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Removal of Reactive Red Dye from Aqueous Solution Onto Activated Carbon Prepared from Stalks of *Gossypium hirsutum L.*

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ABSTRACT

Dyes are the important water pollutants. Sulphuric acid activated carbon prepared from the stalks of *Gossypium hirsutum* L. (Prepared carbon was designated as GHSC- *Gossypium hirsutum* L Stalk Carbon) was used as an adsorbent. In this present study the removal of Reactive Red Dye (RR) from its aqueous solutions by adsorption onto GHSC using batch technique. The effects of various experimental parameters on adsorption such as contact time, temperature, initial pH, initial dye concentration and sorbent dosage were examined and the optimal experimental conditions were evaluated. The percentage of removal was maximum at pH2. Experimental data obtained were fitted with linearized forms of Ho and Legergren kinetics models. Hence this is adsorption followed the second order kinetics. The adsorption data were fitted to Freundlich and Langmuir adsorption isotherms. The equilibrium data was best described by Langmuir model. The adsorption results indicated that the dye, Reactive Red can be effectively removed from its aqueous solutions by using GHSC - *Gossypium hirsutum* L Stalk Carbon.

Key words: *Adsorption, Gossypium hirsutum L, Stalk Carbon, Reactive Red Dye, Kinetics models, Isotherms.*

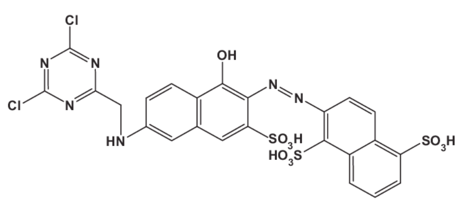
Introduction

Water pollution has been mainly caused by human quest for industrialization which results in bye product that is often discharged into the environment (Jebin Ahmed *et al*., 2021). Dye contaminated waste water originates from various industries such as Lather, textile, printing, food and paper industry and can serious environmental impact in the neighbouring water bodies because of the presence of toxic dyes (Sohini Dutta *et al*., 2024). Dyes and Pigments, if not properly treated can also have detrimental effects on human health. Therefore these coloured contaminants must be removed from waste water from industries. Due to intense colour they reduce sunlight transmission into water. Hence affecting aquatic plants which ultimately disturb aquatic ecosystem in addition they are toxic to humans also (Mohammad Danish Khan *et al*., 2023).

Many treatment methods have been adopted to remove dyes from waste water. These methods can be divided into physical, chemical oxidation, reverse osmosis, membrane separation, coagulation, biological treatments, photo degradation and adsorption have been used but the most efficient methods has been through adsorption process (Valli Nachiyar *et* *al*., 2023). Adsorption technique is an important method in case of heterogeneous system. To fully understand the processes two basic ingredientsand required namely equilibrium and kinetics (Salwa M. Al-Rashed *et al*., 2012).

Recently the growth of adsorption kinetics used for many investigations. The focus of the present study was to investigate the effect of the sorbent amount, contact time dye concentration and temperature on the adsorption (Mohammed Benjelloun *et al*., 2021). Reactive Red is one of the water soluble exanthems class dye a basic red cationic dye, which is common water traces fluorescent. Reactive Redis used mostly in paper printing textile dyeing and leather industries. It is carcinogenic and may cause irritation redness and pain in eye and skin. When involved it causes irritation in respiratory tract Reactive Red is likely to causes irritation to the gastro intestinal tract. Therefore it is imperative that proper treatment of the dye effluent for colour removal is carried out before its discharge (AliasgharNavaeia *et al*., 2019 and Dabrowski, 2001).

Structure of Reactive Red Dye



Materials and Methods

In recent years, *Gossypium hirsutum* L Stalk Carbon has been accepted as one of the most appropriate low cost adsorbent. Investigations have been carried-out to evaluate the adsorption of dyes onto a wide range of GHSC.In this process, 25 g of dried stalks from the *Gossypium hirsutum* L. flower were placed in a mortar and pestle, where they were ground with sulphuric acid. The resulting paste underwent heating at 180 °C for 7 hours. Following the cooling to room temperature, the mixture was further ground to achieve a powdered form. To eliminate the acid content, the powders underwent multiple rinses with de-ionized water and were subsequently filtered. The filtered products were then subjected to heating in a hot air oven at 100 °C for one hour and subsequently heated at 10 °C to 750 °C for 1 hour under N_2 atmosphere to attain activated carbon.

