

Equilibrium and Kinetic adsorption studies of Rhodamine-B from aqueous solutions using cocoa (*Theobroma cacao*) shell as a new adsorbent

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Abstract:

The adsorption of Rhodamine-B (RB) from aqueous solutions by cocoa (*Theobroma cacao*) shell activated carbon (CSAC) was studied in a batch adsorption system. The adsorption studies include both equilibrium adsorption isotherms and kinetics. The adsorption equilibrium was represented with Langmuir, Freundlich, Tempkin, Harkin's - Jura and Dubinin-Radushkevich isotherm models. Pseudo first order, pseudo second order, Elovich and Intraparticle diffusion kinetic models were used to test the adsorption kinetics. The kinetic data were well described by the pseudo second order kinetic model. The mechanism of the adsorption process was determined from the intraparticle diffusion model. The results indicated that CSAC could be employed as a low-cost alternative for the removal of RB from diluted industrial effluents.

Keywords: Cocoa shell activated carbon, adsorption, Rhodamine- B, Adsorption isotherm, Kinetics

1. Introduction

Pollution of water due to the discharge of effluents from dyeing industries affects the environment due to its toxicity [1]. Industrially, several waste water treatment techniques have been suggested which includes electrochemical techniques [2], adsorption [3, 4], coagulation and flocculation [5], ozonation [6], etc. Among these, adsorption using activated carbon has been widely proved efficiency for the removal of pollutants from effluents. The cost of preparing activated carbon from agricultural wastes is negligible when compared to the cost of commercial activated carbon [7]. Some of the agricultural waste in which activated carbon prepared are coir pith [8], rice husk [9], walnut shell[10], barley husk[11],cashew nut shell[12], palm kernel shell[13], pomegranate husk[14], maize cob[15], etc. In this work an attempt was made to study the adsorption effect of carbon from cocoa shell, an agricultural waste product, for the removal of Rhodamine B dye in aqueous solution.

2. Materials and Methods

2.1. Preparation of adsorbent

Dried cocoa shell collected from local agricultural field was carbonized with concentrated sulphuric acid in the weight ratio of 1:1(w/v). The activation was performed by heating the sample for 7 hours in a muffle furnace at 550°C. After carbonization and activation, the carbon obtained was washed with distilled water until a constant pH was reached. Then the sample was dried at 110°C for overnight in a hot air oven. The carbonized material was taken out, grounded and sieved to 150µm size and stored in a vacuum dessicator.

2.2. Preparation of dye solution

Stock solution of RB was prepared by dissolving 1g of dye in 1L of distilled water to give concentration of 1000mg/L. The serial dilutions say 20, 40, 60, 80 mgL⁻¹ were made by diluting the dye stock solution in accurate proportions. The pH of dye solutions were adjusted with 0.1M NaOH or HCl using a pH meter.

2.3. Batch Adsorption experiments

Batch mode experiments were carried out in orbital shaker at a constant speed of 125 rpm at 35°C using 250ml conical flasks containing 100mg of CSAC with 50ml of dye solutions. After agitating the flasks for

predetermined time intervals samples were withdrawn from the flasks. The adsorbents were separated from the solution by centrifugation (REMI make) at 2000rpm for 5 minutes. The dye concentration was determined spectrophotometrically using Elico make UV-Visible spectrophotometer at $\lambda_{\text{max}} = 555\text{nm}$.

3. Results and Discussions

3.1. Effect of contact time and initial concentration

To study the effect of dyes initial concentration and contact time on adsorption uptake, RB solution with initial concentrations 20, 40, 60, 80mgL⁻¹ was agitated with 100mg of CSAC. In this case, the solution pH was kept natural without any pH adjustments. The experimental results of sorption of RB on to CSAC at various initial concentrations are shown in Fig.1. The adsorption at different dye concentrations was rapid at the initial stages and then gradually decreases with the progress of adsorption until the equilibrium was reached. The rapid adsorption at the initial contact time can be attributed to the availability of the positively charged surface of activated carbon. The rate of dye adsorption is probably due to the slow pore diffusion of the solute ion into the bulk of the adsorbent.

