Adsorption of Rose Bengal Dye from Aqueous Solution onto Zinc Chloride Activated Carbon

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Abstract

A low cost activated carbon was prepared from fruit shell of *Terminalia catappa* Linn (Indian almond), waste plant residues and evaluated its adsorbing behaviour of Rose Bengal (RB) dye from aqueous solution by batch mode adsorption experiments. The activated carbon was prepared using zinc chloride as activating agent. This study examined the effect of contact time, adsorbent dosage, initial dye concentration, pH, other ions and temperature. Equilibrium data were obtained at 303, 313, 323, 333 and 343 K temperatures for the initial dye concentrations of 10, 20, 30, 40 and 50 mg/ L. Maximum dye removal capacity was observed at pH 6. Experimental data obtained were fitted into Lagergren, Ho and Weber Morris kinetic models for pseudo first-order, pseudo second-order and intra-particle diffusion kinetic study. The adsorption kinetic was found to follow pseudo second-order kinetic model as per the statistical tool 'Sum of Squared Error' (SSE) result. The equilibrium adsorption data were analysed by Langmuir, Freundlich, Temkin and Dubinin–Radushkevich and isotherms. Thermodynamic parameters; Gibb's free energy (ΔG°), Enthalpy (ΔH°) and Entropy (ΔS°) of the adsorption process were also evaluated. Analysis of these values inferred that the adsorption was endothermic, spontaneous and proceeded with increased randomness.

Keywords: Adsorption; Rose Bengal dye; ZnCl_2 Activated Carbon; Kinetics; Isotherms; Thermodynamic Parameters

Introduction

Now a day's synthetic dyes have been widely used in many industrial processes especially in the textile industry. The varieties of dyes include; acidic, reactive, basic, disperse, azo, diazo, anthraquinone based and metal complex. These dyes have a complex structure and low biodegradability [1]. These dyestuffs cause huge threat to the environment. Rose Bengal (RB) dye is harmful and can cause severe toxic effects on the human corneal epithelium. The dye is extremely hazardous when it comes in contact with skin and creates irritation, itching, scaling, reddening and even blistering. It also causes inflammation, redness, watering and itching in the eyes. On ingestion by inhalation it damages mucous membranes, which leads to respiratory irritation in humans. Numerous efforts and research have been

made to remove these dangerous chemical compounds, there are many traditional techniques applied in the removal process such as coagulation, flocculation, activated carbon adsorption, membrane filtration, photo degradation and sedimentation. Among these methods, adsorption is proved to be superior to other techniques. Adsorption using activated carbon gave fruitful results for the removal of dye from wastewater. The extent of dye removal depends upon the kind of dye, nature of adsorbent and experimental conditions. Preparation of activated carbon from waste plant bio masses and evaluating its adsorbing potential is the recent trend of research. Fruit shell of *Terminalia catappa* Linn is a waste plant bio mass which is chosen as precursor for the preparation of activated carbon in this present investigation [2] and the Zinc chloride activation method is adopted as it has the advantage of producing excellent pores as reported in earlier literatures [3].

Materials and Methods

Preparation of adsorbate

Rose Bengal, all so known as Acid Red 94 [Molecular formula $\text{C}_{20}\text{H}_4\text{Cl}_4\text{I}_4\text{O}_5$] [IUPAC Name: 4,5,6,7-Tetra chloro - 3',6'-dihydroxy-2',4',5',7'-tetraiodo - 3H- Spiro [isobenzofuran-1,9'-xanthen]-3-one]. Maximum wavelength (λ_{max}) for the absorption of this dye is 530 nm. Stock solution of 1000 mg/ L was prepared by dissolving 1 g of dye in 1000 mL of double distilled water. Required experimental solutions say 10, 20, 30, 40 and 50 mg/ L were prepared from the stock solution by proper dilution.

