Isotherms Studies - Adsorption of Reactive Red dye from Aqueous Solution onto Activated Carbon Prepared from Cotton stalk

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ABSTRACT

Dyes are one of the most hazardous chemical compound classes found in industrial effluents and need to be treated since their presence in water bodies reduces light penetration, precluding the photosynthesis of aqueous flora. In the present study a new activated carbon was prepared from Cotton stalk using phosphoric acid in a Tubular furnace and designated as **C**otton **S**talk **T**ubular furnace **C**arbon (CSTC) was used as an adsorbent for the successful removal of Reactive Red dye from aqueous solutions. The effect of various operating parameters such as initial concentration of dye, contact time, adsorbent dosage and initial pH was investigated in order to find the optimum adsorption conditions. Different isotherms were used to identify the possible mechanism of the adsorption process. The optimum pH for removing of RR dye from aqueous solutions was found to be 2 and predicted maximum adsorption capacity for RR dye was obtained as 71.43 mg/g for the chosen experimental conditions. The equilibrium data were fitted to the Langmuir, Freundlich, Temkin and Dubinin-Raduskevich isotherm equations. Significance of the isotherm constant values was discussed. Finally it was concluded that **C**otton **S**talk **T**ubular furnace **C**arbon (CSTC) can be used for Reactive Red dye removal from aqueous solutions.

KEY WORDS: Adsorption; Phosphoric acid activated Cotton stalks Carbon; Isotherms; Reactive Red dye.

1.0 INTRODUCTION

Environmental pollution has recently become a severe problem worldwide [1]. Dyes are one of the most hazardous chemical compound classes found in industrial effluents and need to be treated since their presence in water bodies reduces light penetration, precluding the photosynthesis of aqueous flora [2]. They are also aesthetically objectionable for drinking and other purposes [4] and can cause allergy, dermatitis, skin irritation and also provoke cancer and mutation in humans. Reactive dyes represent an important portion of the commercial synthetic dyes, mainly because of their excellent binding ability by the formation of a covalent bond between their reactive groups and the surface groups of the cellulose fiber. They are used extensively in textile industries, and their release in the ecosystem represents increasing environmental danger, because of their toxicity, mutagenicity, and non-biodegradability. Also, reactive dyes are, in general, the most problematic among other dyes, as they tend to pass through conventional treatment systems unaffected [5]. Additionally, reactive dyes are resistant to natural biodegradation, due to the aromatic rings in their structure [6]. Among dyes used in textile industry, Reactive Red dye (RR dye) is one of the frequently used dyes in textile industries and is a potential threat to the aquatic environment due to its poor biodegradability [7]. Improper treatment and disposal of dye-contaminated wastewaters from textile, dyeing, printing, ink, and related industries have provoked serious environmental concerns all over the world. Removal of dye in wastewater has been made by physical, physicochemical, biological and chemical processes [8-9]. In the present study, **C**otton **S**talk **T**ubular furnace **C**arbon (CSTC) was chosen as adsorbent for removal of Reactive Red dye. The aim of this study is to investigate the adsorption of Reactive Red dye on CSTC under various conditions. So, the influence of several operating parameters such as initial concentration, contact time, adsorbent dosage, and initial pH of solution was investigated. Equilibrium isotherms were used to identify the possible mechanism of the adsorption process. This information will be useful for designing and operating color removal systems based on different local water qualities [10].

2.0 Materials and Methods

2.1 PREPARATION OF ACTIVATD CARBON

Waste cotton stalk were collected, washed, dried and cut into small pieces. Then the materials (25 g) were mixed with 75 mL of phosphoric acid of 50% concentration and the slurry is subjected to heat treatment at 800 ºC in a tubular furnace at a heating rate of 1ºC min^{-1} for 2 h in an N_2 atmosphere. After that, the samples were washed thoroughly with hydrochloric acid of 5 wt. % followed with deionized water. Water wash is continued till the washing reaches the pH values 7.0. Washed product is dried at 105 ºC and designated as **C**otton **S**talk **T**ubular furnace **C**arbon (CSTC).

