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Kinetic and Thermodynamics of Remazol Brilliant Blue R Adsorption

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Orange peel, an agricultural solid waste abundantly available in Turkey, was utilized as a precursor for preparation of activated carbon *via* sulphuric acid chemical activation. The orange peel activated carbon (OPAC) is used for the removal of remazol brilliant blue R from aqueous solution. Research concerning the effects of pH, adsorbent dose, initial dye concentration and temperature are presented and discussed. Kinetic and thermodynamic parameters of adsorption were calculated.

Key Words: Remazol brilliant blue R, Kinetics, Thermodynamics, Adsorption, Orange peel.

INTRODUCTION

Synthetic dyes are extensively used in textile industry but *ca.* 20-40 % of these dyes remain in the effluents[1-3]. Most of the dyes are toxic and carcinogenic compounds. They are also recalcitrant and thus stable in the recovering environment, posing a serious threat to human and environmental health[4]. Accordingly, to protect humans and recover ecosystem from contamination, the dyes must be eliminated from the dye-contained wastewater before being released into the environment[5]. During the past three decades, several physical, chemical and biological decolorization methods have been reported (Table-1) for the removal of pollutants from plastics, dyestuffs, textile, pulp and paper effluents. However, few of them had been accepted by these industries[6-16]. Among the numerous techniques of dye removal, adsorption is the procedure of choice giving the best results as it can be used to remove certain classes of chemical pollutants from water. Adsorption has been found to be superior to other techniques for re-used water in terms of low cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Activated carbon and polymer resins are claimed to be the best adsorbents for removing dyes from relatively concentrated wastewater[17,18].

TABLE-1
REVIEWS ON EXISTING
TECHNOLOGIES FOR COLOR REMOVAL

Technology	Reference(s)
*Adsorption	[5-7]
*Biomass	[8-10]
*Bioadsorption	[11,12]
*Biodegradation	[7,13]
*Physicochemical treatment	[14,15]

Annual production of waste orange is estimated to be more than 2 million tons in Turkey. The accumulation and concentration of pollutants from aqueous solutions by the use of biological materials is also named biosorption[19]. Bio-adsorbents originated agriculture wastes are cheaper than the already available commercial activated carbon products. So, they can be used economically on a large scale. Since the orange peel is available free of cost from orange processing industries, only the carbonization of it is involved for the wastewater treatment. Hence, recycling of this solid waste for wastewater treatment would not only be economical but also will help to solve solid waste disposal problems. Previously several researchers had proved to use of orange peel as a biosorbent for removing pollutants such as methyl orange, methylene blue and congo red[20].

Therefore the main objective of this study was to evaluate the possibility of using dried orange peel to develop a new low-cost activated carbon and study its application to remove remazol brilliant blue R (RBBR) which is extensive use in textile industry. Studies concerning pH value, dose of sorbent, initial RBBR concentration and temperature are presented and discussed. Experimental data was analyzed using pseudo second-order kinetics, intra-particle diffusion and thermodynamic equations. The characteristic parameters for each model have been determined.

EXPERIMENTAL

Orange peel was collected from a local fruit field in the south of Turkey. Orange peel was firstly washed and subsequently dried at 105 ºC for 48 h to remove the moisture content

and the dried orange peel was milled and sieved to the size of 0.5-1.0 mm.

The dried orange peel biomass 1 kg was added in small portion to 800 mL of 98 % H_2SO_4 during 6 h and the resulting reaction mixture was kept overnight at room temperature followed by refluxing for 12 h in an efficient fume hood. After cooling to room temperature, the reaction mixture was poured onto cold water (3 L) and filtered. The resulting material was heated in an open oven at 150 ºC for overnight followed by washing with 3 L distilled water and then soaked in 1 % $NaHCO_3$ solution overnight to remove any remaining acid. The obtained carbon was then washed with distilled water until pH of the orange peel activated carbon (OPAC) reached 6, dried in an oven at 150 ºC for 24 h in the absence of oxygen and sieved and kept in a glass bottle until used.

The adsorption capacity was investigated using RBBR as the model guest. An accurately weighed quantity of the RBBR was dissolved in distilled water to prepare the stock solution. The solution for adsorption tests was prepared from the stock solution to the desired concentration by successive dilutions.

