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STUDIES ON THE EQUILIBRIUM, KINETICS, AND THERMODYNAMICS OF BASIC DYE ADSORPTION BY TEAK SAWDUST FROM AQUEOUS SOLUTION

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ABSTRACT

This study aims to investigate the sorption of Rhodamine-B, a basic dye, onto teak sawdust. Rhodamine-B dye, which is used in the textile sector, can have its color removed with an adsorbent. Using equilibrium, the kinetic adsorption isotherms method, and the thermodynamics equation, the tests are carried out using various factors such as the dosage of the adsorbent, pH, temperature, agitation speed, sieve size, and contact time. Common isotherm equations were used to correlate the Rhodamine-B adsorption isotherm on the treated adsorbent. The Freundlich and Langmuir adsorption isotherm models were then used to correlate the sorption data. The Langmuir constant was used to analyze thermodynamic equations at different temperatures, and the Langmuir isotherm showed a better fit for the adsorption data than the Freundlich isotherm. Lagrenge's I and II order equations were applied to the kinetic parameter. According to the experimental studies, the wastewater's maximum color removal was achieved at an ideal adsorbent dosage of 12.5 mg with a contact period of 50 minutes.

Keywords: Rhodamine-B, Teak sawdust, Concentration, pH, Contact Time, sieve size.

INTRODUCTION

Numerous industrial and human activities release dyes into the environment, some of which are hazardous even at low doses (less than 1 mg/L). The primary causes of water pollution are industrial effluents. Textiles, paper, dye manufacturing, tanneries, and pharmaceutical companies release color into the environment [1]. In order to eliminate these colors, new and improved wastewater treatment techniques are always being researched and developed. Numerous techniques, such as electrocoagulation [2], ultrafiltration [3], membrane separation [4], and phyto extraction [5], are used to separate and recover color from aqueous solutions. Adsorption is the most viable alternative and most promising strategy among all of these [6]. Powdered activated carbon [7], sawdust [8], fly ash [9], rice husk [10], chemically modified plant wastes [11], and other materials have all been employed as adsorbents for color removal.

MATERIALS

Materials and methods

The carboxylic acid that contains the diethylammo-nium chloride dye [9-(2-carboxyphenyl)-6-diethylamino-3-xan-thenylidene] is called rhodamine-B. In biology, rhodamine B is used as a fluorescent dye for staining. It is occasionally combined with auramine O to create the auramine-rhodamine stain, which is used to show acid-fast organisms, particularly Mycobacterium. Figure 1 illustrates the chemical structure of this stain.

The commercial-grade basic dye Rhodamine-B [C.I.No - 45170; C.I.Name - basic violet 10, chemical formula - C28H31ClN2O3; molecular weight - 479.02 g/mol; λmax – 554 nm] [12], was used as shown in fig. 1.

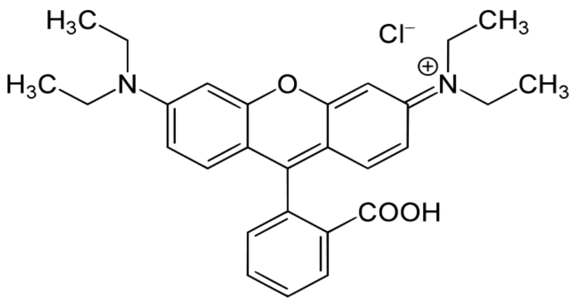

Fig 1: Rhodamine-B dye structure

Preparation of dye solution

Rhodamine-B dye was used without any purification. A stock solution was prepared by a calculated amount of the dye and distilled water. From these stock solution five numbers of dye solution in the concentration of 10 mg/l to 50 mg/l were prepared. The λ_{max} of Rhodamine-B dye is554 nm.

Preparation of Adsorbent

Teak sawdust was taken from local saw mill located in Bhopal. The sawdust was rinsed with distilled water for removing unwanted impurities on them and after washing it was kept in electrical oven at 50°C temperature for 24 hours. It was than treated with H2O2 solution and again kept in oven at same temperature and duration for drying the sample. These dried sample were put in desiccators for use as adsorbent during the entire study.

These dried adsorbent were powdered and sieved through different sieve sizes for collecting sample of size (300-150) μ, (150-75) μ and minus 75 μ size.