As shown in Fig. 1, the contact time needed for RB solution to reach equilibrium was 120min. The results indicated that there was no change in the sorption capacity after 120mins, therefore 180mins was fixed as the agitation time for isotherm studies. The adsorption capacity at equilibrium (q_e) increased from 9.44 to 34.39 mgg⁻¹ with an increase in the initial concentrations from 20 – 80 mgL⁻¹.

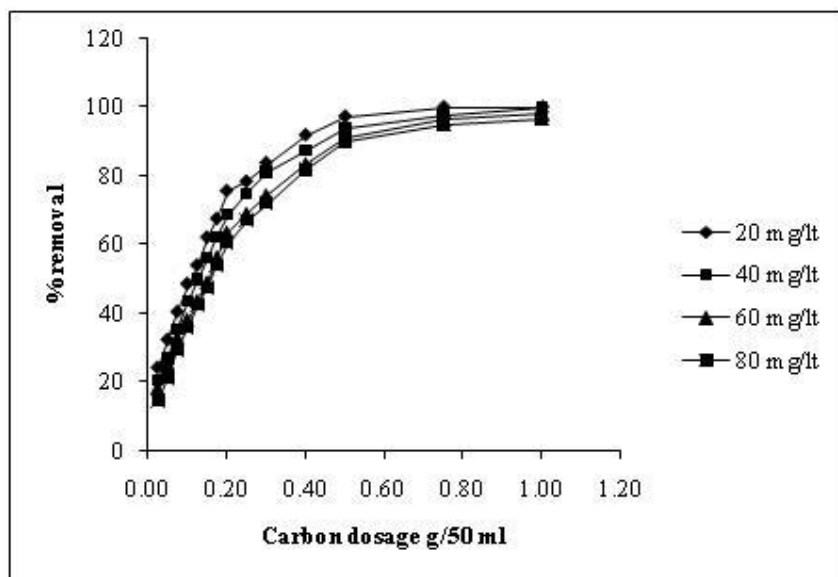


Fig. 1. Effect of agitation time on adsorption- Initial concentration variation

3.2. Effect of adsorbent dose

The effect of adsorbent dose on the removal of the dye for different concentrations (20, 40, 60, 80 mgL⁻¹) were investigated by agitating with different adsorbent dosage over the range of 25 -1000mg. The study reveals that percentage adsorption increases with increase in the carbon concentration (Fig. 2). This attributes the increased carbon surface area and availability of more adsorption sites.

3.3. Effect of pH

The effect of pH were investigated by employing initial concentration of dye (40 mg/L) and 100mg/50ml of CSAC. The initial pH values were adjusted with 0.1M HCl and 0.1M NaOH to form a series of pH from 2 to 10. The results show that there was no significant change in the percent removal of dye over the entire pH range. This indicates that either H⁺ or OH⁻ ions could not influence the dye adsorption onto CSAC [16, 17].