Materials characterization

The crystalline properties of the activated carbon were examined by Powder X-ray diffraction (XRD) analysis using a PAN Analytical X'Pert PRO model X-ray diffractometer equipped with Cu Kα radiation (α = 1.5418 Å), covering the range of 10°-80°. The assessment of functional groups in activated carbon was carried out using a PerkinElmer FTIR spectrometer, employing the pellet method with KBr as an internal standard. The analysis spanned the range of 400-4000 cm^{-1}. Morphological analysis, Energy-Dispersive X-ray Spectroscopy (EDAX), and mapping assessments were performed utilizing the Zeiss ULTRA PLUS scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) with the Techni G2S-TWIN instrument by FEI. The Brunauer-Emmett-Teller (BET) absorption characterizations were carried out using the Micromeritics ASAP 2020 instrument.

Fig. 1(a). *Gossypium hirsutum* L.

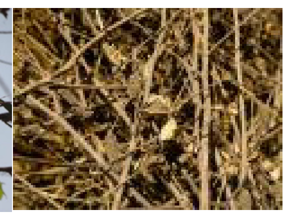


Fig. 1 (b). Stalks of *Gossypium hirsutum* L.

Adsorbate

Reactive Red is a cationic dye and it was purchase from S-D fine chemical Pvt.Ltd. It is molecular formula $C_{19}H_9Cl_2N_6Na_3O_{10}S_3$. The stock solution was prepared in double distilled water by dissolving 1g of dye in it. All the test solution was prepared by diluting the stock with double-distilled water.

Preparation of Dye Solution

The dye solutions of appropriate concentration were prepared by diluting the stock solution (1000 mg/l) with distilled water. The pH adjustment was carried out using 0.1N HCl and NaOH solution using a pH meter.

Results and Discussion

Effect of contact time

The effect of contact time on percentage removal of Reactive Red Dye for different initial concentrations has been shown in figure 1.0. The adsorption experiment was carried out with 50 mg/l Reactive Red Dye solution. The result are expressed with percentage removal of Reactive Redversus different contact time in the range 10-160 minutes and are depicted percentage removal of Reactive Redincrease when increasing contact time and occurs that the adsorption equibilirum of Reactive Redwas rapidly attained after 80 minutes of contact time. The curve is single smooth and continuous leading to situation (Noll *et al*., 1992).

Effect of adsorbent dosage

The absorption of the Reactive Red Dye on GHSC has been studied by varying the adsorbent dose (10-50 mg/50 ml) for 50 mg/l of dye concentration. The percentage of adsorption increased with the increase in the carbon dose. This was attributed to increased carbon surface area and the availability of more absorption sites. The plot wasdrawn percentage of dye removal versus dose from the range of (10-30 mg). To evaluate the effect of adsorbent dose on the adsorption of Reactive Redis 50 mg/l as initial concentration.

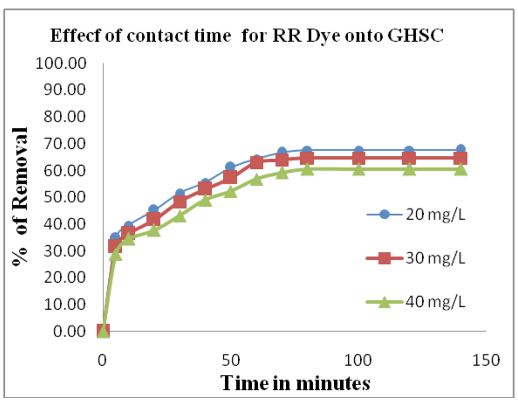


Fig. 1.

