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Adsorption kinetics of crystal violet dye on commercial activated carbon and activated carbon obtained from *Syzygium cumini* seed

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ABSTRACT

Adsorption of crystal violet (CV) in aqueous solution on commercial activated carbon (CAC) and activated carbon obtained from Syzygium cumini seed (SCSC) have been studied comparatively. The effect of various experimental parameters has been investigated using a batch adsorption technique to obtain information on treating effluents from the dye industry. The extent of dye removal increased with decrease in the initial concentration of the dye and increased with increase in contact time, amount of adsorbent used and the initial pH of the dye solution. Adsorption data were modeled using the Freundlich and Langmuir adsorption isotherms and first order kinetic equations. The kinetics of adsorption was found to be first order with regard to intra-particle diffusion as rate determining step. The adsorption capacities of dyes have been compared. The results indicate that Syzygium cumini seed carbon can be used in wastewater treatment for the removal of colors and dyes.

Key Words: Crystal Violet (CV), commercial activated carbon (CAC), *Syzygium cumini* seed carbon (SCSC), adsorption isotherms, Kinetics of adsorption, intraparticle diffusion.

INTRODUCTION

Many industries, such as dyestuffs, textile, paper and plastics, use dyes in order to color their products and also consume substantial volumes of water. As a result, color is the first contaminant to be recognized in waste water [1]. It's not only aesthetically displeasing but also hinder light penetration and may in consequence disturb biological process in water – bodies. More over, dyes itself are toxic to some organisms and hence disturb the ecosystem [2]. In addition, the expand uses of dyes have shown that some of them and their reaction products such as aromatic amines are highly carcinogenic which make the removal of dyes before disposal of the wastewater is necessary [3].

Most of the dyes are stable to photo degradation, bio-degradation and oxidizing agents [4]. Some physical or chemical processes are used to treatment of wastewaters. However, these processes are costly and cannot effectively be used to treat the wide range of dyes wastewater. Biological treatment process is reported to be efficient in the removal of suspended solids and reduction of chemical oxygen demand but is largely ineffective in removing color from wastewater [5]. Hence investigations have been conducted on physicochemical methods of removing color from textile effluent. These studies include the use of coagulants [6], oxidizing agents, ultra filtration, electrochemical [7], surfactant [8], electrodialysis [9] and adsorption techniques [10]. Among several chemical and physical methods, the adsorption onto activated carbon has been found to be superior to other techniques for removal of dyes from aqueous in terms of methodology, its capacity for efficiently adsorbing a broad range of different types of adsorbate and simplicity of design of adsorbent [11]. Commercial activated carbon is usually derived from natural materials such as wood or coal and therefore is still considered expensive [12]. This has led to the search for cheaper substitutes. Hence, low-cost activated carbons based on agricultural solid wastes are investigated for a long time. Agricultural by products and waste materials used for the production of activated carbons include plum kernels [13], cassava peel [14], bagasse [15], jute fiber [16], palm tree cobs [17], olive stones [18,19], date pits [20], nutshells [21] saw dust [22], wheat shells [23] and hen feathers [24]. Recently, several solid materials have been recently used for the adsorption of basic dyes [25-29]. In the present study, activated carbon obtained from *Syzygium cumini* seed carbon (SCSC) is used for the removal of Crystal Violet (CV).

EXPERIMENTAL SECTION

ESICO Microprocessor Photocolorimeter (model no. 1312) was used for all absorbance measurements O.D at 588 nm (λ_{max}). The optical density values are calculated before and after adsorption experiment. A calibrated digital pH meter was used for pH measurements. The commercial activated carbon (CAC) was supplied by E.Merck, India. Raw materials for the preparation of SCSC, were procured locally, washed, cut into small pieces and dried. The raw materials were then carbonized (at 300 °C) acid treated and washed.

The materials were finally sieved to discrete particle sizes (90,120,150,210 and 250 microns). They are then dried at 120 °C for 5 hours in an air oven. Crystal Violet supplied by BDH was used as an adsorbate. All other chemicals used in this study were reagent grade and supplied by BDH (India). Double distilled water was used for preparing all the solutions and reagents.

A stock solution of Crystal violet (1000 mg L^{-1}) was prepared and suitably diluted to the required initial concentrations. Adsorption experiments were carried out of 200 RPM agitation speed (mechanical shaker, Neolab, India) at room temperature (30 ± 1°C) under batch mode [30] as per the experimental conditions detailed in the given Table 1.

