Adsorption of Rhodamine-B Dye from an Aqueous Solution by Biomass Pine Apple Peel: Kinetics, Equilibrium and Thermodynamic Studies

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Abstract

Today there are lots of dyes available commercially. They are used in many industries such as paper, rubber, plastic, cosmetics and especially Textiles. Many methods have been proposed in order to remove color from waste water among which adsorption is more acceptable due to the ability for its use in the large scale. The objectives of this study were to investigate pine apple peel as on inexpensive adsorbent for removal of Rhodamine-B dye from aqueous solution. In this study the effect of pH, initial concentration, contact time and amount of adsorbent where optimized in order to investigate the mechanism of adsorption process. Several kinetic models including lageregren,s pseudo first order, lageregren,s pseudo second order, Intra particle diffusion, Elvoich model, Natarajan and Khalf model, Bhattarcharya and Venkobechar model were used. In addition equilibrium data were fitted on Langmuir, Freundlich, Temkin, Dubihin-Radhushevich.The kinetic study on Rhodamine-B dye suggest that the adsorption follows pseudo second order kinetics. Adsorption follows the Freundlich isotherm model than other models. The thermodynamic study on Rhodamine-B reveals that the reaction is spontaneous and endothermic. The study reveals that the biomass pine apple peel proved to be an effective alternative and environmentally benign adsorbent for Rhodamine-B removal from aqueous solution.

Keywords: Rhodamine-B; Pine apple peel; Adsorption; Kinetics; Isotherm; Thermodynamics

Introduction

Industrial wastewater is considered as one of the major pollutants of the environment [1]. Colored wastewater is produced by various industries, such as textile, dyeing, pharmaceutical, food, cosmetics and healthcare, paper and leather industries [2, 3]. Many dyes and their breakdown products may be toxic for living organisms. Therefore decolorization of dyes is important before the discharge of effluent. Removal of dye has been attempted extensively using physico-chemical methods such as coagulation, ultra-filtration, electro-chemical adsorption, photo oxidation, activated carbon adsorption, etc [5]. But these

technologies are not efficient, satisfactory and also cost effective [4]. Adsorption has been shown to be one of the most promising and extensively used methods for the removal of both inorganic and organic pollutants from contaminated water [6, 7]. Use of low cost, easily available biomaterials for the adsorption of dyes is practiced as an alternative method and several botanical, low cost materials have directly been used as an adsorbent for removal of dyes from wastewater [8, 9]. Now days, agricultural waste materials are receiving much more attention as adsorbents for the removal of dyes from waste water due to its low cost and good availability. In the present study, pine apple peel (PAP) has been used as an adsorbent whose results showed good absorption in Rhodamine-B dye aqueous solution [10].

Material And Methods

Preparation of an adsorbent

Pineapple biomass was obtained from fruit market in Thanjavur. The pineapples were peeled of using peeler. The peeled pineapple peels (PAP) were washed using tap water followed by double distilled water. After washing the peel pieces were dried under sun light for 72 hours to remove moisture content present. The dried PAP pieces were washing repeatedly with hot water (700 C) to remove any soluble matter present and dried in oven at 850 C for 48 hours. The dried PAP were powdered and sieved through 100 mesh sieves and stored air tight polythene bottles for adsorption experiments.

Chemical Structure Of Rhodamine -B

Batch Biosorption Studies

The experiment was carried out by the batch adsorption method in the Erlenmeyer flasks for a predetermined period using orbital shaker. In the adsorption, parameters such as pH, Initial dye concentration, equilibrium time fixation were studied for optimization. The kinetic studies and isotherm study were carried out at different dye concentration 200ppm, 250ppm, 300ppm, 350ppm, 400ppm and 450ppm. By keeping temperature constant, at 150 rpm for 2 and half an hours. The mechanism of adsorption was investigated by Lagergren's pseudo first order, pseudo-second order, Natarajan and Khalf first order, Bhattacharya and Venkobechar first order, Elvoich and Intra particle diffusion models. The isotherm study results were fitted in Langmuir, Freundlich, Temkin, Dubinin-Radushkevich isotherms. The thermodynamics study carried out at three different temperatures 310, 320 and 330K. The measurement of absorbance of colour was done Spectrophotometrically. The equilibrium adsorption capacity was evaluated using the equation

$$q_e = (C_0 - C_e) V / m \quad (1)$$

Where q_e (mg/g) is the equilibrium adsorption capacity, C_0 and C_e is the initial and equilibrium concentrations (mg/L) of Rhodamine-B dye solution. V is the volume and m is the weight of adsorbent.