Preparation of adsorbents

The *Terminalia catappa* Linn fruit shells were collected from A.V.V.M. Sri Pushpam College campus, Thanjavur District., washed with distilled water to remove the surface adhered particles, dried in sun light for 4 days, chopped into small pieces and powdered in a pulveriser. 50 g of the powder was mixed with 100 mL of 60% ZnCl_2 solution. The slurry was kept at room temperature for 24 hours, to ensure the complete access of the ZnCl_2 to the *T. Catappa* shell powder. Excess of solution was decanted and the slurry was heated in muffle furnaces at 723K

for 3 hours. Thus the carbonized samples were washed with 0.5M HCl followed with distilled water until the pH of the washings attain 7.0. Then it was dried in a hot air oven at 383K for 1 hour. The dried material was ground and sieved to get particle size in between 73 µm and 150 µm. It was designated as *T. catappa* Zinc Chloride Activated Carbon (TCZAC).

Adsorption experiments

Batch experiments were conducted. The experiments were carried out in an orbital shaker at a constant speed of 130 rpm using 250 mL conical flasks containing predetermined dose of TCZAC with 50 mL of dye solution. After agitating, the samples were drawn from the flasks and the adsorbents were separated from the solution by centrifugation at 1000 rpm for 10 min. The absorbance of the supernatant solution was determined spectrophotometrically at $\lambda_{\max}$ 530 nm using Systronics 2202 make UV-Visible spectrophotometer to estimate the residual dye concentration. Percentage of removal and the quantity of adsorbate adsorbed were calculated using the following equations.

$$q_t = (C_i - C_t) \frac{V}{W}$$

$$\% \text{ of Removal} = (C_i - C_t) / C_i \times 100$$

Where;

C_i and C_t are the concentration of adsorbate (mg/ L) at initial stage and at time 't' respectively

V is the volume of solution (L)

W is the mass of adsorbent (g).

Experimental results obtained from the effect of initial concentration and contact times were employed in testing the applicability of isotherm and kinetic models.

Effect of solution pH

Solution pH is an important factor which influences the transfer of adsorbate from aqueous solution to adsorbent by altering the speciation of the adsorbate as well as the surface charges of adsorbent. To study the effect of pH on adsorption, 50 mg of TCZAC was added to 50 mL of 20 mg/ L of the RB dye solution of the different pH. Initial pH of the solution was maintained by adding 0.1M HCl or 0.1NaOH.

Effect of adsorbent dosage

The effect of dose was studied by taking adsorbents from 10 to 100 mg/ 50 mL for 20 mg/ L of the RB dye solution.

Effect of contact time and initial concentration

Effect of initial concentration was studied by taking 10, 20, 30, 40 and 50 mg/ L of RB dye solutions. The % of removal was determined at regular time intervals up to 160 minutes of agitation time.

Kinetic Studies

Kinetic studies are necessary to determine the different operation conditions for the sorption of dye. The kinetics of RB

onto TCZAC was analysed using pseudo-first order, pseudo-second order and intra particle diffusion kinetic models as below.

Pseudo - first-order kinetic model

The linearised form of the pseudo-first order equation of Lagergren is [4]

$$\log(q_e - q_t) = \log q_e - k_1 / 2.303 \times t$$

Where;

q_e and q_t are the adsorption capacity at equilibrium and at time t respectively (mg/ g). k_1 is the rate constant of pseudo first-order adsorption. From the plot drawn between $\log(q_e - q_t)$ and t, values of k_1 and q_e can be calculated from the slopes and intercepts of the plot respectively.

The second-order kinetic model

The pseudo-second order kinetic model (Ho equation) is represented by the following linear equation [5].

$$t/q_t = 1/k_2 q_e^2 + 1/q_e \times t$$

Where; q_e and q_t are the adsorption capacity at equilibrium and at time t respectively (mg/ g).

The initial adsorption rate, h (mg/ (g min)),

$$h = k_2 q_e^2$$

The Plot drawn between of t/q_t and t gave a straight line, from which 'calculated adsorption capacity $q_{e(cal)}$ mg/ g, and the second-order rate constants k_2 (g/ (mg min)) can be determined from the slopes and intercepts of plots respectively.

Intra-particle diffusion study

The mechanism of adsorption of a sorbate on a sorbent follows a series of steps. The slowest of these steps control the overall rate of the process. Generally, pore and intra particle diffusion are often rate limiting in a batch reactor while for a continuous flow system, film diffusion is the rate limiting step [6]. Previous studies [7-9] by various researchers showed that the plot of q_t versus $t^{1/2}$ represents multi linearity which characterizes two or more steps involved in the sorption of sorbate by a sorbent. These involve transport of the solute molecules from the aqueous phase to the surface of the solid particulates and diffusion of the solute molecules into the interior of the pores, which is usually a slow process.

