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Kinetic, Thermodynamic and Equilibrium Studies on Uptake of Rhodamine B onto $ZnCl_2$ Activated Low Cost Carbon

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Abstract: A carbonaceous adsorbent prepared from biomass waste like wood apple outer shell (*Limonia acidissima*) by $ZnCl_2$ treatment was investigated for its efficiency in removing Rhodamine B (RDB). Influence of agitation time, adsorbent dose, dye concentration, pH and temperature were explored. Two theoretical adsorption isotherms namely Langmuir and Freundlich were used to describe the experimental results. The Langmuir adsorption capacity (Q_o) was found to be 46.7 mg/g and the equilibrium parameter (R_L) values indicate favourable adsorption. The experimental data were well fitted with Langmuir isotherm model and pseudo second order kinetic model. Desorption studies showed that ion exchange mechanism might be involved in the adsorption process.

Keywords: Wood apple, Adsorption isotherms, Kinetics studies, Rhodamine B, Thermodynamic parameters and ZAWAC

Introduction

Pollution caused by dyes is a common problem faced by countries which is likely to cause health hazards, harm to ecology, damage to structure or amenities and interferences with legitimate use of water[1]. Rhodamine B dye causes burning sensation, coughing, wheezing, laryngitis, shortness of breath, headache, nausea and vomiting. The target organs of human beings by Rhodamine B are kidney, liver, lungs and spleen. Therefore, the treatment of effluent containing such dye is of vital interest due to its esthetic impacts of receiving waters.

Adsorption process using activated carbons is widely used to remove pollutants from wastewaters. However, commercially available activated carbon is expensive. This has led to search for low cost material as alternative adsorbent material. In the last years, many researchers have studied the production of various type of activated carbons from different sources *viz.*, palm-tree cobs[2], palm kernels[3], cassava outer shell[4], bagasse[5], jute fibre[6], rice husks[7], olive stones[8], date pits[9], fruit stones and nut shells[10] and wood apple outer shell[11]. Manufacturing advantage lies in utilizing rejected waste as raw material for making new effective carbon will renew the waste and cost effective.

In this work, we used $ZnCl_2$ activated wood apple carbon (ZAWAC*)* as adsorbent to remove the Rhodamine B dye from waste water. Wood apple is rich in oxalic, malic, citric acids and concentrated tannic acid. It is useful in preventing cancer of breast and uterus and helps to cure sterility. The carbon made from this biomass waste could yield a carbon with high porous structure and high surface area.

Experimental

The adsorbate, Rhodamine B was received from Qualigens fine chemicals, India. Double distilled water was used for preparing all the solutions and reagents.

Preparation and characterization of activated carbon

Wood apple outer shell raw material (biomass waste) collected from industries was washed with hot distilled water. It was dried in sun light for 10 h and then the resultant material was grounded and stirred into a boiling solution containing $ZnCl_2$ in the ratio of 2:1. The filtered material after drying was carbonized by using *Brick Kiln* at elevated temperature for 3 days and then material was leached out using dilute HCl. Then the carbon was repeatedly washed to ensure the removal of excess of $ZnCl_2$ and dried. The carbonized material was sieved to 200 μm size and used for experiment

Batch equilibrium studies

Adsorption isotherms were performed in Erlenmeyer flasks (250 mL) where solutions of dye (100 mL) with different initial concentration (10-60 mg/L) were placed in these flasks. Equal mass of 100 mg of activated carbon was added to dye solution and kept in a mechanical shaker for 7 h to reach equilibrium of solid-solution mixture. Similar procedure was followed for another set of Erlenmeyer flask containing the same dye concentrations without activated carbon to be used as a blank, the pH was adjusted to 7 by adding either few drops of diluted HCl (or) NaOH (0.1 M). The flasks were then removed from the shaker and the final concentration of dye in the solution was analyzed. Each experiment was duplicated under identical conditions. The amount of adsorption at equilibrium (q_e) and adsorption at time(q_t) were calculated.

Results and Discussion

Textural characteristics of prepared activated carbon

Textural of the carbon was characterized by before and after adsorption using FT-IR, SEM, XRD, surface area through BET studies. Surface functional groups and other parameters were determined using standard methods[12,13].