2.2 PREPARATION OF SYNTHETIC DYE

An accurate weight of 1g (±0.0005) Reactive Red dye was dissolved in 1 L of distilled water to produce the stock solutions of synthetic dye. These stock solutions were then diluted into the required concentrations using distilled water whenever necessary.

3.0 ADSORPTION EXPERIMENTS:

3.1 Effect of pH

Fig. 1 shows the effect of pH for the removal of Reactive Red dye onto CSTC. The percentage of removal was found to decrease as the pH of the solution is increased. It is observed that the adsorption removal was maximum at pH 2.0. When pH of the solution increases, the surface becomes negatively charged and the adsorption of dye decreases, because negatively charged surface sites on the adsorbent did not favor approach of Reactive Red dye due to the electrostatic repulsion [15].

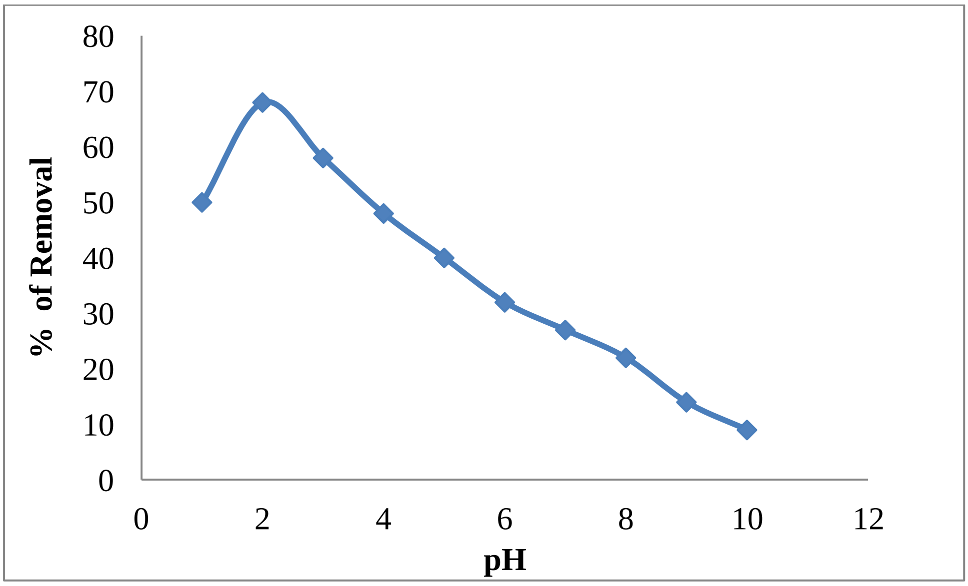

Fig. 1 Effect of pH for RR dye

[RR dye pH = 2, Time = 60 min Ci = 20 mg/L Dose: 30 mg/50ml]

3.2 Effect of adsorbent dosage

Adsorbent dosage is one of the important parameters in an adsorption process. Because amount of adsorbate adsorbed vary with the dosage of an adsorbent for a given initial concentration of the adsorbate under a given set of operating conditions. Figure 2 shows the effect of adsorbent dosage on adsorption of Reactive Red dye of initial concentration 20 mg/L. The percentage of RR dye removal increased from 49.00 to 99.00%. The increase in the removal efficiency may be attributed to availability of more adsorbent surface for the Reactive Red dye to be adsorbed with an increase in the adsorbent dosage. Based on these results, the remaining parts of the experiments were carried out with the adsorbent dose of 30 mg for 50 mL of adsorbate solution for Reactive Red dye [11].