The effect of contact time experimental results can be used to study the rate limiting step in the adsorption process, as shown by Weber and Morris [10]. Since the particles are vigorously agitated during the adsorption period, it is probably reasonable to assume that the rate is not limited by mass transfer from the bulk solution to the particle external surface; one might then postulate that the rate limiting step may be either film diffusion or intraparticle diffusion. As they act in series, the slower of the two will be the rate determining step. According to Weber and Morris, an intra-particle diffusion Co-efficient k_p is defined by the equation:

$$q_t = k_p t^{1/2} + C$$

Weber and Morris plot was drawn between q_t and $t^{1/2}$ gave a straight line. Where k_p (mg/ g/ min^{0.5}) is the intra particle diffusion rate constant and C is the thickness of the boundary film [11]. The k_p and C values obtained from the slopes and intercepts.

Effect of temperature studies

The adsorption study was carried out at different temperatures (303, 313, 323, 333, and 343K) for the RB solutions initial concentration of between 10 mg/ L, 20 mg/ L, 30 mg/ L, 40 mg/ L and 50 mg/ L, with the stirring for a period of 160 min.

Isotherm studies

It is important to fit the equilibrium data in different isotherm equations to give useful information of the adsorption process for the conception of the four isotherm models of adsorption were used in this study namely Langmuir, Freundlich, Temkin and Dubinin-Radushkevich.

Langmuir isotherm

The linear form of Langmuir isotherm equation is often written in as [12]

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

where q_e is the amount of solute adsorbed per unit mass of adsorbent (mg/ g), C_e the equilibrium concentration of solute in the bulk solution (mg/ L), q_m is the maximum monolayer adsorption capacity or saturation capacity (mg/ g) and b is the adsorption energy, b is the reciprocal of the concentration at which half saturation of the adsorbent is reached. Values of ' q_m ' and ' b ' can be calculated from the slopes and intercepts of the graph is drawn between C_e/q_e and C_e .

The essential characteristics of Langmuir isotherm can be described by a separation factor, R_L , which is defined by the following equation

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

Where;

C_0 is the initial concentration of the adsorbate solution. The separation factor R_L indicates the shape of the isotherm and the nature of the adsorption process as given below:

R_L value	Nature of the process
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

Freundlich isotherm

The liner form of Freundlich isotherm model is represented by [13]

$$\ln q_e = \ln k_f + \left(\frac{1}{n}\right) \ln C_e$$

Where; q_e is the amount of adsorbate adsorbed (mg/ g), C_e is the equilibrium concentration of dye solution (mg/ L) and k_f and n are the constants incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. Values of ' n ' and ' k_f ' were determined from slopes and intercepts of the graph drawn between the $\ln C_e$ and $\ln q_e$.

Temkin isotherm

The Temkin isotherm assumes that the heat of sorption in the layer would decrease linearly with coverage due to sorbate - sorbent interactions. Further the fall in the heat of adsorption is not logarithmic as stated in Freundlich expression. Linear form of Temkin isotherm equation is [14].

$$q_e = \frac{RT}{b_T} \ln a_T + \frac{RT}{b_T} \ln C_e$$

Where,

b_T is the Temkin constant related to the heat of sorption (J/ mg) and a_T the equilibrium binding constant corresponding to the maximum binding energy (L/ g) The Temkin constants a_T and b_T were calculated from the slopes and intercepts of graph drawn between q_e versus $\ln C_e$.

Dubinin - Radushkevich isotherm

The Linear form of Dubinin-Radushkevich isotherm is [15].

$$\ln q_e = \ln q_D - B\epsilon^2$$

Where,

q_D is the theoretical saturation capacity (mg/ g) B is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol²/ J²) and ϵ is Polanyi potential which is related to the equilibrium concentration as follows.