Results And Discussion

Effect of pH: Initial pH of dye can influence the adsorption of it on the surface. In the present study pH 1-10 was used to observe the better adsorption with initial concentration of dye 250ppm with 1 g/L PAP as adsorbent dosage. The reaction mixture was agitated for 1 hr at 310K with agitating speed 150rpm. The most favorable adsorption was seen at basic pH 8, with 107.9 mg/g uptake of dye adsorption. It was shown in the Figure 1.

The surface of the adsorbent which may be negatively charged at higher pH, which favored for adsorption of the positively charged dye cations through electrostatic force of attraction. The adsorption of PAP to adsorbent consequently increased with an increase of pH values [11, 12]. So, optimum pH was 8.

Effect of biosorbent dosage

At optimum pH the biosorbent dose were increased from 0.5 g/L at intervals of 0.5g/L up to 5.5g. The reaction mixture was agitated for 1hr at 310K with agitating speed 150 rpm. The percentage of removal efficiency was found high at 4 g/L. So, optimum biosorbent dose was 4 g/L. It was shown in Figure 2.

Equilibrium time fixation: At optimum pH 8 and biosorbent dose 4 g/L the reaction mixture was agitated for 2 and half an hour with regular time intervals of 15 minutes at 310K. The maximum adsorption was found at 120 minutes. After that there is no increase in adsorption. It was shown in Figure 3.

Kinetic study of adsorption

The kinetics of Rhodamine-B adsorption by using PAP was studied at different time intervals and different initial concentration of dye. The kinetic parameters are helpful for the

prediction of adsorption rate, give important information for designing and modeling the adsorption process [13].

The mechanism of kinetics was investigated by Natarajan and Khalf first order, Elvoich model, Bhattacharya and Venkobechar first order, Lagergren's pseudo first order, pseudo second order and intra particle diffusion models. The study was carried at different time intervals up to equilibrium time and at different ppm at 310K are shown in Table 1.

The linearized form of Natarajan and Khalf first order kinetics is presented as

$$\log (C_0/C_t) = (K/2.303)t \quad (2)$$

Where C_0 and C_t are concentration of Rhodamine-B dye (mg/l) at time zero and time t respectively. K is first order adsorption rate constant (min^{-1}) which was calculated from slope of the plot ($\log C_0/C_t$) against t which was given in Table 2 and Figure 4. The R^2 value from 0.849 to 0.866 (Table 5) and also does not fit for whole range of contact time so, it does not follow first order kinetics.

Figure 1

Figure 2

Figure 3

Table-1												
Time\ppm	200		250		300		350		400		450	
	C _t	q _t	C _t	q _t	C _t	q _t	C _t	q _t	C _t	q _t	C _t	q _t
15	94.2	26.45	118.6	32.85	142.0	39.50	168.2	45.45	194.2	51.45	220.3	57.43
30	70.7	32.33	89.8	40.05	108.6	47.84	129.6	55.10	150.8	62.29	172.5	69.38
45	60.3	34.92	77.2	43.20	94.2	51.45	112.9	59.28	132.0	67.00	151.6	74.60
60	54.5	36.37	70.2	44.96	86.2	53.46	103.5	61.62	122.6	69.34	139.9	77.52
75	50.8	37.36	65.6	46.10	81.0	54.75	97.5	63.12	114.7	71.32	132.5	79.38
90	48.2	37.96	62.5	46.88	77.4	55.64	93.4	64.15	110.0	72.49	127.3	80.67
105	46.3	38.43	60.2	47.46	74.8	56.30	90.4	64.91	106.6	73.34	123.5	81.62
120	44.8	38.8	58.4	47.90	72.8	56.80	88.0	65.50	104.0	74.00	120.6	82.34
135	44.8	38.8	58.4	47.90	72.8	56.80	88.0	65.50	104.0	74.00	120.6	82.34
150	44.8	38.8	58.4	47.90	72.8	56.60	88.0	65.50	104.0	74.00	120.6	82.34
165	44.8	38.8	58.4	47.90	72.8	56.60	88.0	65.50	104.0	74.00	120.6	82.34