Adsorption process research: Adsorption experiments were carried out in a thermostatic orbital shaker at different temperatures. The shaking was continued till the state of equilibrium was reached. The initial RBBR concentration and equilibrium concentration were measured using a UV-visible spectrophotometer (Shimadzu UV-1601, Japan). This data was used to calculate the adsorption capacity of the adsorbent. The amount of RBBR adsorbed at equilibrium, q_e was calculated from the mass balance equation given by:

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

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations of dye (g/L), respectively; V is the volume of RBBR solution used (L); and W is the weight of the sorbent used (g).

The kinetic studies were carried out in 0.050 L RBBR solution (0.120 g/L) by adding 0.020 g sorbent at different temperatures. At given time intervals, the liquid phase RBBR concentration was measured.

RESULTS AND DISCUSSION

Effect of solution pH: The effect of solution pH was studied for RBBR removal by OPAC in a range of 4-10 under the conditions given in Table-2. The means of the duplicated experimental results are plotted in Fig. 1, indicating that pH considerably effected RBBR stability particularly under acidic conditions. A similar trend was reported for acid violet adsorption from aqueous solution as a function of pH by other researchers, including activated carbon prepared coir pith[21].

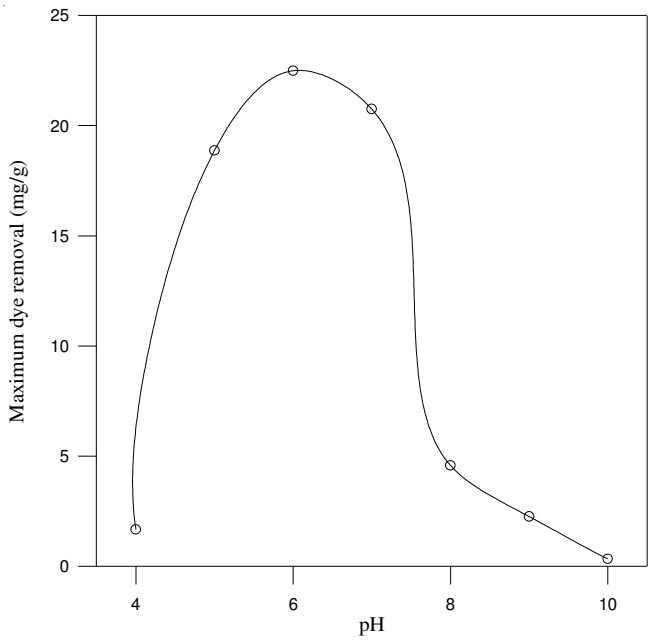

Fig. 1. Effect of pH of RBBR adsorption on OPAC. Conditions: 0.12 g/L concentration, 0.400 g/L dose and 298 K temperature

As can be seen in Fig. 1, the RBBR removal decreased when the solution pH was below 5 and above 8. The results indicated that the molecular form of RBBR in solution changed markedly in the pH range from 5-8. The degree of RBBR adsorption onto OPAC reached to 97 %, when the RBBR solution pH was 6. In this paper, the optimum pH at which maximum RBBR adsorption attained was 6 and so the rest of experiments were conducted at this optimum pH.

Effect of OPAC dose: The effect of OPAC on RBBR adsorption was performed in a range of 0.4-2.0 g/L under conditions specified in Table-2. The results are shown in Fig. 2, which indicted the decrease of q_e with the increase of OPAC dose. Increase in the adsorption with adsorbent dose can be attributed to increased OPAC surface area and availability of more adsorption sites, while the unit adsorbed of RBBR decreased with increase in OPAC dose. In this paper, the optimum OPAC dose at which maximum RBBR adsorption attained was 0.4 g/L and so the rest of experiments were conducted at this optimum dose.