Effect of agitation time and concentration of dye on adsorption

A series of contact time experiments for dye have been carried out at different initial concentration (10-60 mg/L) and at temperature of 28 °C. Figure 1 and 2, show the percentage of removal and amount of dye adsorbed onto activated carbon increases with time and, at some point in time, reaches a constant value beyond which no more is removed from solution. At this point, the amount of dye desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of the dye being adsorbed onto the activated carbon. The amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions.

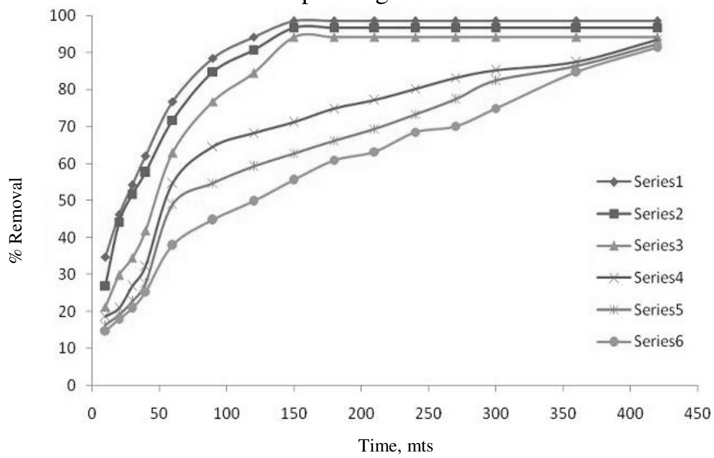

Figure 1. The removal of RHD dye with adsorption time at various initial time

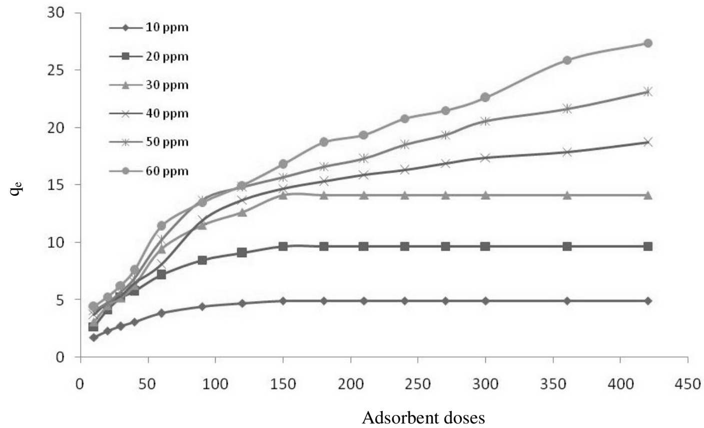

Figure 2. The variation of adsorption capacity at various initial RHD dye concentration

It is evident that the activated carbon prepared from wood apple is efficient to adsorb MB dye from aqueous solution, the process attaining equilibrium gradually. This is due to the fact that activated carbon is composed of porous structure with large surface area (794 m^2/g). Three consecutive mass transport steps are associated with the adsorption of solute from solution by porous adsorbent[14]. First, adsorbate migrates through the solution, *i.e.* film diffusion, followed by pore diffusion and finally the adsorbate is adsorbed into the active sites at the interior of the adsorbent particle. The similar phenomena were observed for the adsorption of dye from aqueous solution on jute fiber[6] and bamboo-based activated carbon and the equilibrium time was 24 h[15].

Effect of adsorbent dose

Figure 3 shows the removal of dye by $ZnCl_2$ activated wood apple carbon at different adsorbent dosages (25-200 mg) for 100 mL of dye solution concentration of 10-60 mg/L. The increase in adsorbent dosage increased the percent removal for dye. The maximum removals of dye are 98.9, 95.6, 91.4, 88.4, 83.4 and 80.1 at 200 mg of adsorbent dosage. Increase in the percentage of removal with increase in adsorbent dosage is due to the increase in adsorbent surface area.