Table-2						
Time	200 ppm	250 ppm	300 ppm	350 ppm	400 ppm	450 ppm
	Log C ₀ /C _t	Log C ₀ /C _t	Log C ₀ /C _t	Log C ₀ /C _t	Log C ₀ /C _t	Log C ₀ /C _t
15	0.327	0.3239	0.3248	0.3183	0.3138	0.3102
30	0.4517	0.4447	0.4413	0.4315	0.4237	0.4164
45	0.5205	0.5103	0.5031	0.4914	0.4815	0.4725
60	0.5644	0.5516	0.5416	0.5291	0.5136	0.5074
75	0.5955	0.581	0.5686	0.5551	0.5425	0.531
90	0.6183	0.6021	0.5884	0.5737	0.5607	0.5484
105	0.6356	0.6183	0.6032	0.5879	0.5743	0.5615
120	0.6498	0.6315	0.615	0.5996	0.585	0.5719

Table-3						
Time	200ppm	250 ppm	300 ppm	350 ppm	400 ppm	450 ppm
	Log 1-u(T)	log-u(T)	log-u(T)	log-u(T)	log-u(T)	log-u(T)
15	-0.4972	-0.5028	-0.5163	-0.5141	-0.5161	-0.519
30	-0.7781	-0.7854	-0.8024	-0.7992	-0.8011	-0.8024
45	-1.0000	-1.0083	-1.026	-1.022	-1.0241	-1.0264
60	-1.2034	-1.2104	-1.2292	-1.2277	-1.202	-1.2321
75	-1.4157	-1.4248	-1.4425	-1.4401	-1.4425	-1.4425
90	-1.6656	-1.6696	-1.6947	-1.6861	-1.6925	-1.6925
105	-2.0223	-2.0269	-2.0969	-2.0362	-2.0555	-2.0555

Table-4						
logt	q _t	q _t	q _t	q _t	q _t	q _t
1.1761	26.45	32.85	39.5	45.45	51.45	57.43
1.4471	32.33	40.05	47.84	55.1	62.29	69.38
1.6532	34.92	43.2	51.45	59.28	67	74.6
1.7782	36.37	44.96	53.46	61.62	69.34	77.52
1.8751	37.31	46.1	54.75	63.12	71.32	79.38
1.9542	37.96	46.88	55.64	64.15	72.49	80.67
2.0212	38.43	47.46	56.3	64.91	73.34	81.62
2.0792	38.8	47.9	56.8	65.5	74	82.34

Bhattacharya and Venkobechar models

The linearized form of Bhattacharya and Venkobechar first order kinetic equation is presented as

$$\log[1-u(T)] = -(K/2.303)t \text{ -----(3)}$$

Where $u(T) = [(C_0 - C_t) / (C_0 - C_e)]$

C_e is equilibrium Rhodamine-B concentration (mg/l), K is first order adsorption rate constant (min⁻¹) which was calculated from slope of the plot log [1-u(T)] against t, which was shown in Table

3 and Figure 5. The R^2 value is found to be from 0.954 to 0.993. (Table 5)

ELVOICH MODEL

The linearized form of Elvoich kinetic equation is presented as [14]

$$q_t = 1/\beta \ln [\alpha, \beta] + \log t / \beta \text{ -----(4)}$$

Where α and β are constants calculated from Table 4 and from the intercepts and slopes plot q_t against $\log t$ shown in Figure 6. The constant β is related to the extent of surface coverage. The simple Elvoich models used to describe second order kinetics, assuming of that the actual solid surface is energetically heterogeneous. The Elvoich model has $R^2 = 0.961$ to 0.964 for adsorbents under study. Where α is initial adsorption rate 1 (mg/g /min) and β is related to the extent of the surface coverage and the activation energy for chemisorptions (g mg⁻¹). The initial adsorption rate, decreased from -0.7885 to -0.7261 while increasing the initial dye concentration from 200 to 450. It was shown in Figure 6 and table 4 and 5.

