

Adsorption of Reactive orange 16 dye onto activated carbon from the stems of *Solanum Torvum*

Abstract:

The activated carbon prepared from *Solanum Torvum* by treating it with H_2SO_4 was used as an effective adsorbent for the removal of reactive orange 16 (RO16). The activated carbon was characterized by scanning electron microscopy (SEM), powder-XRD and FTIR spectral analysis. Experiments were carried out as function of initial dye concentration, adsorbent dose and pH. The adsorption process was more favourable at acidic pH (2.0). The data were modeled using the pseudo-first order and pseudo-second order kinetics. The adsorption was found to follow pseudo-second order. The results indicate that the Langmuir model provides the best correlation for the experimental data. Thermodynamic parameters such as free energy change, enthalpy change and entropy change determined indicate the process for spontaneous and endothermic.

Key words: Activated carbon, *Solanum Torvum*, Adsorption, Kinetics, Thermodynamics.

1. Introduction:

Water pollution is a common environmental problem in the world predominantly owing to the influence of residual dyes from dyeing and textile industries. Dyeing ions mostly coming from textile and allied industries let out enormous amount of effluents into water streams which have detrimental effects on life in earth. The dye discharging of untreated effluents containing dyes reduce the light penetration, affects the photosynthesis of aqueous flora, besides of being aesthetically objectionable for drinking and other purposes^{1, 2}. Dyes are highly toxic to some organisms and can cause allergic dermatitis, skin irritation, cancer, mutation, etc. In addition, biodegradation of some of them produce harmful aromatic compounds which are highly carcinogenic^{3, 4}. The continuous exposure of workers in the textile industries is linked to a higher bladder cancer risk. The adsorption method is a most proficient for the removal of artificial dyes from water effluents. According to this process, an adsorbent adsorbs the dye species from the effluents and reduce the volume of dye molecules. An adsorbent has excellent properties of high internal surface area and well-defined pore structures that leads to the use of activated carbon for the removal of dye species from aqueous solutions⁵⁻⁷. Apart from these physical properties the adsorption capacity of adsorbent is dependent on experimental condition and the source of organic material in the production of activated carbon. The preparation of activated carbon depends on the method of activation. There are principally two methods which are used for the activation of developed adsorbent i.e. physical and chemical. The physical activation includes carbonization and activation at high temperatures⁸. On the other hand chemical activation includes treatment with different chemicals at higher temperatures⁹. Recently, various kinds of activated carbon have been achieved from different agriculture wastes and used as low-cost adsorbents for removal of dyes from aqueous solutions like banana pith¹⁰, plum kernals¹¹, orange peel¹² and fruit wastes¹³ etc. The aim of this study is to produce active carbon from *Solanum torvum* which was activated with H_2SO_4 solution used for the removal of reactive orange 16. The various studies have been investigated.

2. Materials and Methods:

2.1. Preparation of Adsorbate

Reactive orange (RO16) dye (CI17757) from Sigma Aldrich was used without any further purification. A stock solution of RO 16 was prepared by dissolving 1g of dye in 1000 ml of double distilled water and diluted to the required concentration.

2.2. Preparation of Activated Carbon (STAC)

Solanum Torvum stem was collected from local areas situated in and around Odathurai village, Tamilnadu, India. The plant stem was washed with distilled water to remove the impurities and dried for 7 days. The dried *Solanum Torvum* stem was treated with concentrated sulphuric acid in the ratio 1:1 (w/v). When the reaction subsided, the material was left in a hot air oven at 110 -140°C for a period of 24 hours. The dried mass was washed with large quantity of water to remove free acid and then dried at 110°C. The powdered material was subjected for activation at 800°C for a period of 10 minutes and used as adsorbent.

3. Characterization of adsorbent:

3.1. Powder X-ray diffraction analysis

The X-ray diffraction pattern of the adsorbent is shown in Fig. 1. The adsorbent exhibit broad peaks at $2\theta = 25^\circ$ and the absence of a sharp peaks revealed a mostly amorphous structure, which is a beneficial property for well-defined adsorbent.