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right)$$

A plot of $\ln q_e$ vs. ϵ^2 gives a linear line and the constants q_D and B calculated from the slopes and intercepts respectively. The mean free energy of adsorption E was calculated from B using the following equation

$$E = \frac{1}{(2B)^{1/2}}$$

From this mean free energy of activation we can predict whether an adsorption is physisorption or chemisorption. If this energy is lesser than 8 kJ/ mol, the adsorption is physisorption and if the energy is more than 8 kJ/ mol, the adsorption is chemisorption.

Adsorption thermodynamics

Thermodynamic parameters such as change in free energy ΔG° (kJ/ mol), enthalpy ΔH° (kJ/ mol) and entropy ΔS° (J/ K/ mol) were determined using the following equations.

$$k_d = \frac{C_{\text{solid}}}{C_{\text{liquid}}}$$

Figure 1: Structure of Rose Bengal dye.

Figure 2: Terminalia catappa fruit shell.

Figure 3: Effect of pH on the adsorption of RB dye. [RB]: 20 mg/ L; Dose: 50 mg/ 50 ml; contact time: 160 min

Figure 4: [RB]: 20 mg/ L; Contact time: 160min; pH: 6.

$$\Delta G^{\circ} = -RT \ln k_d$$

$$\ln k_d = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$

Where;

k_d is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/ L), C_{liquid} is the liquid phase concentration at equilibrium (mg/ L), T is the temperature in Kelvin and R is the gas constant. The Van't Hoff plot is drawn between $\ln k_d$ versus $1/T$.

The values of change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated from the slopes and intercepts of the plot respectively.

Results

Results of effect of pH study were depicted as graph in figure 3. Color of the RB dye solution disappeared below the solution pH 4 even in the absence of adsorbent. Hence the pH dependence of RB dye adsorption onto TCZAC was studied in the pH range of 4 to 11. The percentage removal increased as the pH of the solution increased in acidic medium up to 6. Afterwards the percentage removal found to decrease up to pH 11. Maximum percentage removal was observed at pH 6.

Percentage of removal of RB dye from aqueous solution with respect to different doses was shown in figure 4. The percentage adsorption increased with the increase of the carbon dosage.

Result of the percentage of removal of RB dye from aqueous solution with respect to different contact time and with different initial concentration (10, 20, 30, 40 and 50 mg/ L) was given Table 1 and shown in figure 5, and it is observed that the amount of solute adsorbed by the adsorbent, increased with the increase of initial concentrations of dye.

The results obtained from pseudo-first order and pseudo-second order kinetic models are presented in table 2 and concerned plots are shown in figure 6 and figure 7 correspondingly.

The results obtained from Intra particle diffusion model are presented in table 2 and concerned plots are shown in figure 8.

Figure 9 demonstrates the effect of temperature. That the percentage of removal of RB dye increased with, the increase of temperature from 303 to 343 K.

The results obtained from Langmuir model are presented in tables 3 and concerned isotherm plots are shown in figure 10. The dimensionless separation factor R_L values calculated for various initial concentrations at different temperatures are given in table 4.

The results obtained from the Freundlich isotherm model are given in table 3. Representative isotherm plots are shown in figure 11.

The results obtained from the Temkin isotherm model are recorded in Table 3 and concerned isotherm plots are shown in figure 12.

Table 1: Percentage of removal of dye and amount of dye adsorbed at 303K.

Initial concentration (mg/ L)	Percentage of removal of dye at equilibrium	Amount of dye adsorbed at equilibrium (mg/ g)
10	77.5	07.75
20	75.0	15.00
30	71.7	21.50
40	68.8	27.50
50	65.5	32.75

Figure 5: [RB]: 10-50 mg/ L; Dose: 50 mg/ L; pH: 6.