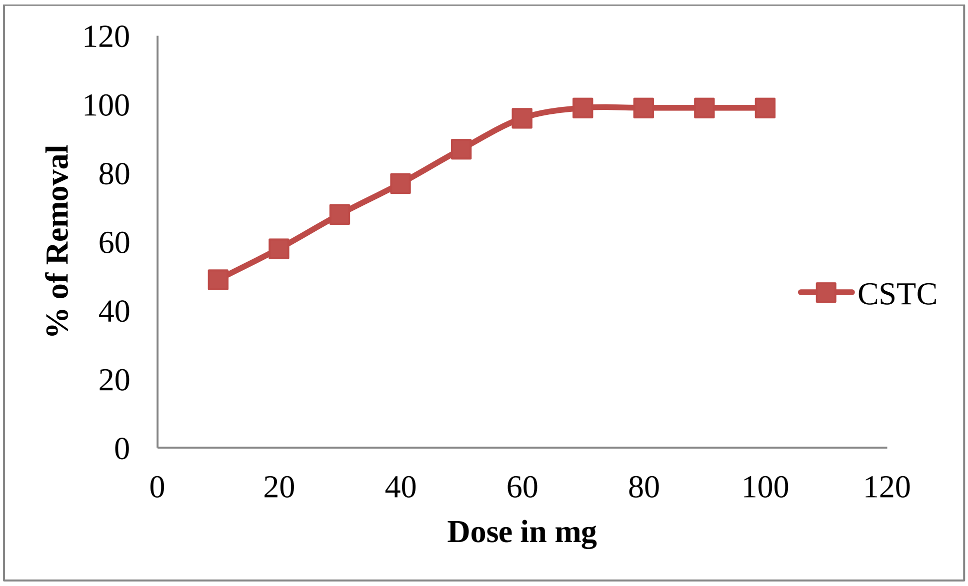

Fig. 2 Effect of Dose – RR dye
[RR dye pH = 2, Time = 60 min Ci = 20 mg/L]

3.3 Effect of contact time

The contact time was evaluated as one of the most important factors affecting adsorption efficiency. The effect of contact time on the percentage removal from aqueous solution was studied by taking 20, 30, 40 and 50 mg/L of RR dye as initial concentrations. The result of the above study was shown in Fig. 3. The rate of percentage removal was found to be rapid at initial stages and found to decrease as the contact time increases then become constant showing the attainment of equilibrium. The time to attain equilibrium found to be 80 minutes for RR dye for the chosen initial concentrations. At the initial stage, the ratio of surface area of the adsorbent to the amount of solute in liquid phase is high and hence the driving force makes solute to rush towards the adsorbent surface. As the time increases the above ratio begins to decrease due to adsorption and hence the rate of adsorption becomes slow [12].

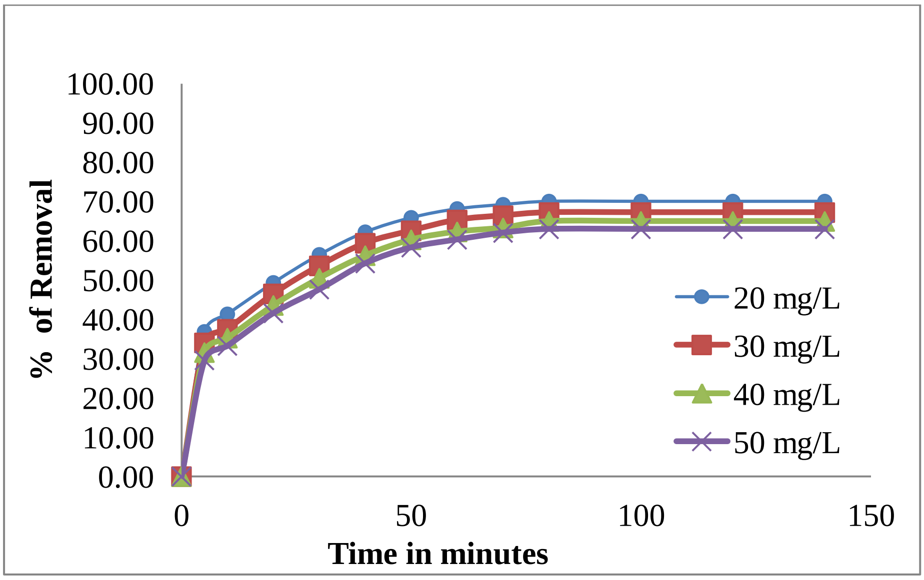

Fig. 3 Effect of contact time for RR dye onto CSTC
[RR dye pH = 2, Dose = 30 mg/50 mL]