Pseudo first order kinetics

The kinetic data were treated with the following Lagergren's pseudo first order rate equation [15] for 250 ppm. Activation energy for chemisorptions (g mg⁻¹). The initial adsorption rate

decreased from -0.7855 to -0.7261, while increasing the initial dye concentration from 200 to 450 ppm.

$$\log (q_e - q_t) = \log q_e - K_1 t / (2.303) \text{ -----(5)}$$

Where q_t and q_e are the amount adsorbed at time t and at equilibrium (mg/g) and K_1 is pseudo first order rate constant for the adsorption process (min⁻¹). The plot of $\log (q_e - q_t)$ versus t was shown. (Table 6 Figure 7)

Pseudo second order kinetics

The pseudo second order model can be represented in the following form [16, 17]

$$t / q_t = 1 / K_2 q_e^2 + t / q_e \text{ -----(6)}$$

Where K_2 is the pseudo second order rate constant (g/mg.min). The plots of t versus t/q_t result was shown in Table 7 and Figure 9 for 250ppm. From the above results pseudo first order has R^2 value was 0.997 and pseudo second order kinetics has R^2 value was 1.0000. for first order q_e experimental is 26.06 mg/g where as q_e theoretical is 47.90 mg/g but for second order q_e is experimental is 52.63 and q_e theoretical is 47.90 mg/g. So for the second order only q_e experimental and q_e theoretical (mg/g) values are nearly same. From this, it clearly indicates that pseudo second order better fitted than pseudo first order.

Table-5

Rhodamine B	Natarajan and khalf model		Bhattacharya and Venkobechar model		Elvoich model		
	K (min ⁻¹)	R ²	K (min ⁻¹)	R ²	α (mg/g/min)	β (g/mg)	R ²
200	0.004606	0.866	0.0368	0.992	-0.7855	0.0747	0.964
250	0.004606	0.861	0.0368	0.993	-0.7631	0.0613	0.963
300	0.004606	0.854	0.0368	0.988	-0.8035	0.0534	0.961
350	0.004606	0.853	0.0368	0.993	-0.7520	0.0467	0.962
400	0.004606	0.855	0.0368	0.991	-0.7339	0.0409	0.964
450	0.004606	0.849	0.0276	0.954	-0.7261	0.0370	0.960

Table-6

Time	Log(qe-qt)
15	1.1775
30	0.8949
45	0.6721
60	0.4684
75	0.4684
90	0.0086
105	-0.3566

Table-7

Time	t/qt
15	0.4566
30	0.7491
45	1.0417
60	1.3345
75	1.6269
90	1.9198
105	2.2124
120	2.5052

Table-6(a)

K_1	-0.015
q_e (experimental)	23.77
R^2	0.997
q_e (theoretical)	47.40

Table-7(a)

K_1	0.0002
q_e (experimental)	52.63
R^2	1
q_e (theoretical)	47.90

Table 8:	
$t^{1/2}$	q_t
3.873	32.85
5.4772	40.05
6.7082	43.2
7.746	44.96
8.6603	46.1
9.4868	46.88
10.247	47.46
10.9544	47.9

Table-8(a)	
K diff	1.9648
C	28.10
R ²	0.8865

Table-9	
C_e	C_e/q_e
44.8	1.1217
58.4	1.2192
72.8	1.2817
88	1.3435
104	1.4045
120.6	1.4645