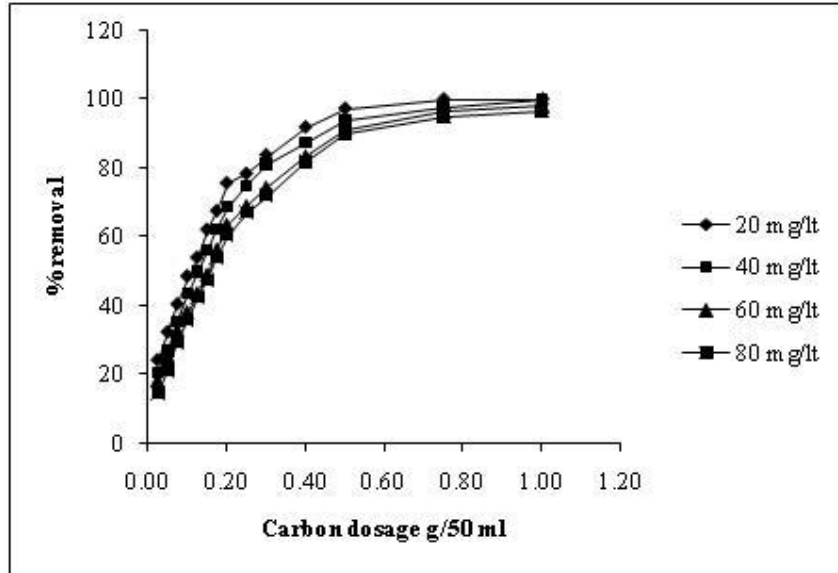


Fig. 2. Effect on adsorbent dose on the removal of Rhodamine B

3.4. Adsorption isotherms

3.4.1. Langmuir isotherm

The Langmuir isotherm is based on the assumption that it predicts monolayer coverage of the adsorbate on the outer surface of the adsorbent [18]. This model also suggests that there is no lateral interaction between the sorbed molecules. Linear form expression for the Langmuir model is

$$C_e / q_e = 1 / b Q_0 + C_e / Q_0 \quad (1)$$

where,

- Q₀ is a constant related to adsorption capacity (mg/g)
- b is Langmuir constant related to energy of adsorption(L/mg)
- C_e is equilibrium constant of dye (mg/L)
- q_e is amount of dye adsorbed at equilibrium (mg/g)

The linear plot of C_e/q_e versus C_e is shown in Fig. 3(a). The constants Q₀ and b can be calculated from slope and intercept of the plot and the values are tabulated in Table 1. The shape of the Langmuir isotherm was investigated by the dimensionless constant separation term (R_L) to determine high affinity adsorption and is expressed as R_L=1 / (1+b C₀). R_L values indicate the nature of adsorption process as given below.

R _L values	Adsorption
R _L > 1	Unfavourable
R _L =1	Linear
0 < R _L <1	Favourable
R _L =0	Irreversible

In the present investigation, the R_L values were less than one which shows the adsorption process was favorable.

3.4.2. Freundlich isotherm

The Freundlich isotherm is based on multilayer adsorption on heterogeneous surface [19]. Linear form of Freundlich equation is

$$\log q_e = \log k_f + 1/n \log C_e \quad (2)$$

where,

- q_e is dye concentration in solid at equilibrium (mg/g)
- C_e is dye concentration in solution at equilibrium (mg/L)
- k_f is measure of adsorption capacity (mg/g)
- n is adsorption intensity

The linear plot of $\log q_e$ versus $\log C_e$ is shown in Fig. 3(b). The values of $1/n$ and k_f can be calculated from the slope and intercept respectively and the results are given in Table 1. When $1/n$ is >1.0 , the change in adsorbed dye concentration is greater than the change in the dye concentration in solution.

3.4.3. Dubinin-Raduskevich(D-R) isotherm

The D-R isotherm is more general because it does not assume a homogenous surface or constant adsorption potential [20]. It was applied to estimate the porosity apparent free energy and the characteristics of adsorption. The linear form can be represented as

$$\ln q_e = \ln q_D - B\epsilon^2 \quad (3)$$

where,

- B is a constant related to the mean free energy of adsorption ($\text{mol}^2(\text{kJ}^2)^{-1}$)
- q_D is the theoretical saturation capacity (mg/g)
- ϵ is the polyani potential, and calculated as follows:

$$\epsilon = RT \ln (1+1/C_e) \quad (4)$$

The slope of the plot of $\ln q_e$ versus ϵ^2 gives B and the intercept yields the adsorption capacity, q_D . Fig. 3(c) shows D-R plot and the results are given in Table 1. The mean free energy of adsorption (E) (KJmol^{-1}) is calculated from the equation

$$E = 1 / (2B)^{0.5} \quad (5)$$

Table 1. Results of various isotherm plots for the adsorption of RB on to CSAC

Models	Isotherm constants			
	Langmuir	$Q_m(\text{mg g}^{-1})$	$b \times 10^{-3} (\text{L mg}^{-1})$	
41.67		19.5		0.995
Freundlich	$k_f(\text{mg g}^{-1})$	n		R^2
	0.0029	0.32		0.966
Dubinin-Raduskevich	$q_D(\text{mg g}^{-1})$	$B (\text{mol}^2 \text{kJ}^{-2})$	$E (\text{kJmol}^{-1})$	R^2
	31.25	0.000	0.7071	0.914
Tempkin	$\alpha(\text{L g}^{-1})$	$\beta(\text{mg L}^{-1})$	b	R^2
	0.3663	8.139	314.62	0.973
Harkin's- Jura	A	B		R^2
	500	2.5		0.936