Table 2: Kinetic parameters for the removal of RB dye onto TCZAC.					
Initial dye concentration (mg L ⁻¹)					
Kinetic parameters	10	20	30	40	50
Pseudo – first order constant					
k ₁ (min ⁻¹)	0.032	0.025	0.020	0.018	0.014
q _{e, exp} (mg g ⁻¹)	7.750	15.00	21.50	27.5	32.75
q _{e, cal} (mg g ⁻¹)	5.26	10.18	13.87	17.82	19.41
R ²	0.996	0.994	0.987	0.994	0.997
SSE	7.58				
Pseudo-second-order constants					
k ₂ (g mg ⁻¹ min ⁻¹)	0.0130	0.0037	0.0020	0.0013	0.0012
q _{e, cal} (mg g ⁻¹)	8.197	16.667	24.390	32.258	37.037
h (mg/ g min)	0.876	1.037	1.220	1.307	1.597
R ²	0.996	0.996	0.996	0.995	0.994
SSE	2.83				
Intra-particle diffusion constants					
k _p (mg g ⁻¹ min ⁻¹)	0.63	0.94	1.10	2.04	2.19
C (mg g ⁻¹)	2.308	5.337	8.747	6.085	8.703
R ²	0.998	0.998	0.997	0.999	0.998

The constants obtained from Dubinin-Radushkevich isotherm are collected in table 3 and the concerned isotherm plots are shown in figure 13.

The results obtained from thermodynamics study are presented in table 5 and representative plots are shown in figure 14.

The effect of ionic strength is shown in the figure 15.

Figure 6: [RB]: 10-50 mg/ L; Dose: 50 mg/ 50 mL; pH: 6.

Figure 7: [RB]: 10-50 mg/ L; Dose: 50 mg/ 50 mL; pH: 6.

Figure 8: [RB]: 10-50 mg/ L; Dose: 50 mg/ 50 mL; pH: 6.

Figure 9: Adsorption isotherm of RB onto TCZAC at different temperature. [RB]: 10-50 mg/ L; Dose: 50 mg/ 50 mL; Contact time: 160 min

Discussion

Effect of solution pH

Disappearance of color of the RB dye below the solution pH 4 in the absence of adsorbent may be due to change in the structure of the RB dye as described in indicator theories. Trend in percentage of adsorption with respect to pH of the solution can be interpreted by; the point of zero charge (pH_{zpc}) of TCZAC and the speciation of the RB dye at different pH of the solution as below.

pH_{zpc} of the adsorbent is 7. When the solution pH is below pH_{zpc} that is 7, the surface of the adsorbent is positively charged [16]. The lower percentage removal at lower pH infers that the dye might have acquired positive charge as reduced molecular ions (CH^+) and surface of the adsorbent would have rendered electrostatic repulsion towards dye cations. Increase of solution pH would decrease the positive charge on the adsorbent which explains

Figure 10: [RB]: 10-50 mg/ L; Dose: 50 mg/ 50 mL; Time: 160min.

Figure 11: [RB]: 10-50 mg/ L; Dose: 50 mg/ 50 mL; Time: 160 min.

Figure 12: [RB]: 10-50 mg/ L; Dose: 50 mg/ 50 mL; Time: 160 min.

Table 3: Isotherm parameters for removal of RB dye onto TCZAC.

Isotherm model	Temperature (K)				
	303	313	323	333	343
Langmuir constants					
q_m (mg g ⁻¹)	66.67	71.43	76.92	83.33	90.91
b (L mg ⁻¹)	0.059	0.062	0.067	0.075	0.086
R^2	0.999	0.995	0.996	0.995	0.997
Freundlich constants					
k_f (mg g ⁻¹)	32.73	41.59	54.83	74.30	110.9
n	1.410	1.399	1.389	1.372	1.348
R^2	0.994	0.996	0.996	0.996	0.995
Temkin constants					
b_t (J/ mg)	20.41	25.92	30.86	35.08	38.34
a_t (L/ mg)	0.758	0.833	0.9345	1.065	1.267
R^2	0.983	0.977	0.976	0.975	0.976
Dubinin-Radushkevich constants					
q_D (mg g ⁻¹)	26.91	28.06	29.38	30.80	33.03
E (kJ mol ⁻¹)	0.500	0.707	0.745	0.845	1.000
R^2	0.891	0.885	0.882	0.879	0.898

Figure 13: [RB]: 10-50 mg/ L; Dose: 50 mg/ 50 mL; Time: 160 min.

the increase of percentage removal of the dye up to pH 6. When the solution pH is above 6, the surface of the adsorbent becomes slightly positively charged and the dye might have acquired negative charge which would be attracted by the adsorbent. This positive charge on the adsorbent would have decreased with the increase of pH and hence the attraction between the dye anion and the adsorbent would have decreased. The decrease of percentage removal of the dye in alkaline medium that is pH of the solution is above 7 is attributed to electrostatic repulsion between the dye anion and the negative charge on the surface of the adsorbent.