Dosage of the Adsorbent

The amount of adsorbent dosage for removal of dye at 500 mg dosage of adsorbent obtained highest colour removal of Rhodamine-B dye. For the removal of Rhodamine-B dye, after appling 100 mg to 1000 mg adsorbent it was found that 500 mg is the optimum dose of the adsorbent for maximum colour removal of Rhodamine-B dye as shown in Fig 2. Fig 2 shows a plot between % Removal of colour for different dosages of Adsorbent.

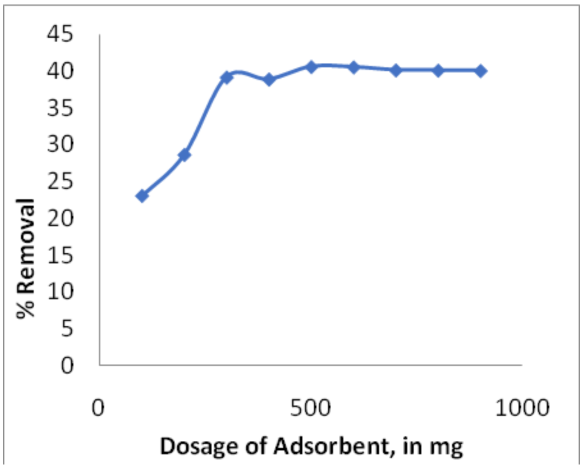

Fig 2: Dosage of the Adsorbent v/s % Colour Removal

Effect of particle size

The surface area available for adsorption is greatly determined by particle size of the adsorbent. The effect of particle size on Rhodamine-B adsorption was studied and results are shown in Fig 3. It was established that adsorption of Rhodamine-B increased with increase in particle size of teaksawdust. This can be attributed to larger total surface area of coarser particles for the same amount of adsorbent [13]. This relationship indicates that powdered coarser adsorbent of size (300-150) μ would be advantageous over finer particles range in adsorption of Rhodamine-B dye.

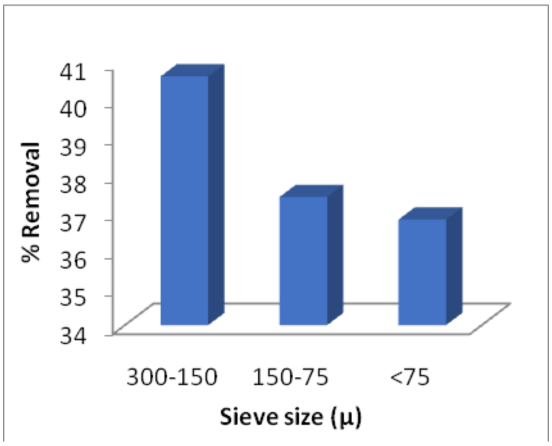

Fig 3: % Colour Removal v/s Particle size of sawdust

Effect of pH

Effect of pH on the removal of Rhodamine-B dye was studied of optimum dosage of 500 mgof sawdust. The pH of the solution was adjusted using 0.1N HCl and 0.1N NaOH and all pH measurements were carried out using a digital pH meter. It was found that on pH 2 $\pm$ 0.5 adsobent gives maximum removal efficiency. This is clear from Fig 4 which gives % colour removal at different pH of the solution.

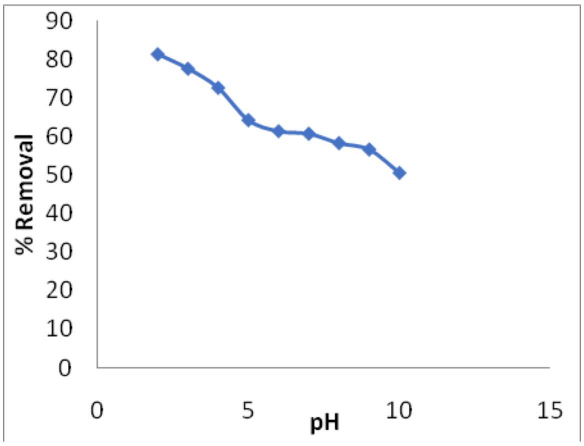

Fig 4: % colour removal at different pH

Adsorption procedure

Temperature controlled shaking waterbath shaker was used to control the desired temperature. The impact of various parameters such as pH value, temperature, and dosage of the adsorbent, agitation speed, size of particles and concentration of the dye were studied.