3.4.4. Tempkin isotherm

The derivation in Tempkin isotherm assumes that fall in the heat of adsorption is linear rather than logarithmic, as implied in Freundlich equation [21]. The Tempkin isotherm is applied in the following form

$$q_e = RT/b(\ln(AC_e)) \quad (6)$$

The linear form of Tempkin equation is

$$q_e = \beta \ln \alpha + \beta \ln C_e \quad (7)$$

where,

$$\beta = (RT)/b, \quad (8)$$

T is the absolute temperature in Kelvin

R is the universal gas constant, $8.314 \text{ J (mol K)}^{-1}$

b is the Tempkin constant related to heat of sorption (J/mg)

A the equilibrium constant corresponding to the maximum binding energy (L/g)

The Tempkin constants α and b are calculated from the slope and intercept of q_e versus $\ln C_e$ (Fig. 3(d)) and parameters are given in the Table 1.

3.4.5. Harkin's - Jura isotherm

Harkin's - Jura isotherm assumes the presence of multilayer adsorption with the existence of heterogeneous pore distribution [22]. The Harkin's-Jura isotherm is expressed as

$$1/q_e^2 = (B/A) - (1/A (\log C_e)) \quad (9)$$

where,

C_e is the equilibrium concentration of the dye in solution (mgL^{-1})

q_e is the amount of dye adsorbed onto the adsorbent (mgg^{-1})

A and B are the isotherm constants

The plot of $1/q_e^2$ versus $\log C_e$ gives a linear plot and the isotherm constants and correlation coefficients are given in Table 1.