3.2. SEM analysis

A scanning electron microscopy is a primary tool for characterizing the surface morphology and fundamental physical properties of an adsorbent. The SEM image of STAC is shown in Fig. 2. It is clear that, adsorbent appear to have number of pores and hence there is enhanced possibility for dye species to get trapped and adsorbed into these pores.

3.3. FTIR spectral analysis

The FTIR spectra were obtained to evaluate qualitatively the chemical structures of before and after adsorption of activated carbons. The spectra are shown in Fig. 3 and 4. FTIR spectrum of the STAC showed the broad intense peak at 3425 cm^{-1} which is indicative of hydroxyl groups. The peak observed at 2924 cm^{-1} can be assigned to the -C-H stretching. The peak observed at 1620 cm^{-1} can be attributed to axial deformation of carbonyl groups. The presence of aliphatic primary amine C-N stretching is confirmed by absorption at 1033 cm^{-1} . The peaks at $1200 - 1100\text{ cm}^{-1}$ could indicate the presence of alcohols and phenolic groups⁸. A comparison of the spectra before and after adsorption shows that there is no appreciable change in adsorption of STAC. This may be due to the fact that adsorption did not alter the chemical nature of the surface of the adsorbent, i.e the adsorption may be physical in nature¹¹.

4. Batch adsorption studies

Adsorption experiments were carried out in a 250 mL of Erlenmeyer flask containing known amount of adsorbent with RO16 dye solution. All the experiments were carried out at natural pH (except for effect of pH). The effect of contact time was studied using 100 mg of the adsorbent per 100 mL of dye solution at various concentrations. The effect of adsorbent dose was studied by varying the adsorbent dose from 50 to

500 mg for the 50 ml of 30, 40 and 50 mg/L adsorbate. The effect of pH was studied in the pH range of 2-11 taking 100 mg of adsorbent and 100mL of adsorbate.

5. Results and Discussion:

5.1. Effect of initial dye concentration

The effect of initial dye concentration on adsorption of the RO16 onto STAC was investigated in the concentration range of 30-60 mg/L at 30°C. The results are shown in Fig. 5. The adsorption of the RO16 dye increased with increase in contact time and then the equilibrium is attained beyond which there was no significant increase in the removal at all dye concentrations. The increase in the quantity of the dye adsorbed per unit mass of the adsorbent was from 5.92 mg/g to 9.84 mg/g.

5.2. Effect of adsorbent dose

The percentage removal of RO16 initially increased rapidly with the increase in adsorbent dose and after the critical dose the removal percentage almost reached a constant value as shown in Fig. 6. This may be attributed to the increase in the availability of surface active sites resulting from the increased dose and conglomeration of the adsorbent¹⁴.

5.3. Effect of p^H

The effect of solution pH on the adsorption of RO 16 on STAC was shown in Fig. 7. The maximum uptake of RO16 was obtained at p^H 2 and the dye adsorption decreased with increase in p^H. At low p^H value the surface of adsorbent gets positively charged as more H⁺ ions get adsorbed on the surface. The dye molecules are negatively charged they get easily adsorbed due to electrostatic attraction.

5.4. Adsorption kinetics

In order to examine the kinetic of the adsorption process of RO 16 on the STAC, pseudo-first-order and pseudo-second-order kinetic models were studied.

5.4.1. Pseudo-first order kinetics

The rate constant of adsorption is determined from the pseudo-first-order rate expression given by Lagergren¹⁵.

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

where, q_e is the amount of dye adsorbed at equilibrium (mg/g), q_t is the amount of dye adsorbed at time t (mg/g), t is the time (min) and k_1 is the pseudo first order rate constant (min^{-1}). The rate constant k_1 and q_e can be calculated from the slope and intercept of the graph plotted between $\log (q_e - q_t)$ vs t . The data in Table 1 reveal that the calculated values of q_e does not agree well with the experimental q_e values. The R^2 values are relatively low, indicates that the data does not fit into pseudo-first kinetics.