Adsorption experiments were conducted by adding 500 mg of teak sawdust into a series of 200 ml conical flask each with 10 mg/l initial concentration, (300-150) µ particle size of sawdust selected shown in fig 3, 2 pH, 30°C temperature and 100 R.P.M. speed of shaker. For all conical flask using aluminum foil caped over and placed into a waterbath shaker are shaken to equilibrium. After equilibrium time, the absorbance of clarified supernatant solution was analyzed using a UV–vis spectrophotometer and calculated by the following mass balance relationships [14] :

$$q_e = \frac{(C_0 - C_e)\,V}{W} \qquad (1)$$

$$q_t = \frac{(C_0 - C_t)\,V}{W} \qquad (2)$$

And dye removal efficiency i.e. Percentage of the adsorption was calculated as given below :

$$\%\ \text{Removal} = \frac{(C_0 - C_t)}{C_0} X100 \qquad (3)$$

where qe is the amount of adsorbate in the adsorbent at equilibrium (mg/g), qt is the amount of adsorbate in the adsorbent at any time (mg/g), C_0 is the initial dye concentration (mg/L), C_e is the concentration of dye at equilibrium, C_t is the concentration of dye at any time in (mg/L), V is the volume of solution (L) and W is the weight of teak sawdust (g).

Effect of Contact Time in different Temperatures

The variation in percentage removal of dye with the time is shown in figure 5. The equilibrium concentrations was found in 120 minutes, due to saturation of active sites which do not allow further adsorption to take place.

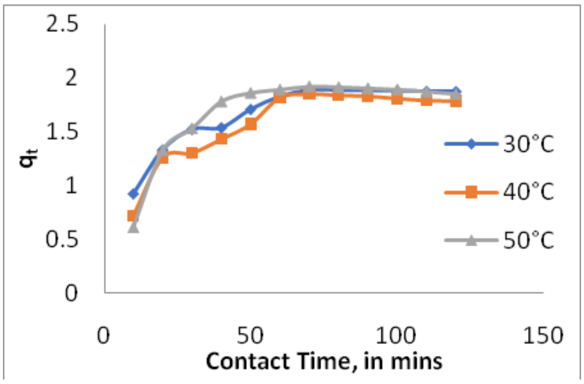

Fig 5: Equilibrium concentration of the dye

RESULTS

Equilibrium Adsorption study

Equilibrium adsorption data has been used for adsorption isotherms study. These data describes the rate of the reaction and the adsorption mechanism and affinity of the adsorbent. Thermodynamic studies provides information about the reaction is endothermic or exothermic and spontaneity of the adsorption process. The importance of obtaining the best-fit isotherm becomes more and more significant, because as more applications are developed, more accurate and detailed isotherm descriptions are required for the adsorption system designs [15].

Langmuir Adsorption Isotherm

The Langmuir equation [15] which is valid for monolayer sorption onto a completely homogeneous surface with a finite number of identical sites and with negligible interaction between adsorbed molecules, is given by the following equation:

$$q_e = \frac{q_0 b C_e}{1 + b C_e}$$

on rearranging this equation, we get

$$\frac{C_e}{q_e} = \frac{C_e}{q_0} + \frac{1}{b\, q_0}$$

where q_0 and b are the Langmuir constants related to maximum achievable adsorption capacity (monolayer capacity) and bonding energy of adsorption (or affinity between the adsorbate and adsorbent). The above equation can be linearized to get the maximum capacity, by plotting a graph of C_e / q_e Vs C_e.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a equilibrium parameter (R_L) [16], which is defined by:

$$R_L = 1/ (1 + b\, C_o)$$

where the value of R_L provided information about characteristics of isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The value of R_L shown in table, confirmed that the teak sawdust is favorable for adsorption of the Rhodamine-B dye under conditions used in this study.

Freundlich Adsorption Isotherm

The Freundlich equation [17] is the earliest known empirical equation and is shown to be consistent with exponential distribution of active centres, characteristic of the heterogeneous surfaces. It is expressed by the following equation :

$$q_e = K_F \, C_e^{1/n}$$

on rearranging this equation, we get

$$\log q_e = \log K_F + 1/n \log C_e$$

where K_F and n are the Freundlich constants characteristic on the system. K_F and n are indicators of adsorption capacity and adsorption intensity respectively.