Effect of initial RBBR concentration and temperature: The dye in the effluent of different industries may have different concentrations, which raises the question of how dye concentrations influence the performance of OPAC for removing RBBR. In this study, the adsorption of 0.100, 0.120, 0.140, 0.160, 0.180 and 0.200 g/L RBBR concentrations were investigated for OPAC. The means of the duplicate data are depicted in Fig. 3, indicating a considerable effect of RBBR concentration

TABLE-2
EXPERIMENTAL RUNS AND CONDITIONS

Experiment	Conditions				
	Solution pH	Adsorbent dose (g/L)	RBBR concentration (g/L)	Temperature (K)	Contact time (min)
Effect of pH	4-10	0.400	0.120	298	120
Effect of adsorbent dose	6	0.400-2.00	0.400-0.600	298	
Effect of RBBR concentration	6	0.400	0.100-0.200	298, 308, 318, 328	
Effect of temperature	6	0.400	0.100-0.200	298, 308, 318, 328	

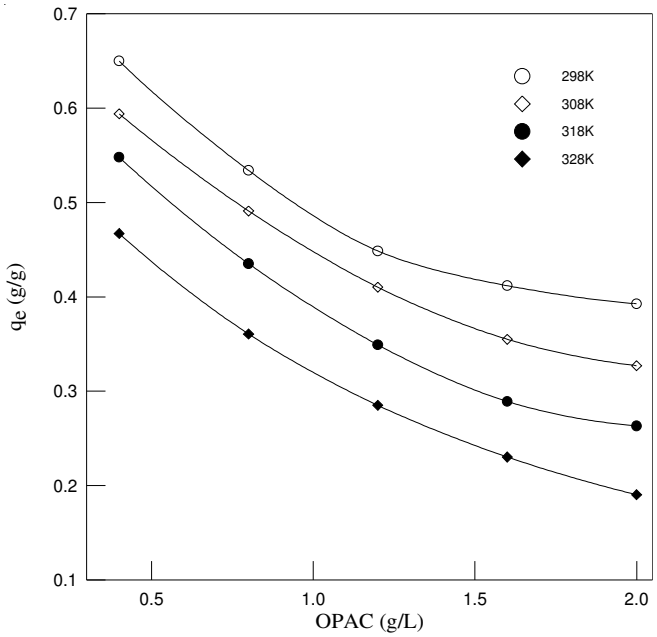

Fig. 2. Amount of RBBR adsorbed at equilibrium time (q_e) at different OPAC dose at different temperatures (initial RBBR concentration 0.400 g/L, pH = 6.0, 2 h)

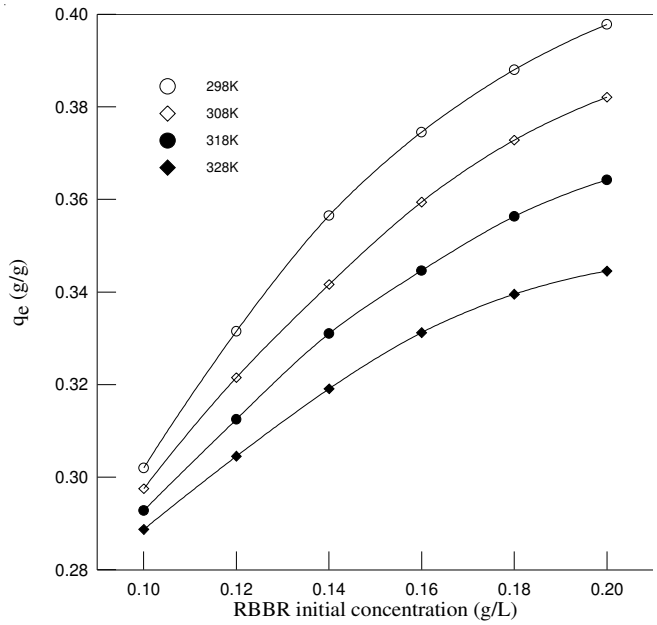

Fig. 3. Amount adsorbed at equilibrium time (q_e) on OPAC at different temperatures with different RBBR concentration

on OPAC adsorption capacity. Based on data illustrated in Fig. 3, by increasing the initial RBBR concentration, the q_e of OPAC increased at different temperatures. This can be attributed to free adsorption sites available at the initial phase of the test, as well as to a higher mass transfer rate at initial contact time where the RBBR concentration is high.

Fig. 3 also shows the effect of temperature on the adsorption equilibrium of RBBR on OPAC. It can be seen that the q_e decreased with the increase of the temperature for initial concentration of 0.100-0.200 g/L which indicated the exothermic process. However, at low initial concentration of RBBR (0.100 g/L), the effect of temperature on the adsorption equilibrium was not significant.