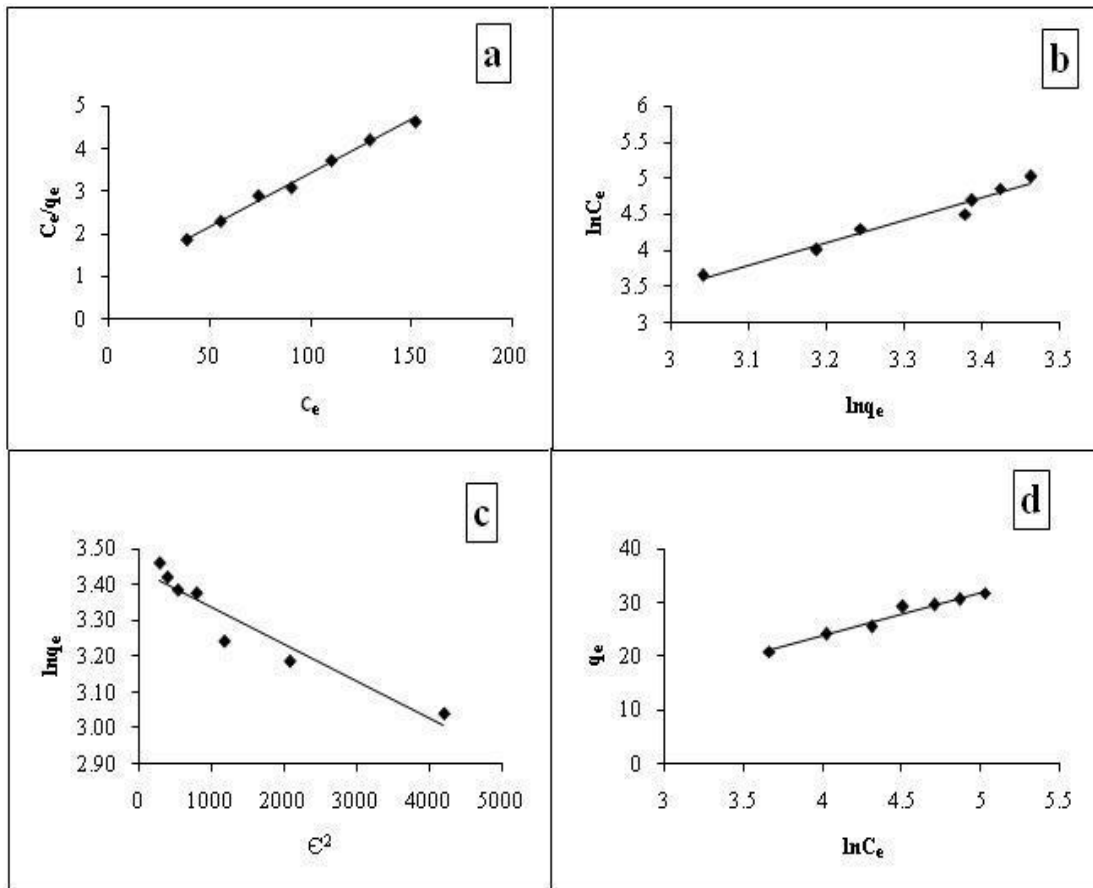


Fig. 3. Adsorption isotherm plots for RB on to CSAC
 (a) Langmuir plot (b) Freundlich plot (c) Dubinin-Raduskevich (D-R) plot (d) Tempkin plot

3.5. Kinetics of adsorption

The kinetic studies describe the rate of adsorption and this rate controls the equilibrium time. These kinetic models are useful for the design and optimization of effluent treatment models. Pseudo first order, pseudo second order, Elovich and Intraparticle diffusion kinetic models were analyzed for the mechanism of RB adsorption by CSAC.

3.5.1. Pseudo first order model

The adsorption data fitted to the Lagergren's pseudo first order rate equation is [23]

$$dq_t/dt = k_1(q_e - q_t) \tag{10}$$

The integrated linear form of the model is

$$\log(q_e - q_t) = \log q_e - k_1 / 2.303t \tag{11}$$

where,

- q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g)
- q_t is the amount of adsorbate adsorbed at contact time t (mg/g)
- k_1 is the pseudo first order rate constant (min^{-1})

A plot of $\log(q_e - q_t)$ versus t gives a linear trace from which the values of k_1 and q_e can be determined from the slope and intercept. The data for the adsorption of RB on to CSAC applied to pseudo first order kinetic model is shown in Fig. 4(a) and the results are presented in Table 2. The determined values of q_e calculated from the equation differ from the experimental values, which show the adsorption of RB on to CSAC fitted poor to the pseudo first order kinetics.

Table 2. Calculated kinetic parameters for the adsorption of RB on to CSAC

Concentration (mg/L)	20	40	60	80
Pseudo first order kinetics				
$k_1 \times 10^{-2}(\text{min}^{-1})$	1.38	1.61	1.84	2.07
$q_{e,cal}(\text{mg/g})$	3.87	8.41	12.1	16.67
$q_{e,exp}(\text{mg/g})$	9.44	18.22	26.47	34.49
R^2	0.999	0.989	0.989	0.989
Pseudo second order kinetics				
$k_2 \times 10^{-3}(\text{g/mg min})$	8.2	4.0	2.9	2.2
$q_{e,cal}(\text{mg/g})$	10.1	19.6	28.5	37.0
h	0.83	1.56	2.41	3.1
R^2	0.995	0.997	0.997	0.998
Elovich				
$\alpha(\text{mg/g min})$	9.12	12.1	20.9	22.4
$\beta(\text{g/mg})$	0.75	0.36	0.25	0.2
R^2	0.967	0.983	0.981	0.981
Intraparticle				
$K_d(\text{mg/g min})$	0.369	0.8	1.077	1.441
$C(\text{mg/g})$	4.944	9.102	13.64	17.4
R^2	0.943	0.940	0.933	0.926