Table-9(a)	
q_{max}	250
K_L	0.00421
R_L	0.3458
R ²	0.984

Table-10	
$\log C_e$	$\log q_e$
1.6513	1.5658
1.7664	1.6803
1.8621	1.7543
1.9444	1.8162
2.017	1.8692
2.0813	1.9157

$1/n_f$	0.8021
n_f	1.2467
R ²	0.9956
K_f	1.7924

Table-11	
$\log C_e$	Q_e
1.6513	36.8
1.7664	47.9
1.8621	56.8
1.9444	65.5
2.0170	74.0
2.0813	82.35

Table-11(a)	
R ²	0.9940
b_t	24.24
A_t	0.0483
B	106.32

Table-12	
ξ^2	$\log q_e$
609.6	1.5658
360.24	1.6803
231.95	1.7543
158.50	1.8162
114.28	1.8698
85.56	1.9157

Intra particle diffusion

According to Weber and Morris the intra particle diffusion constant (K_i) is given by the following equation [17] for 250ppm.

$$q_t = K_i t^{1/2} \text{ -----(7)}$$

The intra particle diffusion would be the controlling step if this line passed through the origin .when the plots do not pass through the origin. This is indicative of some degree of boundary layers control and this further show that the intra particle diffusion is not the only rate controlling step but also other processes may control the rate of adsorption [18].

K_i (mg/g/min^{1/2}) values can be determined from Table 8 and from the Figure 9, slope of plot q_t against $t^{1/2}$.The R² value was 0.8865.

Adsorption isotherm

Equilibrium isotherm equations are used to describe the experimental adsorption data. The parameters obtained from the different models provide important information on the adsorption mechanism and the surface properties and affinities of the adsorbent. Linear regression is frequently used to determine the best fitting isotherm and the applicability of isotherm equation is compared by judging the correlation co-efficient.

Langmuir isotherm

The Langmuir equation [18] is expressed as

$$C_e/q_e = (1/K_L q_m) + (1/q_m) C_e \text{ -----(8)}$$

Where q_m is monolayer adsorption capacity (mg/g) K_L is Langmuir isotherm constant related to the affinity of the binding sites and the energy of adsorption(l/mg). The values are the q_m and K_L can be calculated by plotting C_e/q_e versus C_e . The dimensionless constant separation factor is R_L [19]

$$R_L = 1/ (1+K_L C_e) \text{ ----- (9)}$$

The R_L value indicates the type of isotherm to be either unfavorable($R_L > 1$), linear($R_L = 1$), favorable ($0 < R_L < 1$) or is reversible ($R_L = 0$) [20, 21]. It was shown in figure 10 and table 9. The R² value was 0.9847 and R_L is 0.34548 . So this isotherm is

Table-13: 310K Temperature.

Time\ppm	200		250		300		350		400		450	
	C _t	q _t	C _t	q _t	C _t	q _t	C _t	q _t	C _t	q _t	C _t	q _t
15	94.2	26.45	118.6	32.85	142.0	39.50	168.2	45.45	194.2	51.45	220.3	57.43
30	70.7	32.33	89.8	40.05	108.6	47.84	129.6	55.10	150.8	62.29	172.5	69.38
45	60.3	34.92	77.2	43.20	94.2	51.45	112.9	59.28	132.0	67.00	151.6	74.60
60	54.5	36.37	70.2	44.96	86.2	53.46	103.5	61.62	122.6	69.34	139.9	77.52
75	50.8	37.36	65.6	46.10	81.0	54.75	97.5	63.12	114.7	71.32	132.5	79.38
90	48.2	37.96	62.5	46.88	77.4	55.64	93.4	64.15	110.0	72.49	127.3	80.67
105	46.3	38.43	60.2	47.46	74.8	56.30	90.4	64.91	106.6	73.34	123.5	81.62
120	44.8	38.8	58.4	47.90	72.8	56.80	88.0	65.50	104.0	74.00	120.6	82.34
135	44.8	38.8	58.4	47.90	72.8	56.80	88.0	65.50	104.0	74.00	120.6	82.34
150	44.8	38.8	58.4	47.90	72.8	56.60	88.0	65.50	104.0	74.00	120.6	82.34
165	44.8	38.8	58.4	47.90	72.8	56.60	88.0	65.50	104.0	74.00	120.6	82.34

Table-14: 320K Temperature.