Intra-particle diffusion model: An empirically found functional relationship, common to the most adsorption process, is that the uptake varies almost proportionally with $t_{1/2}$, The Werber-Morris plot[22].

$$q_t = k_{id}t^{1/2} + C \quad (2)$$

where k_{id} is the intra-particle diffusion rate constant. According to eqn. 2, a plot of q_t *versus* $t_{1/2}$ should be a straight line with a slope k_{id} and intercept C when adsorption mechanism complies with the intra-particle diffusion process. The means of the duplicated experimental results is plotted in Fig. 4. From Fig. 4, it may be seen that there are two separate regions. The first straight portion is attributed to the macro-pore diffusion and the second linear portion to micro-pore diffusion. In the first region, it is attributed to the instantaneous utilization of the adsorbing sites on the adsorbent surface. In the second region, it is attributed to a very slow diffusion of the RBBR from the surface film into the micro-pores, which are the least accessible sites of adsorption. This also stimulates a very slow rate of migration of adsorbates from the liquid phase on to the adsorbent surface. The deviation of straight line from the origin may be due to the difference in rate of mass transfer in the initial and final stages of adsorption. Further deviation of the straight line from the origin indicates that the pore diffusion is not be only rate-limiting step[23].

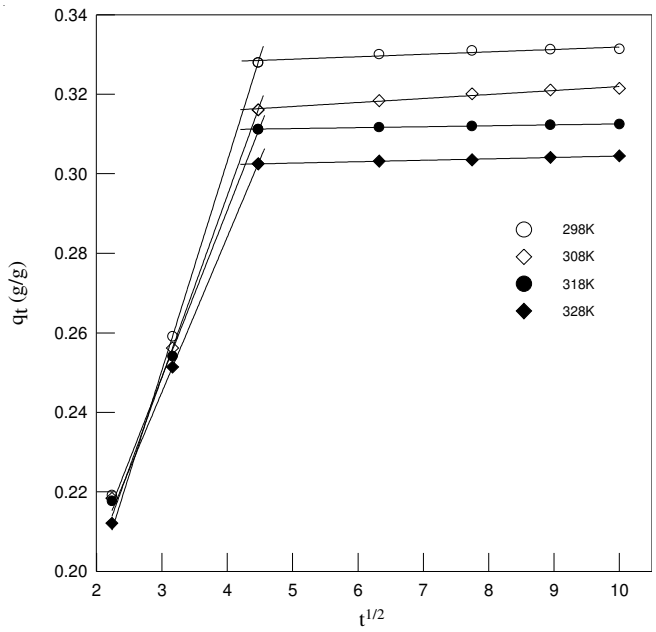

Fig. 4. Werber-Morris kinetic plots of RBBR adsorption on OPAC at different temperatures

To confirm the above results, the intra-particle diffusion coefficients, D_p have been calculated using the following equation.

$$D_p = \frac{(0.03r_0^2)}{t_{0.5}} \quad (3)$$

where r_0 (m) is the average radius of the adsorbent particles and $t_{0.5}$ (min) is the time required to complete half of the adsorption. According to Michelsen *et al.*[24], if the calculated intra-particle diffusion coeffficient (D_p) value is in the range

10^{-15}-10^{-18} m^2/s, then the intra-particle diffusion will be the rate-limiting step. In this study, the calculated D_p values ranged from 2.30×10^{-13}-1.79×10^{-13} m^2/s with different temperatures (Table-3), which indicated the intra-particle diffusion is not only the rate-limiting step of RBBR adsorption onto OPAC.

TABLE-3
INTRA-PARTICLE DIFFUSION COEFFICIENTS (D_P) OF THE ADSORPTION PROCESS AT DIFFERENT TEMPERATURES

T (K)	r_0 (m)	$t_{0.5}$ (min)	D_p (m^2/s)
298	$5.0 – 10^{-6}$	5.78	1.30×10^{-13}
308		5.37	1.40×10^{-13}
318		4.42	1.70×10^{-13}
328		4.20	1.79×10^{-13}

In this paper, the kinetic process was controlled by intra-particle diffusion. When RBBR molecules were adsorbed on the surface of OPAC, the RBBR molecules began to diffuse in the OPAC, the intra-particle diffusion was controlled the adsorption process.