The percentage removal of dye and amount adsorbed (mg g^{-1}) were calculated using the following relationships,

Percentage removal = 100 ($C_i - C_e$) / C_i ------------------------- (1)
Amount adsorbed (q_e) = ($C_i - C_e$) / m ------------------------- (2)

Where C_i and C_e are the initial and final equilibrium concentration (in mg L^{-1}) of dye, respectively and m is the mass of adsorbent (in g L^{-1}). The error in the adsorption data are ±1-2% for removal and ±0.0025-0.005 mg for amount adsorbed. The standard curve is drawn optical density against concentration, the straight line is obtained. From this line, we calculated the concentration of dye solution before and after adsorption experiment.

Table 1. Experimental conditions for the series of adsorption experiments for the removal of Crystal Violet

Variation	Initial Concentration (mg/L)	Contact time (min)	Dose of adsorbent (g/L)	Initial pH	Particle size
Initial concentration CAC SCSC	275-400 10-25	30 30	2 2	6.2 6.2	90 90
Contact time CAC SCSC	275 10	5-60 5-60	2 2	6.2 6.2	90 90
Adsorbent dose CAC SCSC	275 10	30 30	1.4-2.6 1.4-2.6	6.2 6.2	90 90
Initial pH CAC SCSC	275 10	30 30	2 2	3.0-11.9 2.8-9.1	90 90
Particle size SCSC	10	30	2	6.2	90-250

RESULTS AND DISCUSSION

In all, five different sets of adsorption experiments were carried out by varying the following experimental parameters with other parameters kept constant (table 1).

(i) initial concentration of Crystal Violet
(ii) contact / agitation time
(iii) dose of adsorbent (CAC/SCSC)
(iv) initial pH of the dye solution
(v) particle size of SCSC

Effect of Initial Concentration

The studies on the removal of Crystal Violet by CAC and SCSC were carried out at different initial concentration of dye from 275 to 400 ppm (CAC) and 10 to 30 ppm for (SCSC) and the other parameters are constant.

The percentage removal decreases with the increase in dye concentration (figure 1). This indicates that there exists a reduction in immediate solute adsorption, owing to the lack of available active sites required for the high initial concentration of dye (CV). The relative increase in the percentage removal of Crystal Violet below the dye concentration of 275 ppm for CAC and 10 ppm for SCSC and hence, they are fixed as the optimum initial concentrations for further adsorption experiments. Similar results have been reported in literature on the extent of removal of dyes [31-33] and metal ions [34].

Adsorption isotherm:

The study of adsorption isotherm has been of important and significant in the waste water treatment by adsorption technique as they provide an approximate estimation of the adsorption capacity of the adsorbent (Table 1). The equilibrium data for the removal of dye on CAC at 30 $\pm$ 1°C were used in the Langmuir and Freundlich isotherms.

Freundlich isotherm $\log q_e = \log K_f + (1/n) \log c_e$ ------------------------- (3)
Langmuir isotherm $C_e/q_e = (1/Q_ob) + (C_e / Q_o)$ ------------------------- (4)

The data obtained from the adsorption experiments were fitted into Langmuir and Freundlich isotherms respectively by plotting c_e/q_e and log (x/m) against C_e and log C_e. They are found to be linear, indicating the formation of mono layer of adsorbate on the outer surface of adsorbent and after that no further adsorption takes place (figure 2 and 3). The monolayer adsorption capacities of the adsorbents (based on Q_0 values) are found to be the order of SCSC < CAC. Further, the essential characteristics of the Langmuir isotherms can be described by a separation factor (R_L). The values of separation factor (R_L) indicates the shape of the isotherm and nature of the adsorption process as given here,

RL values Nature of the adsorption process
$R_L > 1$ is Unfavorable,
$R_L = 1$ is Linear
$0 < R_L > 1$ is Favorable and
$R_L = 0$ Irreversible.