Time\ppm	200		250		300		350		400		450	
	C _t	q _t	C _t	q _t	C _t	q _t	C _t	q _t	C _t	q _t	C _t	q _t
15	77.5	30.63	98.3	37.93	120.3	44.92	142.6	51.85	168.3	57.94	187.6	65.59
30	57.3	35.68	73.2	44.20	90.3	52.42	107.1	60.72	126.5	68.37	142.6	76.86
45	49.0	37.74	62.9	46.77	78.0	55.50	92.4	64.39	109.2	72.71	123.9	81.52
60	44.6	38.86	57.3	48.18	71.3	57.18	84.4	66.39	99.6	75.09	113.7	84.07
75	41.7	39.57	53.8	49.06	67.0	58.24	79.4	67.66	93.6	76.60	107.3	85.68
90	39.8	40.06	51.3	49.67	64.0	58.97	75.9	68.53	89.4	77.64	102.8	86.78
105	38.4	40.41	49.6	50.11	62.0	59.50	73.3	69.17	86.4	78.40	99.6	87.59
120	37.3	40.68	48.2	50.45	60.4	59.90	71.4	69.65	84.1	78.98	97.2	88.2
135	37.3	40.68	48.2	50.45	60.4	59.90	71.4	69.65	84.1	78.98	97.2	88.2
150	37.3	40.68	48.2	50.45	60.4	59.90	71.4	69.65	84.1	78.98	97.2	88.2
165	37.3	40.68	48.2	50.45	60.4	59.90	71.4	69.65	84.1	78.98	97.2	88.2

Table 15: 330K Temperature.

Time\ppm	200		250		300		350		400		450	
	C _t	q _t	C _t	q _t	C _t	q _t	C _t	q _t	C _t	q _t	C _t	q _t
15	60.3	34.93	78.2	42.95	98.6	50.40	119.5	57.62	141.8	64.54	163.6	71.60
30	44.0	39.00	58.5	47.87	72.7	56.83	88.6	65.34	105.7	73.57	122.8	81.79
45	37.8	40.56	51.0	49.76	62.5	59.38	76.4	68.39	91.4	77.16	106.6	85.86
60	34.4	41.39	48.3	50.42	57.0	60.74	69.9	70.03	83.6	79.09	97.8	88.05
75	32.4	41.91	44.4	51.39	53.7	61.58	65.8	71.05	78.8	80.30	92.3	89.42
90	31.0	42.26	42.8	51.81	51.4	62.16	63.0	71.75	75.5	81.12	88.6	90.36
105	30.0	42.51	41.5	52.12	49.7	62.58	61.0	72.25	73.1	81.72	85.8	91.04
120	29.3	42.68	38.2	52.95	48.4	62.89	59.4	72.64	71.3	82.18	83.8	91.56
135	29.3	42.68	38.2	52.95	48.4	62.89	59.4	72.64	71.3	82.18	83.8	91.56
150	29.3	42.68	38.2	52.95	48.4	62.89	59.4	72.64	71.3	82.18	83.8	91.56
165	29.3	42.68	38.2	52.95	48.4	62.89	59.4	72.64	71.3	82.18	83.8	91.56

favorable.

Freundlich Isotherm

The isotherm was represented by

$$\log q_e = \log K_f + 1/n \log C_e \text{----- (10)}$$

Where q_e is the amount of Rhodamine – B adsorbed at the equilibrium (mg/g), C_e is the equilibrium constant of Rhodamine – B in solution (mg/L) [22, 23]. K_f and $1/n_f$ are constant

incorporating factor affecting the adsorption capacity and intensity of adsorption respectively .It was shown in the Figure 11 and table 10. The R^2 value is 0.9956 .It indicates good linearity and obeys the Freundlich isotherm.