3.4 Effect of initial concentrations

The effect of initial concentration study showed that the percentage of the removal of adsorbate decreased with the increase of initial concentration of adsorbate solution. The percentage removal of RR dye was found to decrease from 70.01 to 62.92, at the temperature 303 K as the initial concentration of RR dye increased from 20 mg/L to 50 mg/L (Table 1). The amount of solute in the liquid phase is high at a higher initial concentration. The ratio of available adsorbent surface to the concentration of solute decreases with the increase of initial concentration. This is the reason for the decrease of percentage of removal when the concentration of the solution is increased. But the amount of Reactive Red dye adsorbed was found to increase with the increase of initial concentration of the solution (Table 1). This is because increase of fraction of solute concentration with the increase of initial concentration [13].

Table. 1 Effect of initial concentration on percentage of removal

[RR dye pH = 2, Dose = 30 mg/50 mL]

Adsorbate	Initial Concentration C_i (mg/L)	Percentage of Removal	q_e
RR dye	20	70.01	14.00
	30	67.17	20.15
	40	64.92	25.97
	50	62.92	31.46

3.5 Effect of temperature

It is well known that temperature plays an important role in the adsorption process. The influence of temperature on adsorption of RR dye were investigated at 305, 315, 325 and 335 K. Plots drawn between amount adsorbed versus temperature were given in Fig. 4. It could be clearly seen that, the amount adsorbed increased with an increase of temperature. This is because; higher temperature eased the sorption by swelling of the adsorbent structure which enhanced the penetration of the big Reactive Red dye [14].

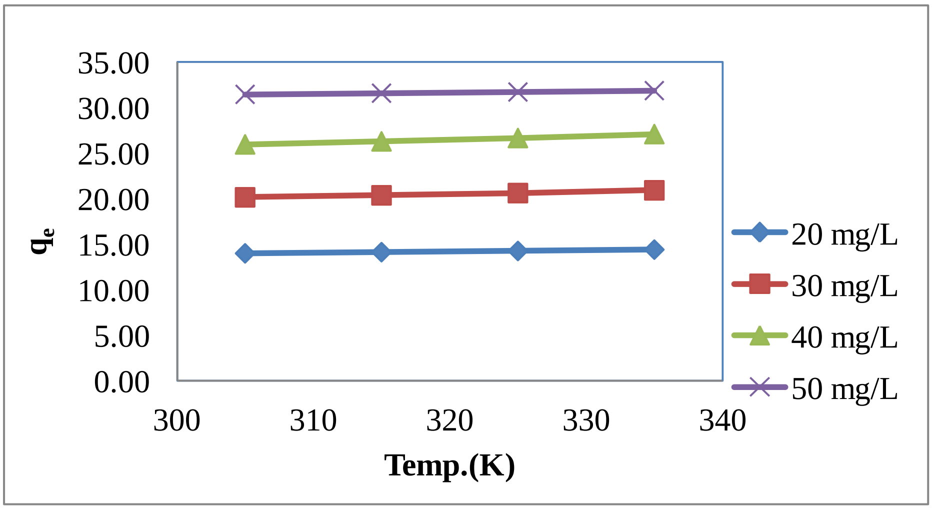

Fig. 4 Effect of Temperature for RR dye onto CSTC
[RR dye pH = 2, Dose = 30 mg/50 mL]

Table. 2 Data processing Tools

S.No.	Parameters		Formulae
1.	Isotherms	Langmuir Separation factor	$C_e/Q_e = 1/Q_0b + C_e/Q_0$ $R_L = 1 / (1+ b\, C_0)$
		Freundlich	$\log Q_e = \log K_f + 1/n \log C_e$
		Tempkin	$q_e = B_T \ln K_T + B_T \ln C_e$
		Dubinin – Raduskevich, Polanyi potential Mean free energy of adsorption	$\ln q_e = \ln q_D - B\varepsilon^2$ $\varepsilon = RT \ln (1+1/C_e)$ $E = 1/ (2B)^{½}$