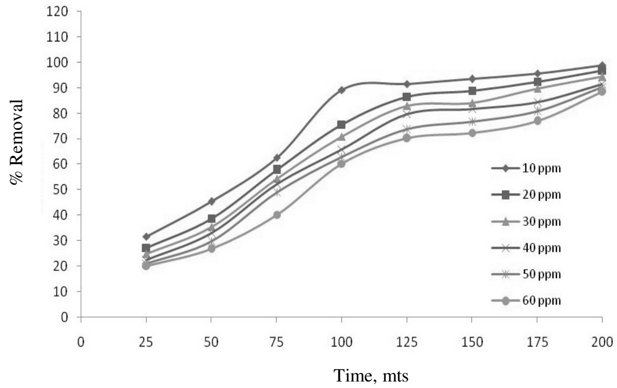

Figure 3. The effect of adsorbent doses on RHD dye onto ZAWAC

Adsorption isotherms

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid-Phase when the adsorption process reaches an equilibrium state.

Langmuir isotherm

Langmuir isotherm is expressed as,

$$C_e/q_e = 1/Q_o b + C_e/Q_o \quad (3)$$

Where Q_o and b are Langmuir constant related to adsorption capacity and energy of adsorption respectively. Plot of C_e/q_e *vs* c_e is linear shown in Figure 4. The values of Q_o and b are 46.7 mg/g and 0.1617 L/mg, respectively shown in Table 1. The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter R_L.

$$R_L = 1/1 + bC_o \quad (4)$$

R_L values indicate the type of isotherm. The R_L value between 0 and 1 indicates favourable adsorption.

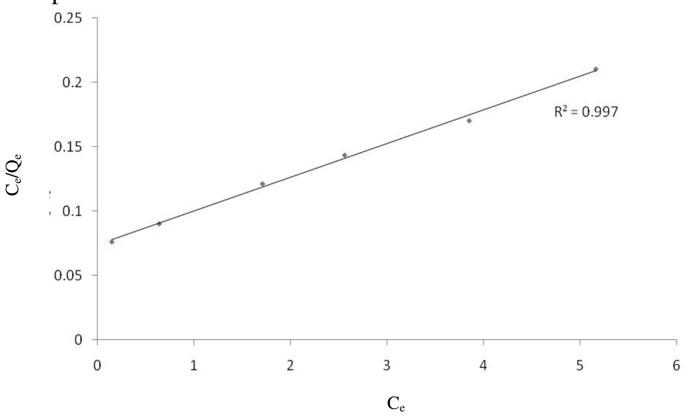

Figure 4. Langmuir adsorption isotherm of RHD dye onto ZAWAC

Table 1. Langmuir isotherm results

Conc. mg/L	Q_o, mg/g	b, L/mg	R^2	R_L
10				0.4337
20				0.3428
30	46.7	0.1616	0.994	0.2152
40				0.1464
50				0.0978
60				

Freundlich isotherm

A well –known logarithmic form of Freundlich model is given by the following equation,

$$\log q_e = \log k_f + 1/n \log c_e \tag{5}$$

Where q_e is the amount of adsorption, k_f is the Freundlich constant related to sorption capacity and 1/n is a constant related to energy or intensity of adsorption. This gives an expression encompassing the surface heterogeneity and the exponential distribution of activated sites and their energies. This isotherm dose not predicts any saturation of the adsorbent surface. The Freundlich exponents k_f and 1/n can be determined from the linear plot of log q_e *Vs* log c_e is shown in Figure 5. The values of the Freundlich constants K_F and 1/n are 3.567 and 0.561 respectively shown in Table 2. The slope 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneous, becoming more heterogeneous as its value gets closer to zero[16]. The results show that the adsorption also follows Freundlich isotherm.