Table 2. Results and correlation analysis for the adsorption isotherm for the removal of Crystal Violet dye by CAC and SCSC

Parameters	Adsorbents	
	CAC	SCSC
Freundlich isotherm		
Slope (1/n)	0.2087	1.0
Intercept (log K)	0.77	0.11
Correlation Coefficient (r)	0.922	0.9915
Langmuir isotherm		
Slope ($1/Q_0$)	0.0025	0.0048
Intercept ($1/Q_0b$)	0.0022	0.096
Correlation Coefficient (r)	0.98	0.8641
Q_0(mg g^{-1})	400	210
b(gL^{-1})	1.1364	0.0496
R_L	0.0032	0.6684

In the present study, the values are found to be in the range of 0-1, indicating that the adsorption process is favorable for the adsorbent [35]. The data were given in Table 2.

Effect of contact time

In these experiments, initial concentration of CV dye on CAC and SCSC were 275and 10 ppm respectively. The effect of contact time (5, 10, 15, 20 …. 60 min) was investigated at 100 mg / 50 ml sample dosage. The extent of removal of dye by CAC and SCSC was found to increase, reached a maximum value with increase in contact time. The contact time at which the maximum percentage removal of dye occurs is fixed as the contact time (figure 4). The following kinetic equations were used for the adsorption of dye under the condition of first order kinetics (figure 5, 6 and 7).

Natarajan and khalaf equation : $$\text{Log } (C_i / C_t) = (k_{ad} / 2.303)\, t \text{ ------------- (5)}$$

Lagergren equation : $$\text{Log } (q_e - q_t) = \log q_e - (k_{ad} / 2.303)\, t \text{ --- (6)}$$

Bhattacharya-Venkobacher equation : $$\text{Log } (1\text{-}U(T)) - (k_{ad} / 2.303)\, t \text{ --- ----- (7)}$$

Where C_i and C_t are the concentration of dye (in mg L^{-1}, at time zero and at time t respectively, q_e and q_t are the amount of dye adsorbed per unit mass of the adsorbent (in m g^{-1}) at equilibrium time and time t respectively : U(T) : $(C_i - C_e) / (C_t - C_e)$, C_e is equilibrium dye concentration (in mg L^{-1}) and k_{ad} are the first order rate constants (in min^{-1}). The values of log (C_i / C_t), log (q_e / q_t) and log (1-U(T)) were correlated with time.

Intra – particle diffusion study

The possibility of intra – particle diffusion was explored by using the intra-particle diffusion model [36].

$$q_t = k_p t^{1/2} + c \text{ ------------------- (8)}$$

Where q_t is the amount of dye adsorbed at time t; c is the intercept and k_p is the intra-particle diffusion rate constant (in mg g^{-1} $min^{-1/2}$). The values of q_t were found to be linearly correlated by using correlation analysis. The applicability of this model indicates the presence of intra-particle diffusion process (figure 8 and 9).

Effect of adsorbent dosage

The dose of 70, 80, 90, 100, 110, 120 and 130 mg in 50ml was used keeping other factors as constant. The extent of removal of dye was found increase; reach an equilibrium value with increase in dosage of adsorbent [37]. It is due to the increased availability of active adsorption sites (figure 10).

Effect of pH

Initial p^H of solution was adjusted to 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11 at optimum condition of dye concentration, adsorbent dosage and contract time. The increase of p^H increases the amount of dye adsorbed (figure 11). It depends upon the nature of surface functional group of the adsorbent and the nature of the dye.

Table 3. Kinetics and dynamics of adsorption of Crystal Violet by adsorption on CAC and SCSC

Parameters	Adsorbent	
	CAC	SCSC
Natarajan and Khalaf equation		
Correlation coefficient (r)	0.900	0.9672
K (min^{-1})	0.2568	0.1478
Lagergren equation		
Correlation coefficient (r)	0.989	0.9545
K (min^{-1})	0.3239	0.1971
Bhattacharya and Venkobacher equation		
Correlation coefficient (r)	0.988	0.9554
K (min^{-1})	0.3233	0.8565
Intra-particle diffusion model		
K_p	0.6705	0.0558
Correlation coefficient (r)	0.919	0.9664
Intercept	268.65	8.89
Log time Vs log percentage removal		
Slope	0.0038	0.0225
Intercept	1.992	1.945
Correlation coefficient	0.972	0.9425

Effect of Particle Size

The effect of particle size of the adsorbent on the extent of removal of dyes by SCSC was studied under constant optimum experimental conditions of initial concentration of dye, contact time and dose of the adsorbent by varying the particle size (90, 125, 150, 210 and 250 microns) of the adsorbent. The effect of particle size of adsorbent on the extent of removal of dyes indicates that the rate of dye uptake increases with the decrease in particle size (figure 12). This is due to the increase in the availability of surface area of the adsorbent with the decrease in particle size [38].