3.5.2. Pseudo second order model

The rate of adsorption for pseudo second order model [24] can be given as

$$dq_t / dt = k_2(q_e - q_t)^2 \quad (12)$$

The linearised form of the above model is

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (13)$$

where,

q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g)

q_t is the amount of adsorbate adsorbed at contact time t (mg/g)

k_2 is the rate constant of pseudo second order adsorption (g/mg min)

The initial adsorption rate, h (mg/g min), as $t \rightarrow 0$ can be defined as

$$h = k_2 q_e^2 \quad (14)$$

A plot of t/q_t versus t gives a linear relationship, from which q_e and k_2 can be determined from the slope and intercept of the plot respectively. The data for the adsorption of RB on to CSAC applied to pseudo second order model is shown in Fig. 4(b) and the results are presented in Table 2. The pseudo second order rate constant decreases from 8.2×10^{-3} to 2.3×10^{-3} (g/mg min) with increase in initial dye concentration. The equilibrium sorption capacity, q_e and initial sorption rate, h increases with increasing the initial dye concentration. From the results it can be suggested that the adsorption of RB on to CSAC follows pseudo second order kinetics.

3.5.3. Elovich equation

The Elovich equation is another rate equation in which the absorbing surface is heterogeneous [25]. It is generally expressed as

$$dq_t/dt = \alpha e^{-\beta q_t} \quad (15)$$

Integrating this equation for the boundary conditions, "Eq. (15)" becomes

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \quad (16)$$

where,

α is the initial adsorption rate (mg/g min)

β is related to the extent of surface coverage and the activation energy for chemisorption (g/mg)

A plot of q_t versus $\ln t$ gives a linear trace with a slope of $(1/\beta)$ and an intercept of $1/\beta \ln(\alpha\beta)$. The plot is linear with good correlation coefficient as shown in Fig. 4(c) and results are given in Table 2.

3.5.4. Intra particle diffusion model

Weber and Morris suggested a kinetic model to identify the diffusion mechanisms and rate controlling steps that affects the adsorption process [26]. It is empirically a functional relationship, common to most adsorption processes, where uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time. According to this theory, the intraparticle diffusion equation is expressed as follows:

$$q_t = k_d t^{1/2} + C \quad (17)$$

where,

k_d is the intraparticle diffusion rate constant (mg/g min^{1/2})

C is the intercept (mg g⁻¹)

The plot of q_t versus $t^{1/2}$ gives a straight line from which k_d can be calculated from the slope of the plot. Values of C give an idea about the thickness of boundary layer, i.e., the larger the intercept, greater the contribution of the surface sorption in the rate controlling step. The data for the adsorption of RB on to CSAC applied to Intra-particle diffusion model is shown in Fig. 4(d) and the results are presented in Table 2. The constant C was increased with increasing the dye concentration, which indicating the increase of the thickness of the boundary layer and decrease of the chance of the external mass transfer and hence increase of the chance of internal mass

transfer. The linear portion of the plot for wide range of contact time between adsorbent and adsorbate does not pass through the origin. This deviation from the origin may be due to the variation of mass transfer in the initial and final stages of adsorption. Such a deviation from the origin indicates the pore diffusion is the only controlling step and not the film diffusion.