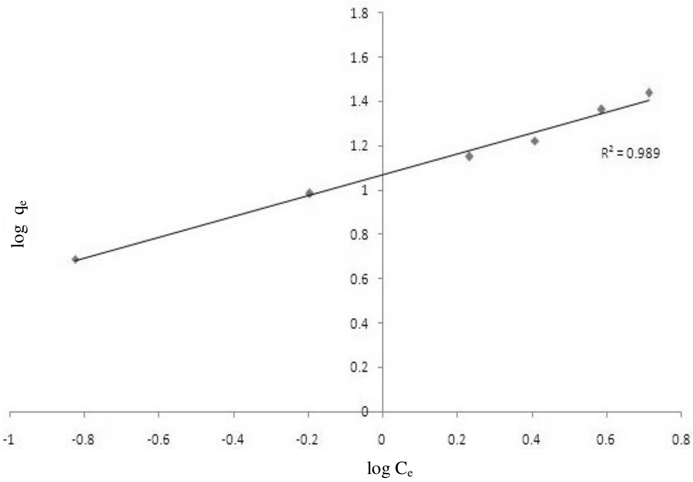

Figure 5. Freundlich adsorption isotherm of RHD dye onto ZAWAC

Table 2. Freundlich isotherm results

S.No.	Conc.mg/L	K_f [(mg/g)(mg-^{1})$^{1/n}$]	1/n	R^2
1	10			
2	20			
3	30	3.567	0.561	0.987
4	40			
5	50			
6	60			

Adsorption kinetics

The adsorption kinetics data of dye is analyzed using the lagergren[17] first order rate equation,

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (6)$$

Where q_e and q_t are the amount of dye adsorbed (mg/g) at equilibrium and at time' t' (h^{-1}) respectively and k_1 is the lagergren rate constant of first order adsorption (h^{-1}). It is found that the calculated q_e values do not agree with the experimental q_e Values. This suggests that the adsorption of MB dye does not follow first order Kinetics[18]. The second order kinetic model[19] can be represented as

$$t/q_t = 1/k_2 q_e^2 + t/q_e \qquad (7)$$

Where k_2 is the equilibrium rate constant of second order adsorption [g(mg h)$^{-1}$]. The values of k_2 and q_e are calculated from the plot of t/q *vs* t is shown in Figure 7. The calculated q_e values agree with experimental q_e values and also the correlation coefficients for the second order kinetic plots at all studied concentrations above 0.9917 which is shown in Table 3. These results indicate that the adsorption system studied, belongs to the second order kinetic model. Similar phenomenon has been observed in the adsorption of Cr(VI) by used tires and saw dust[20] and Congo red on coir pith carbon[21].