5.4.2. Pseudo- second order kinetics

The linear pseudo second order kinetic equation is given as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

where k_2 is rate constant of second order adsorption ($\text{g mg}^{-1}\text{min}^{-1}$). The plot of t/qt vs t (Fig. 8) was linear. The values of q_e and k_2 can be calculated from the slope and intercept. From the results it is clear that the equilibrium adsorption capacity q_e increases and adsorption rate constant, k_2 , decreases with increase in the initial dye concentration. Based on the good agreement between the experimental and calculated q_e and high R^2 and low SSE values obtained (Table 1). For both the kinetic studies, good correlation coefficients were obtained ($R^2 \approx 1$) by fitting the experimental data to pseudo-second order than that for the pseudo-first order kinetic model.

5.5. Adsorption Isotherm:

5.5.1. Langmuir isotherm

The adsorption of dyes at different temperatures have been analysed the linear form of Langmuir model is expressed by,

$$\frac{C_e}{q_e} = \frac{1}{b} Q_0 + \frac{C_e}{Q_0}$$

Where C_e is equilibrium concentration of dye (mg/L), q_e is the amount of dye adsorbed at equilibrium (mg/g), Q_0 and b are the Langmuir constants correlated to adsorption capacity and rate of adsorption, respectively. A linear plot of C_e/q_e vs C_e is shown in Fig. 9. The values of Q_0 and b were calculated from the slope and intercept of the plots and the values are given in Table 2. The maximum monolayer adsorption capacity increases slightly with increase in temperature from 303 K to 333 K in the case of RO16 dye studied. The important features of the Langmuir isotherm was examined by the dimensionless constant separation term (R_L) to determine high affinity adsorption.

R_L was calculated as follows:

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

The values of R_L indicate the nature of the isotherms to be either unfavorable if $R_L > 1$, linear if $R_L = 1$, favorable if $0 < R_L < 1$ (or) irreversible if $R_L = 0$. The R_L at different temperatures 303 K, 313 K, 323 K and 333 K were found to be between 0 and 1 in the concentration range studied for RO16 dye used in the present investigation, suggesting a favorable adsorption on the adsorbent.

5.5.2. Freundlich isotherm

The Freundlich isotherm was represented by the following equation,

$$\log q_e = \log K_f + 1/n \log C_e$$

Where K_f and n are Freundlich constants represent adsorption capacity and intensity of the adsorbent respectively. The plot of $\log q_e$ vs $\log C_e$ shown in Fig. 10 indicates that the adsorption of RO16 dye favours the Freundlich isotherm to some extent. The Freundlich constants (K_f and n) are given in Table 2. The calculated values of n between 2 and 3 that represent good adsorption¹⁶.

5.5.3. Thermodynamic Studies

The thermodynamic parameters used to determine the feasibility of the adsorption process change in Gibbs standard free energy (ΔG^0), standard enthalpy of adsorption, (ΔH^0) and standard entropy of

adsorption (ΔS^0) were determined from the slope and intercept of linear plots of $\ln K_c$ vs $1/T$ using the Van't Hoff equation.

$$\Delta G^0 = -RT \ln K_c$$

$$\ln K_c = \Delta S^0/R - \Delta H^0/RT$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$

Where R is the universal gas constant (8.314 J/mol. K). T is the temperature (K) and K_c is the Langmuir equilibrium constant. The negative value of ΔG^0 and positive value of ΔH^0 indicate that the adsorption process is spontaneous and endothermic in nature. The positive value of ΔS^0 indicated an increased randomness at the adsorbent- adsorbate interface of the adsorption process.

6. Conclusion:

The present study revealed that the activated carbon prepared from *Solanum Torvum* has been used effectively as an efficient adsorbent for the removal of RO 16 dye from aqueous solutions. The amount of dye adsorbed varied with function of initial dye concentration, adsorbent dose, and pH. From the isotherm models, it was observed that the adsorption data fitted well with Langmuir isotherm. The adsorption of RO 16 onto STAC obeyed pseudo second order kinetics. The negative values of ΔG^0 and ΔH^0 positive obtained indicated that the RO 16 dye adsorption process is a spontaneous and an endothermic.