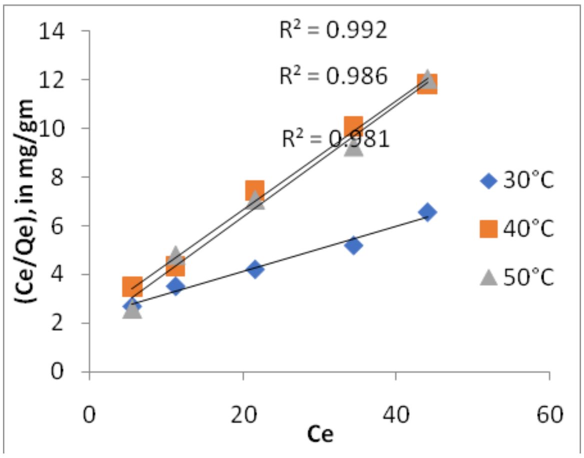

Fig 6: The Langmuir Adsorption Isotherm

Table 1: The values of parameters and correlation coefficient using Langmuir equation

Langmuir Adsorption Isotherms Data				
Temperature, in °C	q_0	**b**	R_L	R^2
30°C	10.75	0.041	0.71	0.981
40°C	4.348	0.129	0.435	0.986
50°C	4.484	0.1	0.498	0.992

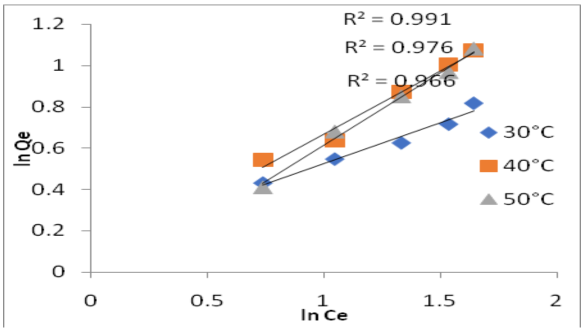

Fig 7: Freundlich Adsorption Isotherm

Table 2: The values of parameters and correlation coefficient using Freundlich equation

Freundlich Adsorption Isotherms Data			
Temperature ,in °C	**K_F (L/mg)**	**1/n**	**R^2**
30° C	1.977	0.396	0.966
40° C	1.125	0.614	0.976
50° C	0.809	0.706	0.991

Table 1 and 2 shows the values of the parameters of the two isotherms and the related correlation coefficients at different temperatures. As seen from Table 1 and 2, the Langmuir adsorption isotherm yields a somewhat better fit than the Freundlich adsorption isotherm. As also illustrated in Table 1 and 2, the values of RL and 1/n are gives favourable for this adsorbate and adsorbent, which indicates favourable adsorption. This work has shown that utilization of teak sawdust will be useful in the treatment of Rhodamine-B dye. It would also eliminates various ecological problems that these waste effluents causes.

Thermodynamics of Adsorption

The thermodynamic [18] parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of adsorption were found using the following equations:

$\Delta G^\circ = -RT \ln K$ (4)
$\Delta H^\circ = R(T_2T_1)/(T_2 - T_1) \ln (K_2/K_1)$ (5)
$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T$ (6)

where R is the gas constant, $K1$ and $K2$ are the Langmuir constants corresponding to the temperatures 303, 313 and 323 K and T is the solution temperature in Kelvin. The degree of spontaneity of the adsorption process depends on the negative values of ΔG°. The positive values of ΔH° show that the adsorption is endothermic [19]; the possible explanation for this being that Rhodamine-B ions displace more than one water molecule for their adsorption, which indicates the endothermicity of the adsorption process.

The positive value of ΔS° suggests increased randomness at the solid/solution interface during the adsorption of teak sawdust towards Rhodamine-B dye. Also the positive ΔS° value corresponds to an increase in the degree of freedom of the adsorbed species. $K1$ and $K2$ are the Langmuir constants corresponding to the temperatures 303, 313 and 323 K. The values of thermodynamic parameterswere given in Table 3.

Table 3: Thermodynamic parameters for the adsorption of Rhodamine-B by teak sawdust

Temperature (K)	**- ΔG°(kJ mol^{-1})**	**ΔH°(kJ mol^{-1})**	**ΔS°(kJ mol^{-1} K^{-1})**
303	8.053	313	5.329
21.40	44.06	323	6.162

Kinetic Adsorption study

The kinetic study of the adsorption process gives valuable result according the workability of the adsorbent and achievability of entire operations. The specific rate constants for the system were calculated using Lagergren's first order rate equation [20].

$$\text{Log } (q_e\text{-}q_t) = \log q_e - k_1 t/(2.303) \quad (7)$$

where q_e and q_t are amount of adsorption at the equilibrium and any time t, respectively. The graph plot between log (q_e-q_t) versus time t, provides appearance of first order kinetics as shown in fig. 7 and table 4. The k_1 (adsorption rate constant) value for teak sawdust were calculated usingthe slope of those straight lines at various temperatures.