Temkin isotherm

The Temkin isotherm is given as

$$q_e = \beta \ln A + \beta \ln C_e$$

Table-16

ppm	310 K		320 K		330 K		ΔH KJ/mol	ΔS J/mol
	K_0	ΔG^0	K_0	ΔG^0	K_0	ΔG^0		
200	3.4643	-3201.40	-4.3619	-4.3619	5.8259	-4835.11	21608.09	80.04
250	3.2808	-3062.10	-4.1867	-4.1867	5.5445	-4699.29	21807.62	80.27
300	3.1203	-2933.32	-3.9669	-3.9669	5.1984	-4522.44	21209.01	77.92
350	2.9773	-2811.92	-3.9019	-3.9019	4.8923	-4355.94	19887.09	73.50
400	2.8462	-2695.85	-3.7562	-3.7562	4.6101	-4193.9	20045.05	73.55
450	2.7313	-2589.65	-3.6296	-3.6296	4.3699	-4046.12	19537.90	71.59

Table-17

ppm	310 K	320 K	330 K
	$\ln K_0$	$\ln K_0$	$\ln K_0$
200	1.2425	1.4729	1.7623
250	1.1881	1.4319	1.7128
300	1.1381	1.3779	1.6483
350	1.1091	1.3614	1.5876
400	1.0459	1.3234	1.5282
450	1.0047	1.2891	1.4747

Where A_t (l/g) is the equilibrium binding constant corresponding to the maximum binding energy and constant B is related to heat of adsorption [25]. A Linear plots of q_e against $\ln C_e$. Enables the determination of constant B and A from slope and intercept (table 11 and Fig 12).The R^2 value is 0.994.

Dubinin – Radushkevich isotherm

The Dubinin- Radushkevich isotherm is given as

$$\ln Q = \ln Q_m - K' [RT \ln(1 + (1/c_e))]^{2E} = -(2k)^{-0.5} \dots \dots \dots (11)$$

This adsorption curve depends of the adsorbent pores. (26) The plot of $\ln q_e$ vs. ϵ_t^2 for Rhodamine - B are shown in table 13 and figure13. The mean adsorption energy (E) gives information about the chemical and physical nature of adsorption. The R^2 value is 0.955.

Thermodynamic Analysis

Thermodynamic parameters such as change in free energy ΔG (J/mole), enthalpy ΔH , (J /mole) ΔS (J/K/mole) were determined using following equations

$$K_0 = C_{\text{solid}} / C_{\text{liquid}} \dots \dots \dots (12)$$

$$\Delta G = -RT \ln K_0 \dots \dots \dots (13)$$

$$\Delta G = \Delta H - T\Delta S \dots \dots \dots (14)$$

$$\ln k_0 = - \Delta G/RT \dots \dots \dots (15)$$

$$\ln k_0 = -\Delta S/R - \Delta H/R \dots \dots \dots (16)$$

Where K_0 is equilibrium constant, C_{solid} is solid phase concentration at equilibrium (mg/L), C_{liquid} is liquid phase concentration at equilibrium (mg/L), T is absolute temperature in Kelvin and R is a gas constant. ΔG values obtained from equation (13), It was presented in Table (14, 15, 16, 17) .

Figure 4

Figure 5

Figure 6

Conclusion

The aim of this paper was utilization of natural biosorbent PAP as adsorbent for the removal of Rhodamine-B dye. Even though Bhattarchaya and Venkobechar first order kinetic model, Lagergren's pseudo first order kinetic model gave better results, but pseudo second order kinetic model was best fitted kinetic of adsorption. The correlation coefficient $R^2 = 1$ for second order adsorption model and q_e theoretical values are consistent with q_e experimental value showed that pseudo

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

second order adsorption equation fit with whole range of contact time. Among isotherms, Freundlich isotherm was found to be best fitting model with respect to R^2 values. ΔG , ΔH and ΔS values showed that favorable, spontaneous and endothermic. The PAP adsorbents have excellent adsorption capacity compare to any other non conventional adsorption. So PAP can be used as a low cost attractive alternative for costly activated carbon.

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