Effect of adsorbent dosage

The increase of percentage adsorption with the increase of carbon dosage is due to increased carbon surface area and the availability of more adsorption sites [17].

Effect of contact time and initial concentration

The adsorption process is characterized by a rapid up take

Table 4: Dimensionless separation factor (R_L) for adsorption of RB dye onto TCZAC.

C_i for RB dye	Temperature (K)				
	303	313	323	333	343
10	0.146	0.617	0.596	0.573	0.538
20	0.079	0.446	0.425	0.402	0.368
30	0.054	0.349	0.330	0.309	0.280
40	0.041	0.287	0.270	0.251	0.225
50	0.033	0.243	0.228	0.212	0.189

Table 5: Thermodynamic parameters of rose Bengal by *Terminalia catappa* Linn.

C_{ia} for RB dye	ΔG (kJ mol ⁻¹)					ΔH (kJ mol ⁻¹)	ΔS (Jk ⁻¹ mol ⁻¹)
	303 K	313 K	323 K	333 K	343 K		
10	-3.116	-3.608	-4.165	-4.803	-5.550	15.215	60.260
20	-2.768	-3.219	-3.724	-4.294	-5.237	15.364	59.487
30	-2.338	-2.745	-3.322	-3.985	-4.765	16.079	60.418
40	-1.987	-2.442	-2.951	-3.627	-4.423	16.304	60.044
50	-1.615	-2.083	-2.604	-3.192	-4.044	16.395	59.154

Figure 14: Plot of $\ln K_d$ vs. $1/T$ for adsorption of RB onto TCZAC.

Figure 15: [RB]: 50 mg/ L; Dose: 50 mg/ 50 mL; Contact time: 60 min.

at initial stages. The percentage of removal increased with the increase of contact time. However, the time to attain equilibrium decreased with the increase of initial concentration of the dye solution. This is due to the decrease in the ratio of available adsorption sites to the concentration of solute in the solution with the increase of the initial concentration [18,19]. Increase of quantity adsorbed with the increase of initial concentration is due to higher driving force obtained because of concentration effect in the solution phase.

Pseudo-first order and Pseudo-second order kinetic models

From the result of kinetics study it is observed the initial sorption rate, 'h', increased from 0.8757 to 1.5974 with an increase of initial concentration of adsorbate from 10 mg/ L to 50 mg/ L.

The regression coefficient (R^2) values were ranged from 0.987 to 0.997 and from 0.994 to 0.996 for the pseudo-first order and pseudo-second order kinetic models respectively. The best fitting kinetic model was determined by comparing the 'calculated adsorption capacity' ($q_{e(cal)}$) values from the respective kinetic models with the experimentally determined adsorption capacity ($q_{e(exp)}$) at equilibrium. The kinetic model which gives the closer ' $q_{e(cal)}$ ' values with the experimental ' $q_{e(exp)}$ ' values can be considered as the best fitting kinetic model. This can be known from the statistical tool 'Sum of Squared Error' (SSE).

$$SSE = \sqrt{\sum [(q_e)_{exp} - (q_e)_{cal}]^2 / N}$$

Where; N is the number of data points, $((q_e)_{exp})$ is the experimental q_e and $((q_e)_{cal})$ is the calculated q_e . The kinetic model which gives lowest SSE value is the best describing kinetic model.

Between the pseudo-first order and pseudo-second order, the pseudo second order kinetic model seems to best describe the adsorption of RB dye as the SSE value of pseudo-second order model is smaller than the pseudo-first order kinetic model.

Intra-particle diffusion study

The linear plots are attributed to the macro pore diffusion which is the accessible sites of adsorption. This is attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface.

The k_p values were found to increase from 0.63 to 2.19 with an increase of RB dye concentration which revealed that the rate of adsorption is governed by the diffusion of RB dye within the pores of the adsorbent.