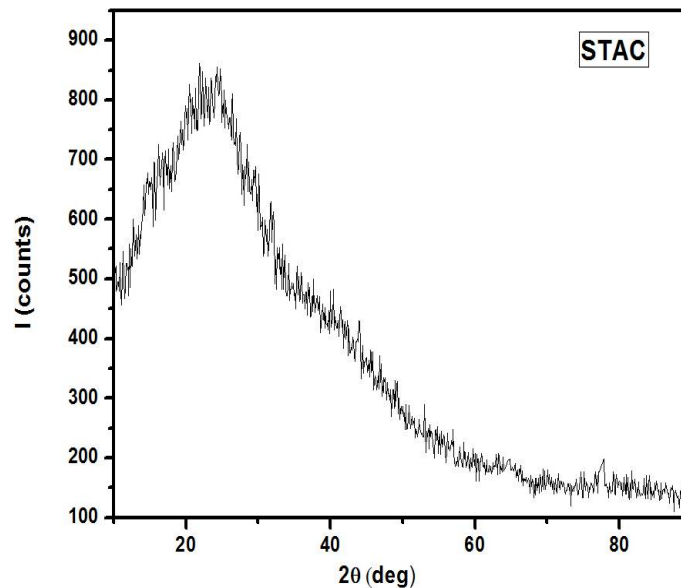


Fig. 1. Powder XRD pattern of STAC

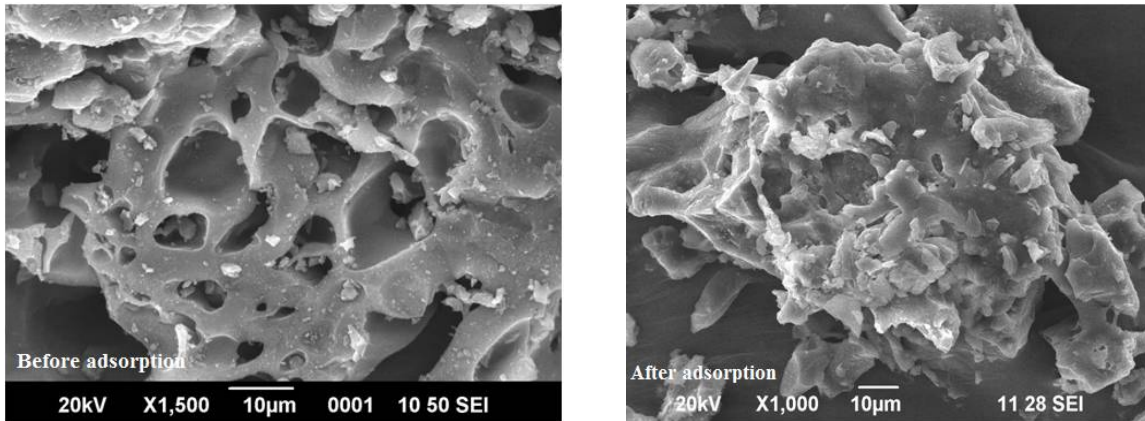


Fig. 2. SEM analysis of STAC

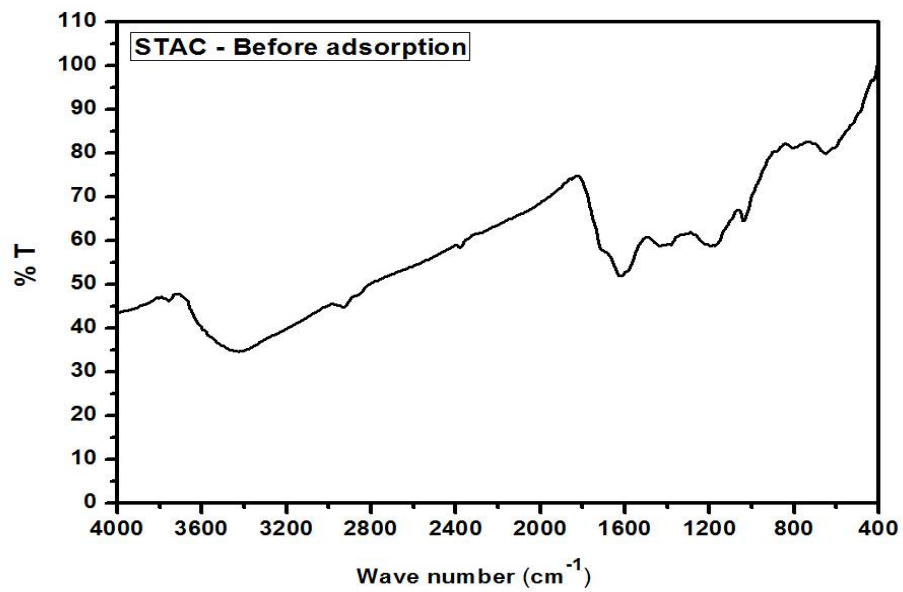


Fig. 3. FTIR spectrum of STAC – Before adsorption

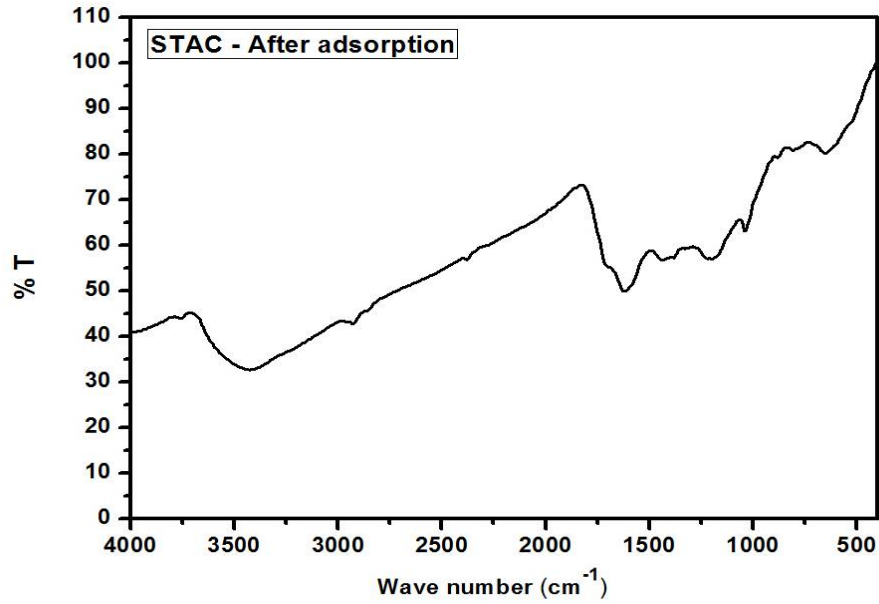


Fig. 4. FTIR spectrum of STAC – After adsorption

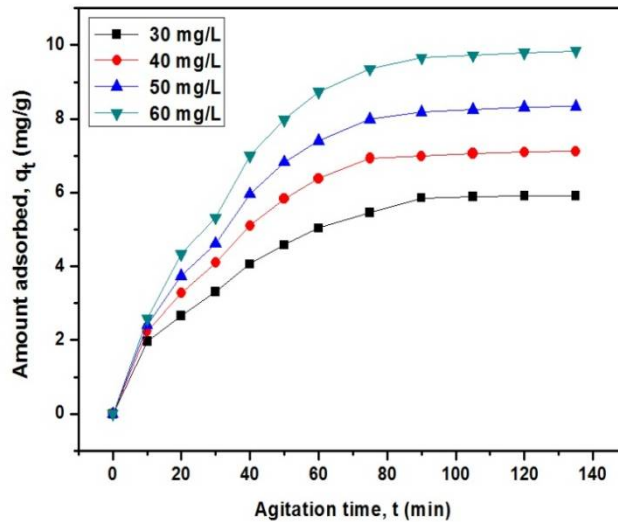


Fig. 5. Effect of initial dye concentration

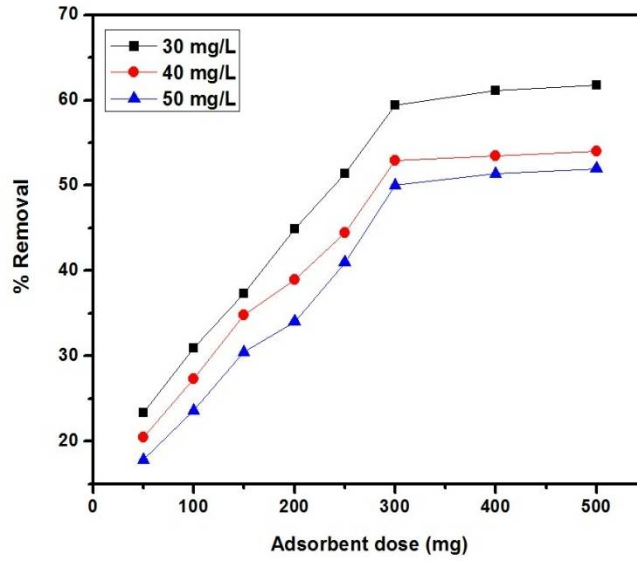