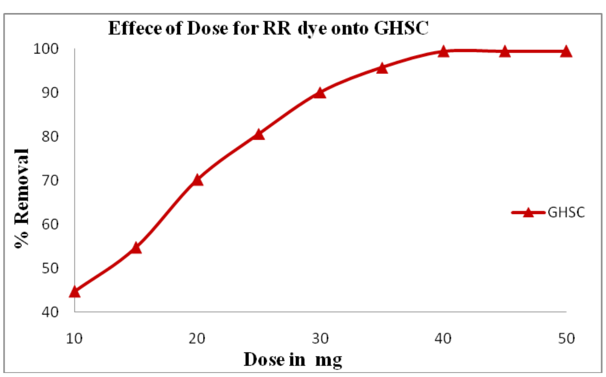


Fig. 1.1

Effect of initial concentration of dye

The effect of initial concentration an adsorption intake Reactive Redsolution with initial concentration 50 -150 mg/l was shaken with commercial activated carbon. In this case the solution pH was 9.0 and temperature was 30 ^{0}C the experimental results of sorption of Reactive Redon GHSC at various initial concentration was rapid increase at the initial stages and then gradually decrease with the progress of adsorption will be the equilibrium was reached.

Effect of temperature

The effect of temperature on the absorption of Reactive Red Dye adsorption by GHSC the experiments were performed at temperature of 303,313 and 323 K. As it was observed that the equilibrium absorption capacity of Reactive Redon to GHSC was found to increase with increasing temperature especially in higher equilibrium concentration or lower adsorption. This fact indicates that the mobility of Reactive Red Dye molecules increased with temperature.

Effect of pH

Respective Figure 2 shows that the effect of pH on the adsorption of RR dye onto GHSC. The pH is one of the most important parameters controlling the adsorption process. The effect of pH of the solution on the adsorption of RRdye on GHSC was determined. To examine the effect of pH on the percentage removal of RR dye. The solution pH was varied from 2 to 12 by adding acid and base to the stock solution. These increases may be due to the presence of negative charge on the surface of the adsorbent that may be responds for the dye binding. However as the pH is lowered the hydrogen ions compete with dye for the adsorption sites in the adsorbent. The maximum of adsorption of RR dye on adsorbent

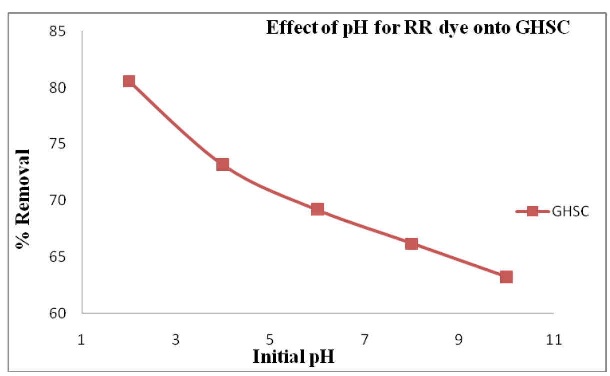


Fig. 2

reached at pH is 9.0 (Jia and Thomas 2002).

Absorption isotherms

Absorption isotherms describes how pollutants interact with absorbent materials with relate to absorption properties and equilibrium data. The experimental data indicated that the absorption isotherms are well described by the Langmuir and Freundlich isotherms.

Langmuir Isotherms

Langmuir sorption isotherm (Langmuir, 1918) is well known of all isotherms describing sorption and it has been applied in many sorption processes. Respective Figure 3 shows the Langmuir isotherm for adsorption RR dye onto GHSC. It is represented as.

$$C_e/Q_e = 1/Q_m b + C_{eq}/Q_m$$

Where C_e is the equilibrium concentration of adsorbate in the solution (mg/L) Q_e is the amount adsorbed at equilibrium (mg/g).Q_m and b are langmuir constants related to absorption efficiency and energy of adsorption respectively. The linear plots of C_e/Q_e Vs C_e suggest the applicability of the langmuir isotherms. The values of Q_m and b are calculated from slope and intercepts of the plots which are listed in Table 1. From the results it is clear that the value of absorption efficiency Q_m and adsorption energy b of the carbon increases on increasing the temperature. The values can conclude that the maximum adsorption correspond the saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no diffusion of adsorbate in plane of the adsorbent surface. The confirm that favourability of the adsorption processes. The separation factor (R_L) was determined and given in table 1.0. The values were established to be between 0 and 1 and confirm that the ongoing adsorption process was favourable (Ramesh *et al.*, 2017).