4.0 ADSORPTION ISOTHERM STUDIES:

The existence of equilibrium between the liquid and solid phase is well described by adsorption isotherms. Equilibrium data collected at different temperatures were fitted in Langmuir, Freundlich, Tempkin and Dubinin-Raduskevich adsorption isotherm models [16-18]. These isotherms are depicted in Fig. 5 and the isotherm equations are given in Table: 2. The R^2 values of these isotherm plots reveal that Freundlich isotherm well describes the present system that is the possibility of multilayer adsorption. In Dubinin-Raduskevich isotherm, the very low value of the constant 'a_T' related to the mean free energy of adsorption per mole of the adsorbate, describes that the adsorption is physical in nature. Results of various isotherms are presented in Table: 3.

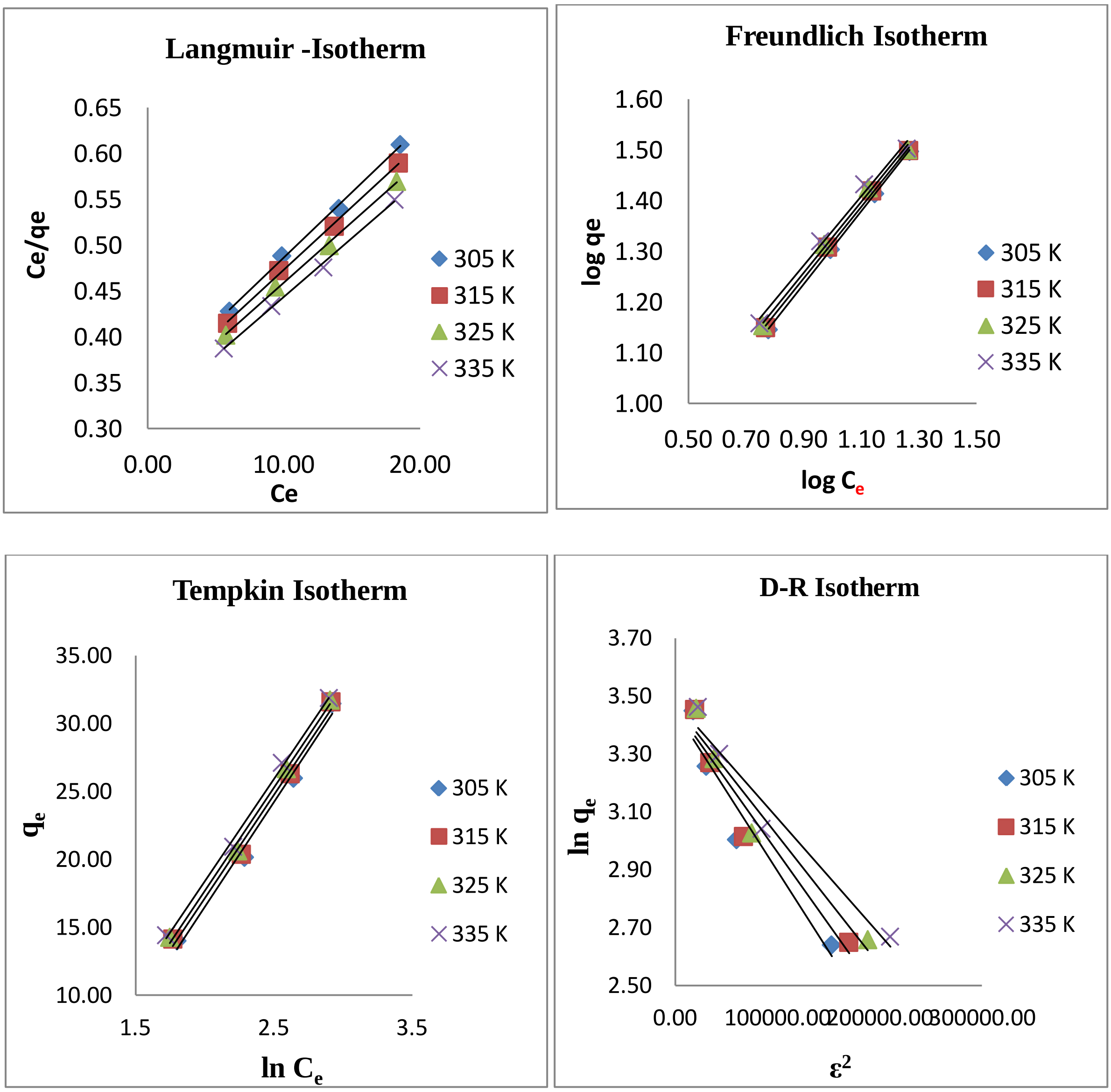

Fig. 5 Langmuir, Freundlich, Temkin & Dubinin-Raduskevich isotherm

[RR dye pH = 2, Dose = 30 mg/50 mL]

Table: 3 Results of various isotherms plots for the adsorption of RR dye onto CSTC

Isotherms	Temp (K)	Parameters and their results			
		Q_m (mg/g)	**b**	**R_L**	**R^2**
Langmuir Isotherm	305	71.429	0.041	0.549	0.9980
	315	76.923	0.039	0.562	0.9980
	325	78.943	0.040	0.556	0.9980
	335	83.333	0.038	0.568	0.9970
Freundlich Isotherm		**n**	**k_f (mg/g^{-1})**		**R^2**
	305	1.3928	3.8726		0.9990
	315	1.4124	4.0644		0.9980
	325	1.4347	4.2658		0.9960
	335	1.4620	4.5290		0.9900
Tempkin Isotherm		**B_T (J/mg)**	**a_T (L/g)**		**R^2**
	305	164.0213	2.1763		0.9890
	315	171.7318	2.2986		0.9920
	325	178.2355	2.4042		0.9950
	335	185.3087	2.5393		0.9970
D-R Isotherm		**q_D (mg/g)**	**E (kJ/mol)**		**R^2**
	305	31.4179	0.5385		0.9340
	315	31.7019	0.5378		0.9390
	325	32.0205	0.5371		0.9460
	335	32.4070	0.5361		0.9550

5.0 ANALYSIS OF ISOTHERM:

5.1 Langmuir isotherm:

R^2 values of isotherm ranged between “0.9970 to 0.9980”. The monolayer adsorption capacity (Q_m values) ranges from 71.43 to 83.33 as the temperature increases. This kind of results were obtained in various similar studies [12]. The separation factor R_L values are in between 0 to 1 which indicates the favourable adsorption.

5.2 Frendlich isotherm:

The values of n are in between 1 and 10 which indicates cooperative adsorption [13]**.** The R^2 values were close to unity which revealed the good fitting into frendlich isotherm.

5.3 Temkin Isotherm:

The value of Temkin constant B_T related to the heat of adsorption increased from 164.0213 to 185.3087 as the temperature of adsorption increased. The temkin parameter a_T value give on idea about nature of adsorption. In our present study the a_T values ranged from 2.1763 to 2.5393 J/mg which indicate the adsorption is physical nature.

5.4 Dubinin-Raduskevich isotherm:

The Mean free energy E value (0.5385 to 0.5361 kJ/mol) and adsorption capacity q_D value ranges (31.4179 to 32.4070 mg/g) indicates that the adsorption is physisorption. In general the fitting data in isotherm equation were in the following order

Frendlich > Langmuir > Temkin > Dubinin-Raduskevich.

6.0 CONCLUSION

Activated carbon prepared from Cotton Stalk (CSTC) found to have good capacity of adsorption of Reactive Red dye. Equilibrium adsorption was achieved in about 80 minutes for the dosage of 30 mg/50 mL of solution at room temperature (303K) for the initial concentration of dye solutions ranging from 20 to 50 mg/L. Freundlich and Langmuir isotherm represents the equilibrium adsorption data well than other Temkin isotherms studied. The fitness of Freundlich model indicated the formation of multilayer coverage of the sorbate on the surface of the adsorbent. The values of n were between 1 and 10 which indicates cooperative adsorption. The a_T values obtained from Temkin isotherm is ranged from 2.1763 to 2.5393 which indicate the adsorption physisorption in nature.

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