Fig. 6. Effect of adsorbent dose

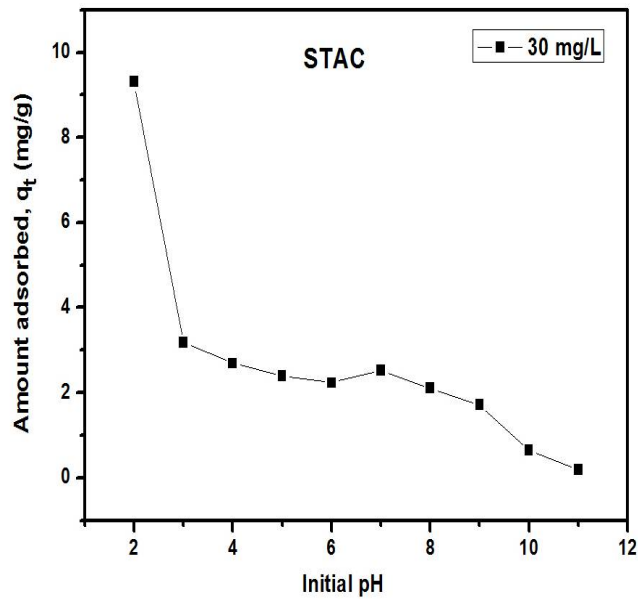


Fig. 7. Effect of pH

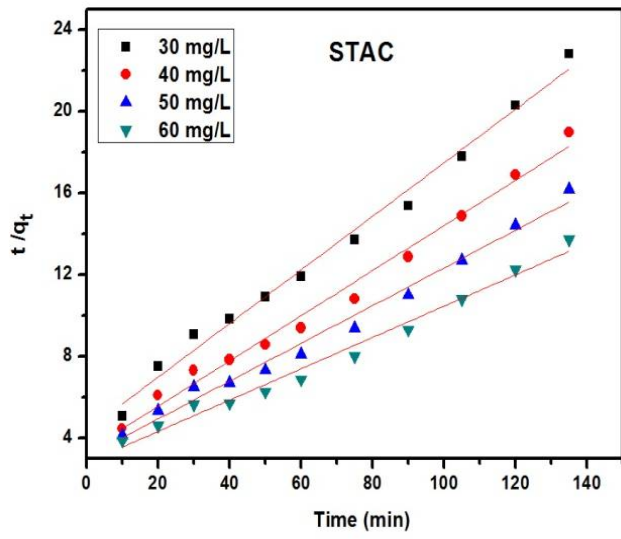


Fig. 8. pseudo-second order kinetics

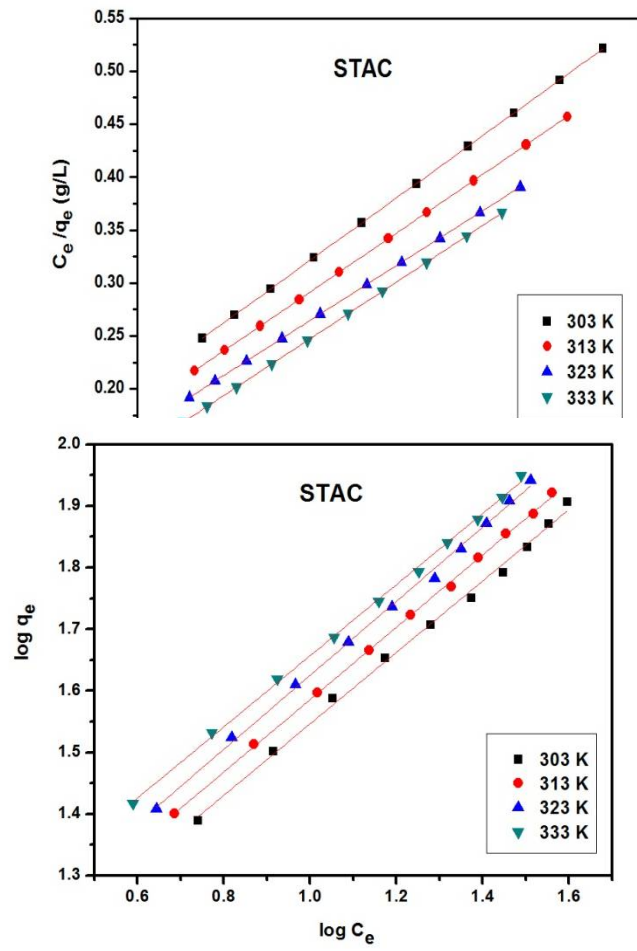


Fig. 9. Langmuir

adsorption isotherm

Fig. 10. Freundlich adsorption isotherm

Table 1 Consolidated table for kinetics of adsorption of Reactive orange 16

Concentration (mg/L)	30	40	50	60
Pseudo-first order kinetic model				
k_1 (min^{-1})	0.0545	0.0519	0.0506	0.0459