Freundlich Isotherm

The Freundlich equation (Ramesh *et al.*, 2017) was employed for the absorption of Reactive Red Dye on the adsorbent. Respective Figure 4 shows the Freundlich isotherm for adsorption RR dye onto GHSC. The logarithmic form of Freundlich equation is represented as given in the following equation.

$$\text{Log } Q_e = \log K_f + 1/n \log C_e$$

Where Q_e is the amount of Reactive Red Dye adsorbed (mg/g), C_e is the equilibrium concentration of dye in solution (mg/l) and K_f and m are constants which integrate the factors affecting the absorption capacity and intensity of adsorption respectively. A linear plot of log Q_e versus C_e shows that adsorption of Reactive Red obeys the Freundlich adsorption isotherm. The K_f and n value and are given in Table 1. Indicate that the increase of negative charges on the adsorbent surface makes electro static force like Vander wall's forces between the carbon surface and dye. The molecular weight and size either limit or increase the possibility of the adsorption of the dye onto adsorbent. However the values clearly show the dominance in adsorption capacity.

The intensity of adsorption is an indication of the binding energies between dyes and adsorbent and the possibility of slight chemisorption rather than

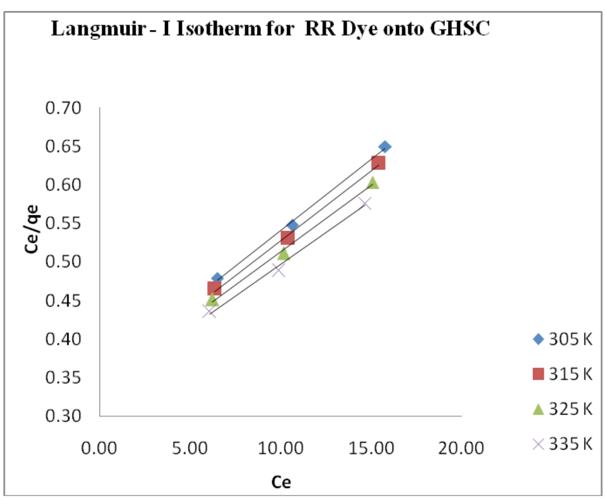


Fig. 3

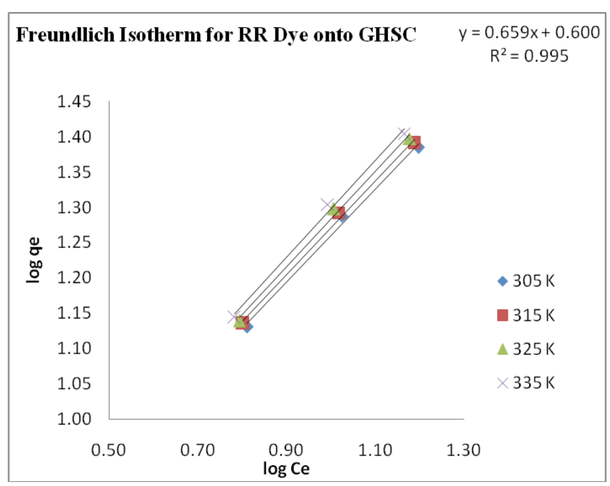


Fig. 4

physisorption. However the multilayer adsorption of Reactive Red Dye through the percolation process may be possible. The values of n are less than one indicating the physisorption is much more favourable (Namasivayamc and Yamuna, 1995).

Adsorption dynamics

The absorption kinetics is a useful parameter in the adsorption process. The rate constants for adsorption of RRdye onto GHSC were evaluated using pseudo-first order and pseudo second order kinetic models.

Table 1. Results of isotherms plots for the adsorption of RR dye onto GHSC

Isotherm Models	Temp (K)	Parameters and their results		
		Q_m (mg/g)	**b**	**R^2**
	303	54.054	0.052	0.9976
Langmuir	313	55.556	0.052	0.9976
	323	57.803	0.051	0.9967
		60.606	0.050	0.9947
Freundlich		**n**	**K_f (mg/g^{-1})**	**R^2**
	303	1.5156	3.9838	0.9953
	313	1.5040	4.0383	0.9954
	323	1.4841	4.0682	0.9952
	333	1.4611	4.1049	0.9945