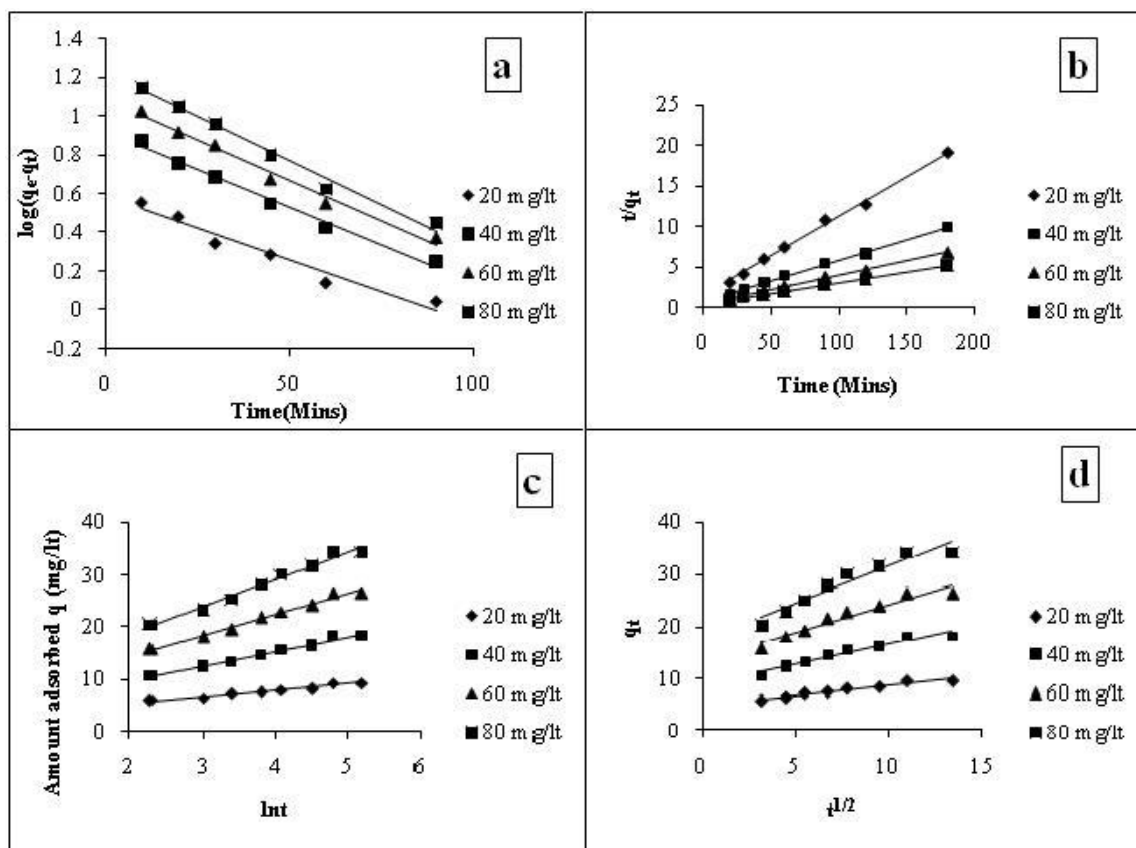


Fig. 4. Kinetic plots for the adsorption of RB on to CSAC
 (a) Pseudo first order plot (b) Pseudo second order plot (c) Elovich plot (d) Intraparticle diffusion plot

3.6. Desorption studies

Desorption studies help to elucidate the adsorption and recycling of the spent adsorbent and the dye. Neutral pH water, Sodium hydroxide (1M), Hydrochloric acid (1M) and 50% acetic acid (v/v) were used for desorption of the dye. From the effect of various reagents used for desorption studies, 50% acetic acid shows better percentage removal of dye from spent carbon, because more than 53% removal of adsorbed dye was achieved [27]. Desorption of dye in acetic acid (organic medium) indicates the RB adsorption on to CSAC was through by chemisorption mechanism.

4. Conclusion

The results of this investigation show that activated carbon developed from cocoa shell has a suitable adsorption capacity for the removal of RB from aqueous solutions. The experimental results were analyzed by using Langmuir, Freundlich, Tempkin, Harkin's - Jura and Dubinin-Radushkevich isotherm models and the correlation coefficients for Langmuir, Freundlich and Tempkin equations fitted better than Harkin's - Jura and Dubinin-Radushkevich equations. The kinetic study was performed based on pseudo first order, pseudo second order, Elovich and intraparticle diffusion equations. The data indicated that the adsorption kinetics follow the pseudo second order rate with Intraparticle diffusion as one of the rate determining step. The present study suggests that CSAC could be employed as a promising low-cost adsorbent for the removal of RB from aqueous solutions.

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