q_e exp (mg/g)	5.92	7.11	8.31	9.84
q_e cal (mg/g)	11.44	11.28	13.45	14.13
R^2	0.9283	0.9370	0.9278	0.9490
SSE	5.52	4.17	5.12	4.29
Pseudo-second order kinetic model				
$k_2 \times 10^{-3}$ (g/mg.min)	3.950	3.659	2.776	2.109
q_e exp (mg/g)	5.92	7.11	8.31	9.84
q_e cal (mg/g)	7.62	9.03	10.81	13.03
R^2	0.9892	0.9867	0.9847	0.9815
SSE	1.70	1.92	2.48	3.19

Table 2 Consolidated table for adsorption isotherms

Carbon	Langmuir isotherm				Freundlich isotherm				
	Temp. (K)	303	313	323	333	Temp. (K)	303	313	323
Q ₀ (mg/g)	124.07	131.41	136.43	140.85	K _f (mg/g)	9.26	9.95	10.57	12.01
b (L/mg)	0.0396	0.0423	0.0523	0.0442	n	1.7240	1.7011	1.6630	1.7312
R ²	0.9965	0.9992	0.9978	0.9987	R ²	0.9569	0.9659	0.9520	0.9612

Table 3 Thermodynamic parameters of the adsorption of RO 16

Temp. (K)	ΔH^0 (kJ/mol)	ΔS^0 (J/Kmol)	ΔG^0 (kJ/mol)
303			-0.78
313	4.37	17.02	-0.95
323			-1.12
333			-1.30

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