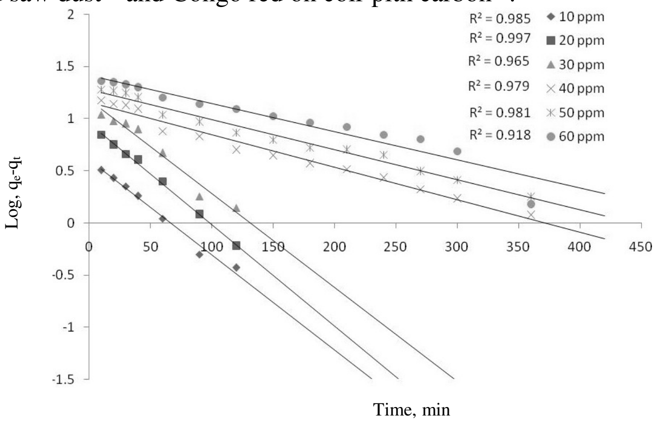

Figure 6. Pseudo-first order kinetics for adsorption of RHD dye onto ZAWAC

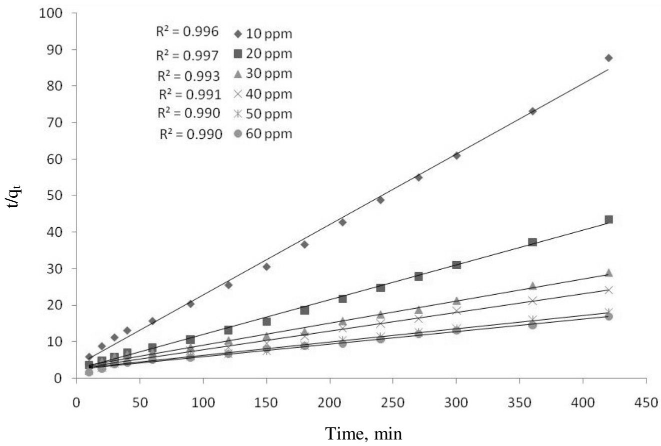

Figure 7. Pseudo-second order kinetics for adsorption of RHD dye onto ZAWAC

Table 3. First and Second orders kinetic result

S.No.	Conc. mg/g	q_e (exp.) mg/L	First order kinetics			Second order kinetics		
			q_e (cal.)	K_1, h^{-1}	R^2	q_e (cal)	K_2 [g(mg h)$^{-1}$]	R^2
1.	10	4.92	2.56	0.0967	0.9818	4.89	0.2564	0.9946
2.	20	9.68	5.56	0.0920	0.9614	9.54	0.3030	0.9945
3.	30	14.13	6.98	0.0880	0.9771	14.45	0.2150	0.9942
4.	40	18.7	9.23	0.079	0.9813	18.65	0.1666	0.9922
5.	50	23.1	12.65	0.0041	0.9848	23.23	0.1589	0.9927
6.	60	27.4	15.9	0.0038	0.9590	27.16	0.1489	0.9917

Effect of temperature

The effect of temperature, a major factor influencing the sorption, was monitored in the range of 35-60 ^oC. The change in standard free energy, enthalpy and entropy of adsorption were calculated using the following equations,

$$\Delta G^* = -RT \ln K_c \tag{8}$$

Where R is the gas constant, K_c is the equilibrium constant and T is the temperature According to van't Hoff equation,

$$\ln k_c = \Delta H^*/RT + \Delta S^*/R \tag{9}$$

Where ΔS^* and ΔH^* are change in entropy and enthalpy of adsorption respectively. A plot of ln K_c *versus* 1/T is linear as shown in Figure 8. Values of ΔS^* and ΔH^* were evaluated from the slope and intercept of van't Hoff plots. The positive values of ΔH^* confirm the endothermic nature of adsorption. The negative values of ΔG^* 35 ^oC, 40 ^oC, 50 ^oC and 60 ^oC indicate spontaneous nature of adsorption of dye as shown in Table 4. The positive values of ΔS^* suggest the increased randomness at the solid/solution interface during the adsorption of dye on $ZnCl_2$ activated wood apple outer shell carbon.

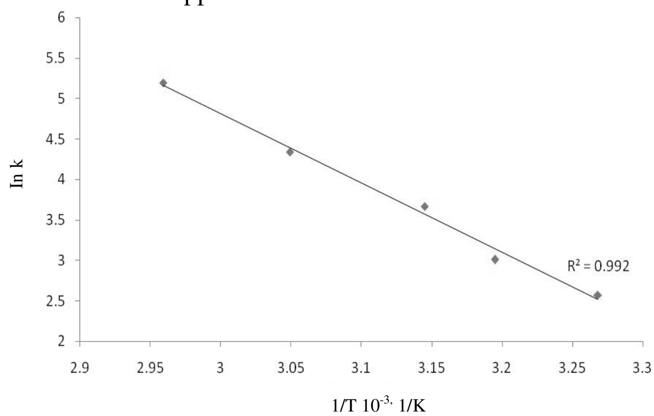

Figure 8. Van't Hoff Plot for adsorption of RHD dye onto ZAWAC

Table 4. Thermodynamics parameters for the adsorptive removal of RHD dye onto ZAWAC

Kc					ΔG^*(-ve), kJ/mol					ΔH^*	ΔS^*
28 °C	35 °C	40 °C	50 °C	60 °C	28 °C	35 °C	40 °C	50 °C	60 °C		
14.6	20.2	42.4	73.1	180	100.99	101.1	104.34	106.03	107.71	49.45	335.7

Conclusion

The present investigation showed that wood apple can be effectively used as a raw material for the preparation of $ZnCl_2$ activated carbon for the removal of dye from aqueous solution over a wide range of concentration. Dye is found to adsorb strongly on the surface of activated carbon. Adsorption behavior is described by a monolayer Langmuir type isotherm. Kinetic data follow second –order kinetic model. The value of the maximum adsorption capacity, Q_o (46.7 mg/g) is comparable with the values for commercial activated carbon reported in earlier studies.

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