Thermodynamics: With respect to the kinetic modeling, the pseudo-second-order[25] model has been examined to find out the adsorption mechanism. The pseudo-second-order kinetic can be expressed in a linear form as:

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

where q_t is the amount of RBBR adsorbed (g/g) at time t, q_e is the equilibrium adsorption capacity (g/g) and k_2 is the rate constant of pseudo-second-order adsorption (g/g min). The straight-line plots of t/q_t *versus* t for the pseudo-second -order reactions have also been tested to obtain rate parameters (Fig. 5). The correlation coefficient r^2, k and q_e under different temperature were calculated and given in Table-4. The pseudo-second-order rate sonstants are expressed as a function of temperature by the Arrhenius equation.

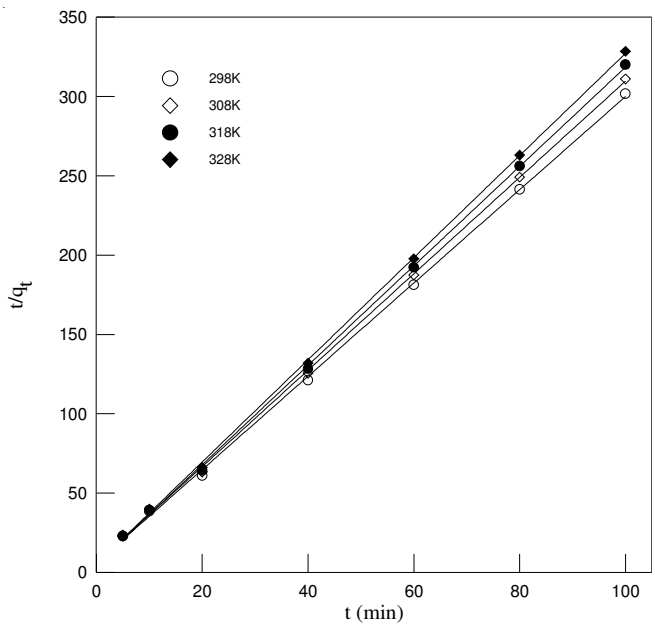

Fig. 5. Pseudo-second-order kinetics for the adsorption of RBBR onto OPAC at different temperatures

TABLE-4
PSEUDO-SECOND-ORDER KINETICS PARAMETER CONSTANTS AND ARRHENIUS ACTIVATION ENERGY (E_A) FOR THE ADSORPTION OF RBBR ONTO OPAC AT DIFFERENT TEMPERATURES

	Temperature (K)	k_2	q_e (g/g)	r^2	E_a (kJ/mol)
OPAC	298	1.4429	0.3401	9.9988	0.1355
	308	1.5529	0.3292	0.9992	
	318	1.8867	0.3191	0.9990	
	328	1.9827	0.3106	0.9992	

$$\ln k_2 = -\frac{E_a}{RT} + \ln A \qquad (5)$$

where E_a is the Arrhenius activation energy of sorption, representing the minimum energy which reactants must have to be proceed, A is the Arrhenius factor, R is the gas constant and is equal to 8.314 J/mol K and T is the solution temperature. The means of the duplicated experimental results is plotted in Fig. 6. From eqn. 5, the E_a is obtained (Table-4). The magnitude of activation energy gives an idea about the type adsorption, which is mainly physical or chemical. The physisorption processes usually have energies in the range of 5-40 kJ/mol, while higher activation energies (40-800 kJ/mol) suggest chemisorptions[26]. It can be inferred from the dispersive interaction between RBBR and surface of OPAC.

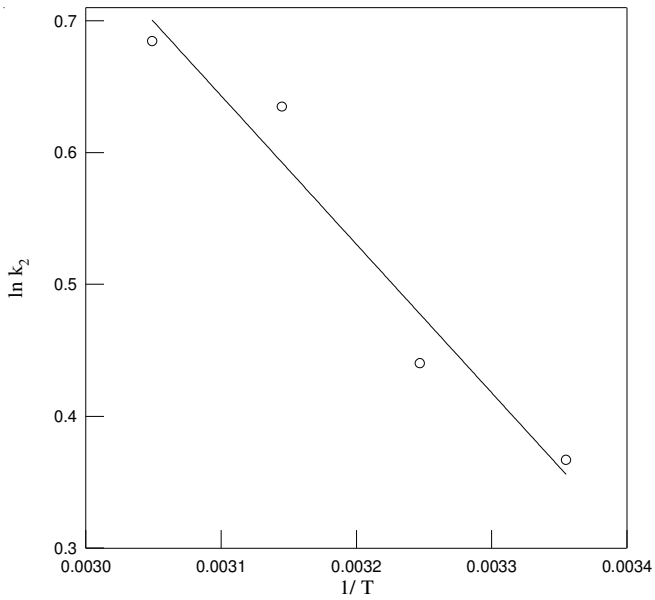

Fig. 6. Arrhenius plots for the adsorption of RBBR onto OPAC at different temperatures

