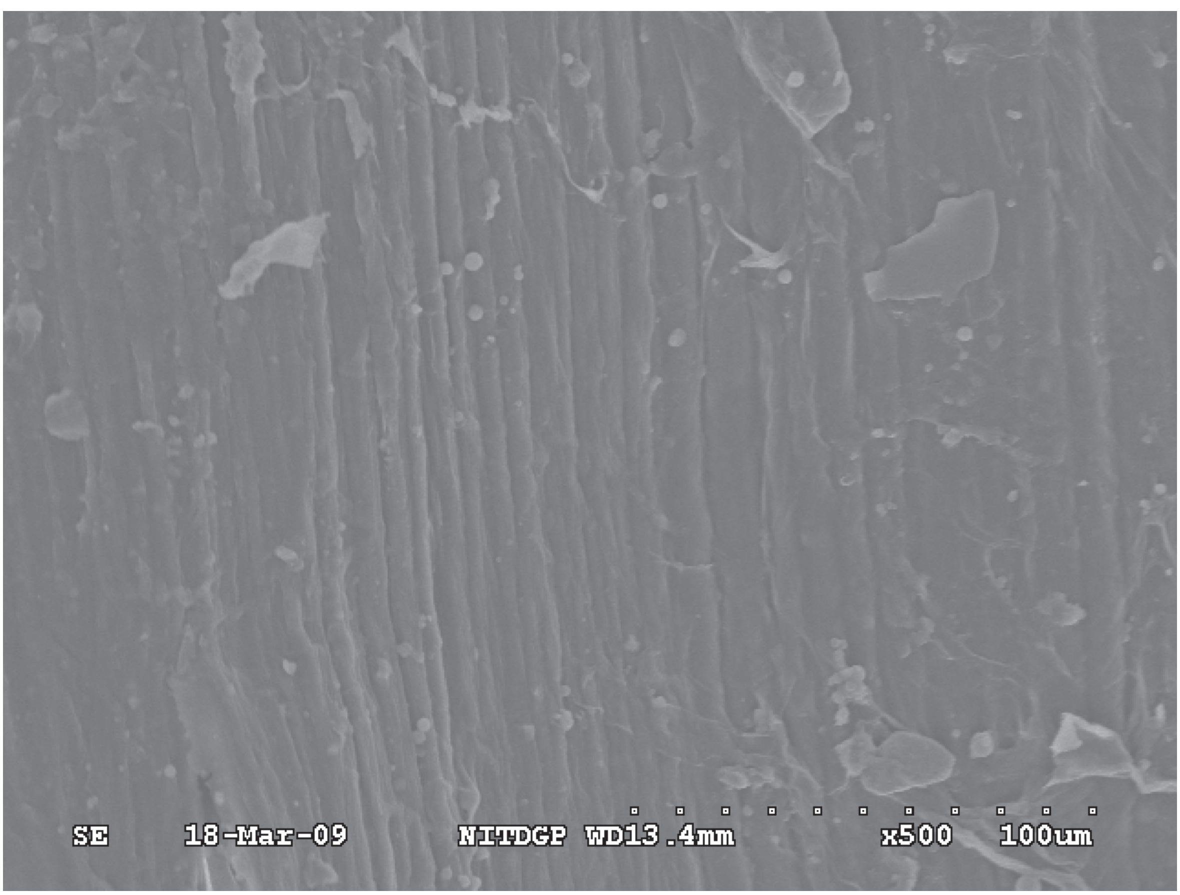

Figure 7a: Scanning electron micrograph structure of chemically modified rice husks.