The pseudo second order kinetic model was applied to the experimental data. The pseudosecond order model [21] is expressed as :

$$\frac{dq_e}{dt} = K_2(q_e - q_t)^2 \quad (8)$$

When the initial condition is q_t= 0 at t = 0, integration leads to equation (8) :

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

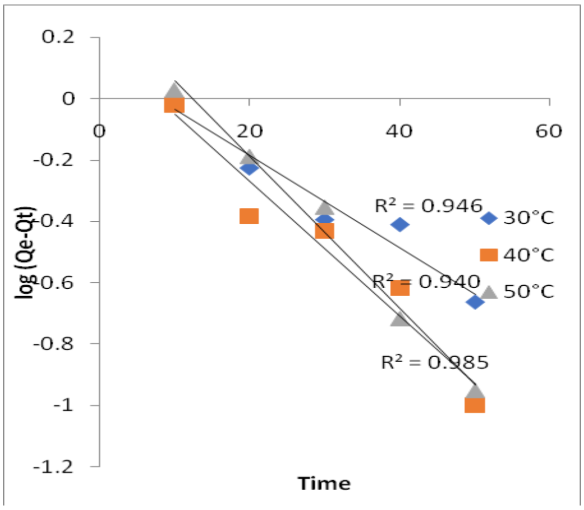

Fig 7: Pseudo-first-order kinetics

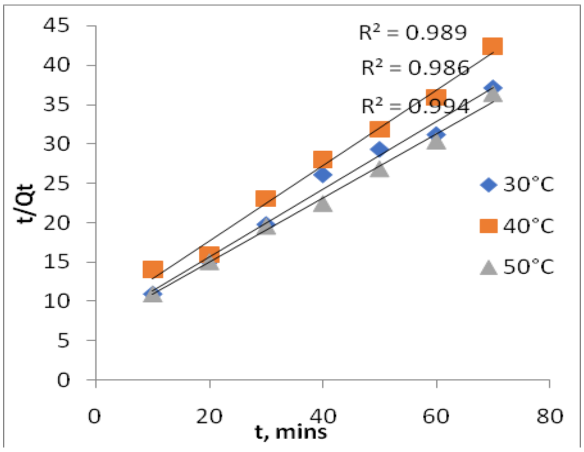

Fig 8: Pseudo-second-order kinetics

In the comparison of both the kinetic models for Rhodamine-B adsorption, the pseudo secondorder kinetics gives better fit than pseudo first order kinetic equation.

Table 4: Kinetic parameters for the adsorption of Rhodamine-B by teak sawdust

Temperature (in °C)	Pseudo-first-order		Pseudo-second-order	
	K_1 (X10^{-2} min^{-1})	R^2	K_2 (X10^{-3} g/(mg min))	R^2
30°C	3.45	0.946	26.60	0.993
40°C	5.10	0.940	28.16	0.997
50°C	5.50	0.985	24.50	0.999

CONCLUSION

In the present study, it was found that adsorption of Rhodamine-B dye on teak sawdust at temperatures (30ºC, 40ºC and 50ºC) are better by Langmuir and Freundlich adsorption isotherm. Langmuir best fitted than Freundlich isotherm. The best fit of the experimental data was achieved with pseudo second order kinetic model indicating that this model was the most appropriate one for the modeling of Rhodamine-B removal by teak sawdust.

The calculations made on the basis of kinetic models, their correlation coefficients and limitsof validity explains that in general, the adsorption process of Rhodamine-B onto teak sawdust was controlled by film diffusion. Moreover, the pseudo second order kinetic model is often associated with adsorption that is chemical in nature.

The thermodynamic study indicate that the adsorption process at temperatures 30ºC, 40ºC and 50ºC. The positive value of ΔH° indicates that the adsorption of Rhodamine-B on teak sawdust is an endothermic process. The negative value of ΔG° showed spontaneous nature of the adsorption. The positive value of ΔS° showed the existence of some structural changes at the solid-liquid interface and favours the ion exchange and stability of the adsorption.

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