Effect of temperature

The increase of percentage of removal with the increase of temperature is due to increased surface activity and increased in kinetic energy of the dye molecule. Since the % of removal increased with the increase of temperature, the adsorption was endothermic nature.

Langmuir isotherm

The regression coefficient (R^2) values are ranged from 0.995 to 0.997 for all the studied temperatures. These results show the best fitting of the equilibrium data with Langmuir isotherm. Further it is noticed that adsorption capacities were slightly increased with an increase of temperature.

These the R_L values were lie in between 0 and 1 which indicates the favourable adsorption of RB dye onto TCZAC.

In general Langmuir constant values infer a better performance of TCZAC.

Freundlich isotherm

The regression coefficient (R^2) for Freundlich isotherms are ranged from 0.994 to 0.969 for all the studied temperatures viz. 303, 313, 323, 333 and 343K. It indicates that the experimental data fit well into the Freundlich isotherm models.

Further it is noticed that Freundlich constant the adsorption capacity k_f (mg/ g) increased from 32.734 to 110.917 with the increase of temperature.

The adsorption intensity 'n' values are ranged from 1.347 to 1.4104 i.e., between 1 and 10, which indicate the favourable physical adsorption [20].

Temkin isotherm

The regression coefficient (R^2) values ranged from 0.975 to 0.983 and these results show the best fitting of the equilibrium data with Temkin isotherm. Equilibrium binding constant ' a_T ' values (L/ g) and the Temkin constant related to heat of sorption, b_T values (kJ/ mg) have low values and B value ranged from 0.002 to 0.001. Hence the adsorption belongs to physisorption.

Dubinin - Radushkevich isotherm

The regression coefficient (R^2) values are ranged from 0.879 to 0.898 for the five studied temperatures. The theoretical saturation capacity q_d values (mg/ g) found to increase from 26.907 to 33.029 with the increase of temperature.

Values of the mean free energy E (kJ/ mol) ranged from 0.5 to 1. These very low values of 'E' support the physisorption interaction.

Adsorption thermodynamics

The negative values of ΔG° show that the adsorption is

spontaneous. The positive values of ΔH° show the endothermic nature of adsorption process. The ΔH° values were within the range of 1–93 kJ/ mol which confirms the physisorption [21,22]. The positive values of ΔS° show the increased disorder and randomness at the solid solution interface. During adsorption some structural changes occur at the surface of the adsorbent. The adsorbed water molecules which are displaced by the adsorbate species, might have gained more translational entropy than is lost by the adsorbate molecules, thus allowing the prevalence of randomness in the system [23]. The enhancement of adsorption capacity of the activated carbon at higher temperatures was attributed to the enlargement of the size of the pore and the activation of the adsorbent surface.

Effect of ionic strength

Adsorption of Rose Bengal found to increase with an increase of NaCl concentration as shown in figure 15. This may be due to compression of the electrical double layer by the Cl^- anion and also due to common ion effect of Na^+ ion which drive dye to the sorbent.

Conclusion

Zinc Chloride Activated (TCZAC) was prepared from fruit shells of *Terminalia catappa* Linn, found to have good capacity to absorb RB dye. Equilibrium of adsorption was achieved around 50 to 160 minutes for the dosage of 50 mg/ 50 mL of solution at room temperature of 303 K for the initial concentrations of RB dye solutions ranging from 10 to 50 mg/ L. Maximum removal (77.5 % for the dye concentration of 10 mg/ L at 303 K) was recorded at pH 6. The % of removal found to increase with the increase of temperature (86.25 % for the dye concentration of 10 mg/ L at 303 K). Kinetic of the adsorption process was found to follow the pseudo second order kinetic model. Adsorption capacity data obtained from the Langmuir, Freundlich, and Dubinin-Radushkevich isotherms indicated that TCZAC was effective in removing RB dye from aqueous solution. Further the adsorption energy values obtained from Dubinin-Radushkevich and Temkin isotherms supported physisorption mechanism. The separation factor R_L values of Langmuir isotherm indicated that the adsorption was favourable. The thermodynamics parameters indicated that the adsorption process is endothermic and spontaneous and physisorption in nature.

Declarations

It is purely individual work and not having any association with academic bodies for financial support. Therefore conflict of interest is not applicable. No human subject was used for this study.

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