Temp	Ci	RL
305	20	0.491
	30	0.391
	40	0.325
315	20	0.492
	30	0.392
	40	0.326
325	20	0.496
	30	0.396
	40	0.330
335	20	0.501
	30	0.401
	40	0.334

Pseudo - first order kinetic models

The linear form of Pseudo-first order kinetic model is given by equation (Lagergren, 1898)

$$\log(q_e - q_t) = \log(q_e) - K_{ad}/2.303 \times t$$

Where q_e and q_t are the amount of RRsorbed (mg/g) at equilibrium and at any time (t) respectively and K_1 (L/min) is the pseudo first order rate constant. The adsorption rate constant K_1 and q_e has been computed from the straight plot of log (q_e-q_t)vs t are listed in the Table 2 and shown in Figure 5.

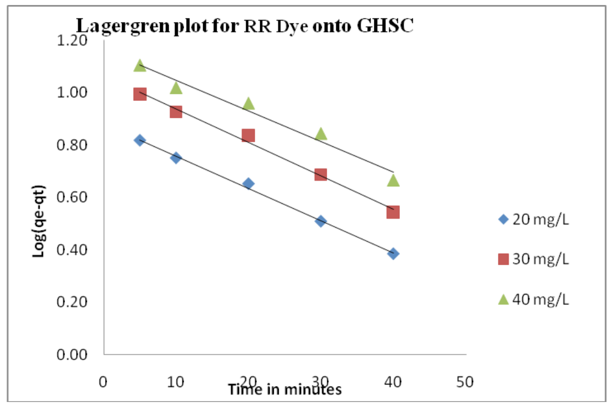


Fig. 5

Pseudo-second order kinetic models

The pseudo-second order kinetic model is given by equation (Ho and Mckay, 1998).

$$t/q_t = 1/K_2qe^2 + (1/qe)t$$

Where K_2 (g/mg/min) is the pseudo-second order rate constant. The plot of t/qtvst is shown the values of Qe and K_2 coefficient are reported in table 2.0 and shown in Figure 1.6. The regression correlation coefficients (0.999) and a good agreement between the calculated and experimental qe values for pseudo second order model indicated that the adsorption dye onto GHSC is governed by pseudo-second order rate kinetics (Sivasankari *et al*., 2021).

Table 2. Kinetic parameters

	Rate constants		$q_{e(cal)}$ mg/g		$q_{e(exp)}$ mg/g		R^2		(SSE %)	
Ci mg/l	k_1 (10^{-2}) (min^{-1})	k_2 (10^{-3}) (gmg^{-1} min^{-1})	First Order	Second order	First order	Second order	First order	Second order	First order	Second Order
20	0.0290	0.0094	11.6493	14.37	13.52	13.52	0.992	0.992	5.13	0.80
30	0.0279	0.0060	7.5945	20.75	19.38	19.38	0.995	0.9904		
40	0.0265	0.0043	14.5211	26.04	24.25	24.25	0.9689	0.9878		

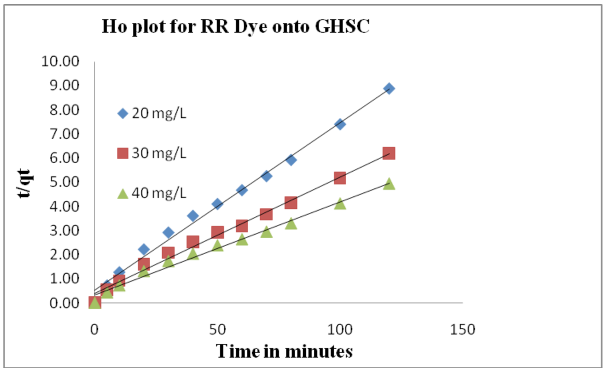


Fig. 6

Conclusion

The adsorption process was shown to be an efficient for removal of dye from aqueous solutions. The equilibirium and kinetics for the uptake of Reactive Red Dye on GHSC. The adsorption data was best fitted in Langmuir absorption model. The kinetics data agreed well with pseudo- second order kinetics. The fitness of Langmuir model indicates the formation of monolayer coverage of the sorbate on the outer surfaceof the adsorbent. The adsorption of Reactive Redontocommercial activated carbon is an efficient to remove the Reactive Redfrom aqueous solution.

Conflict of Interest : None

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