The thermodynamic parameters, *i.e.*, the standard free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) have been estimated to evaluate the feasibility and exothermic nature of the adsorption process. The Gibbs free energy change of the process is related to the equilibrium constant (K) by the following equation.

$$\Delta G^o = -RT \ln K \qquad (6)$$

According to thermodynamics, the Gibbs free energy change is also related to enthalpy change and entropy change at constant temperature by the following equation.

TABLE-5
THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF RBBR ONTO OPAC

Sample	Temperature (K)	Distribution coefficient (K)	Gibbs free energy ΔGº (kJ/mol)	Enthalpy ΔHº (kJ/mol)	Entropy ΔSº (J/mol K)
OPAC	298	4.5022	-3.7277	-33.461	-99.0695
	308	3.5509	-3.2449		
	318	2.1519	-2.0261		
	328	1.3468	-0.8119		

$$\ln K = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (7)$$

The values of ΔHº and ΔSº are calculated from the slope and intercept of plots of ln K *versus* 1/T (Fig. 7). The values obtained are given in Table-5. The Gibbs free energy change (ΔGº) values are found to be decreasingly negative with temperature which indicated the feasibility and spontaneity of the adsorption process of RBBR on OPAC. The enthalpy change (ΔHº) values are found to be negative which indicated the exothermic nature of adsorption process. The (ΔHº) value is found to be less than 40 kJ/mol, which indicates the adsorption of RBBR by OPAC is physiosorption. The present results are found similar to the results reported by Zhong *et al.*[27] on adsorption of RBBR from aqueous solution by peanut hull-based activated carbon.

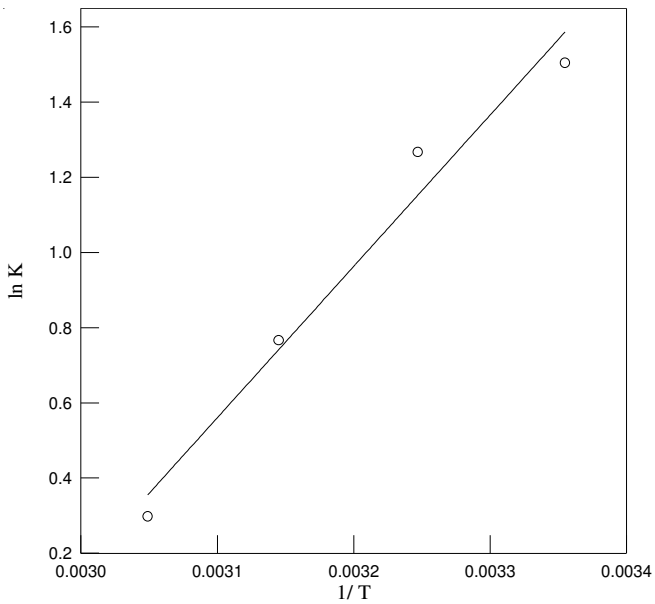

Fig. 7. Plot of ln K *vs.* 1/T for RBBR onto OPAC

Conclusion

The present study shows that the activated carbon prepared from orange peel is an effective adsorbent for removal of RBBR from aqueous solution. The effective pH for RBBR removal was 6. The optimum adsorbent dose and temperature were 0.4 g/L and 298 K, respectively. The straight lines in plots of t/q_t *versus* t showed good agreement of experimental data with pseudo-second-order kinetic model. The adsorption process was conrolled by intra-particle diffusion. The thermodynamic parameters evaluated reveal the spontaneous and exothermic process of RBBR adsorption on adsorbent. Adsorption activation energy was found to be 0.1355 kJ/mol, which were typical activation energy range for physisorption. The result would be useful for design of wastewater treatment plants for removal of dye.

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