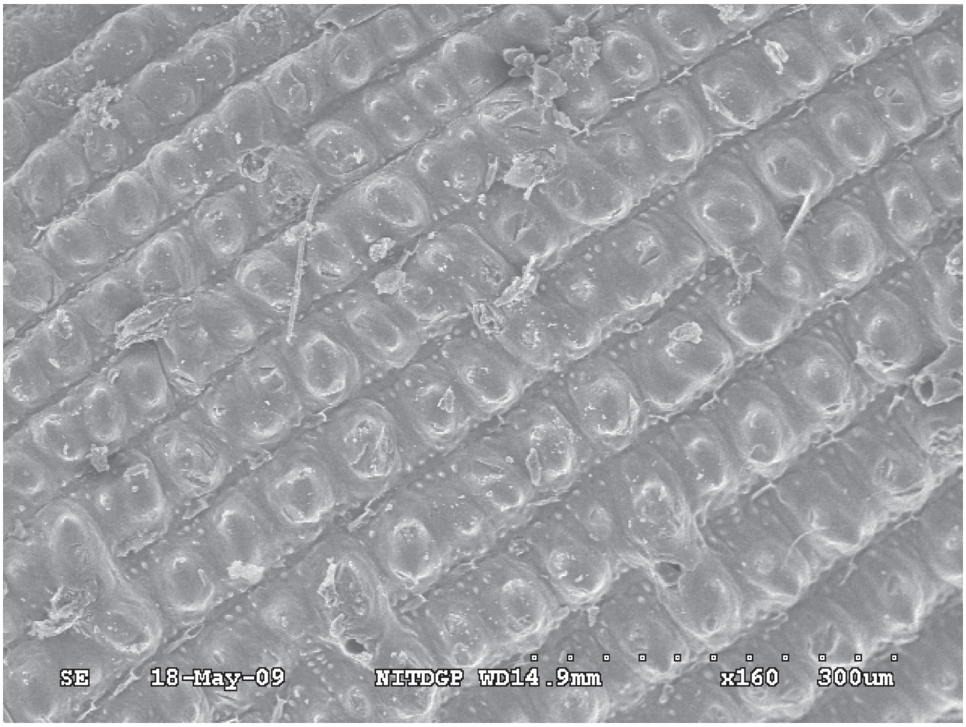

Figure 7b: Scanning electron micrograph structure of chemically modified rice husks after adsorption of methylene blue dye.

Table 3: Background research works on dye removal with different low cost adsorbents.

Adsorbents	*Conditions*	*Findings*	*Ref*
Chaff	C_0 = 20 -200 mg/L, rpm = 100, pH: 2 – 11, *m*: 2 – 12 mg/L	% removal: 82.5 – 97%; Equilibrium time: 180 min	Han, 2006
Wheat bran	C_0 = 5 – 20 mg/L, rpm = 100 – 1000, pH: 2.5 – 10, *m*: 2 – 10 mg/L	Equilibrium time: 140 min; Optimum shaker speed: 400 rpm, pH: 1.08 – 2.97	Hamdaoui et al., 2007
Hazelnut shells	*m*: 5 mg/L, rpm: 200, pH: 3 – 9, C_0: 20 mg/L	pH: varied with adsorption; Adsorption isotherm: Langmuir	Dogan et al., 2008
Fallen Phoenix tree's leaves	C_0: 5 – 20 mg/L, *m*: 1 – 8 mg/L, rpm: 100, pH: 2.5 – 10	% removal: 68 – 95; pH: 4.5 – 10 Equilibrium time: 180 min	Han, 2007
Rice husk	*t*: 0 – 120 min, C_0: 5 – 100 mg/L, *m*: 2 mg/L, rpm: 200, pH: 6.4	Adsorption kinetic: Both Langmuir and Freundlich model	Chandrasekhar et al., 2006
Chemically modified rice husk	C_0: 5 – 200 ppm, *m*: 5 – 30 gm, rpm: 60 – 400, pH: 2 – 9, batch and column study	pH: natural; Equilibrium time 30 – 60 min; % removal: 95 – 99% Shaker speed: 200 rpm; Adsorption isotherm model: Langmuir Kinetics: pseudo-second order	Present study

experimental data well. From ΔG^0 it is also observed that the reaction is spontaneous in nature. Due to low cost of rice husk this may be an effective material in the treatment of wastewater containing dye and this material is biodegradable and eco-friendly. So, it can be concluded that treated rice husk can be recommended to be used as biosorbent to remove dye.

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