Figure 1: Effect of initial concentration

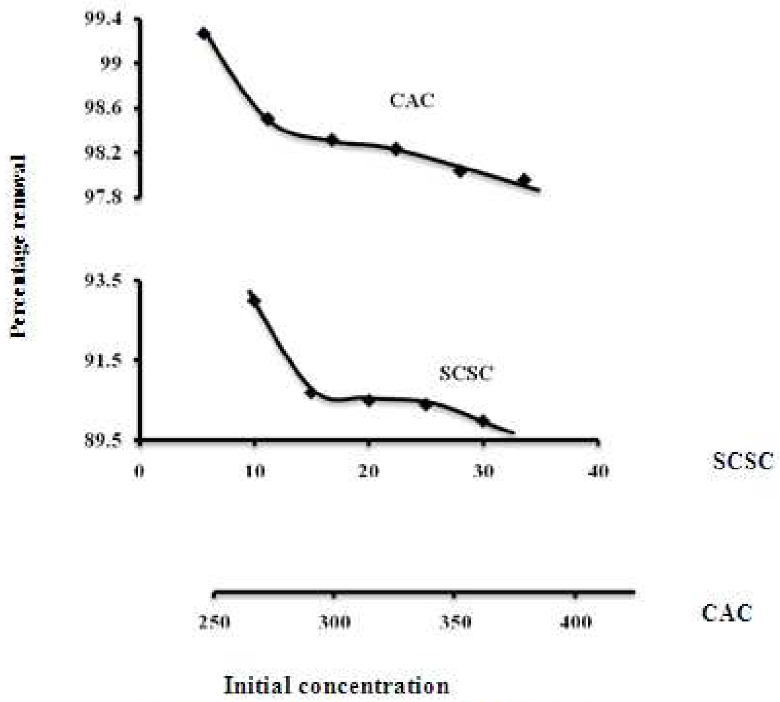


Figure 2: Effect of concentration variation:

Langmuir adsorption isotherm

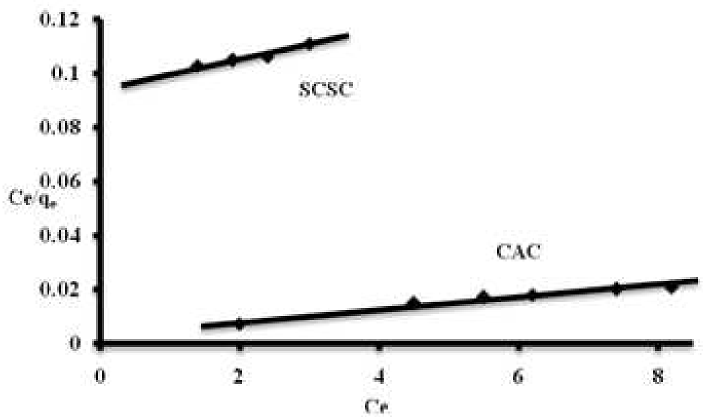


Figure 3: Effect of concentration variation:

Freundlich adsorption isotherm

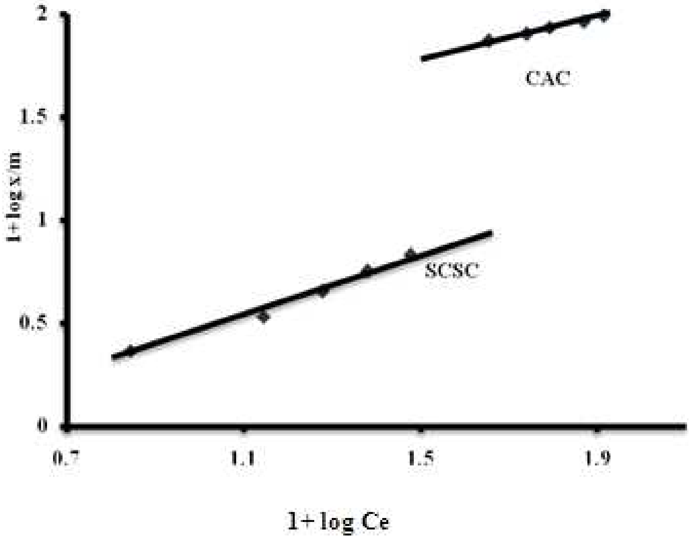


Figure 4: Effect of contact time on the percentage removal of dye

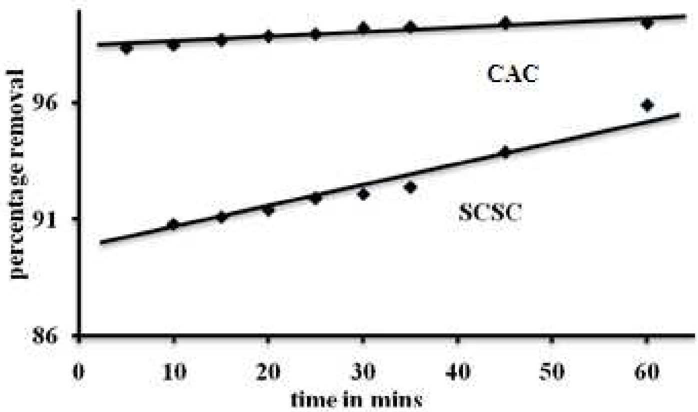


Figure 5: Effect of Contact Time Variation:

Natarajan and Khalaf equation

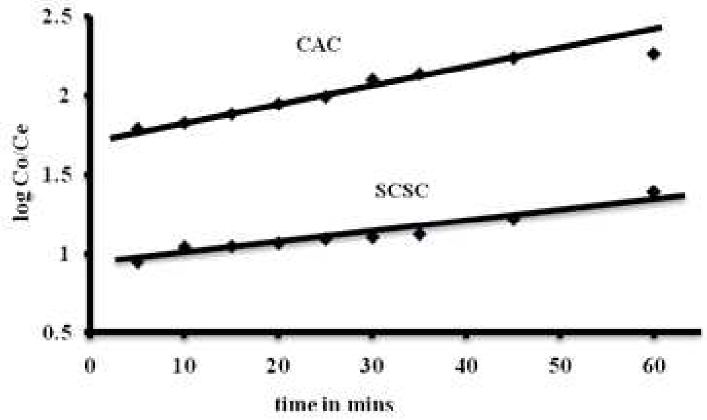


Figure 6: Effect of Contact Time Variation:

Lagergren equation

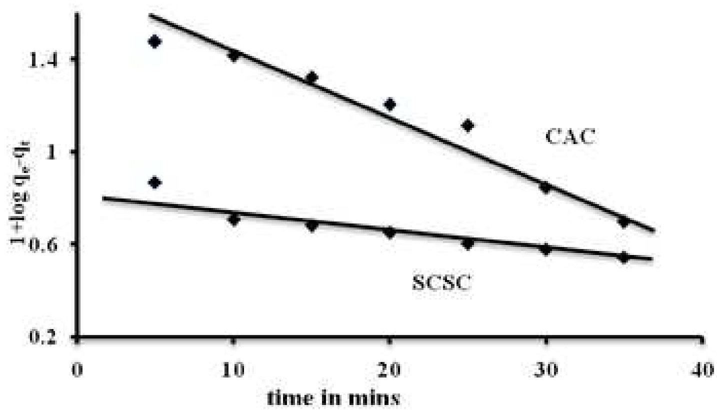


Figure 7: Effect of contact time variation

Venkobachar-Bhattacharya equation

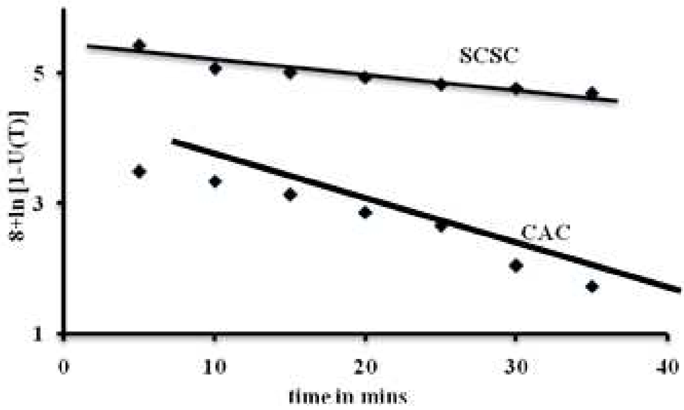


Figure 8: Effect of Contact Time Variation:

Log (Time) Vs Log (Percentage of Removal

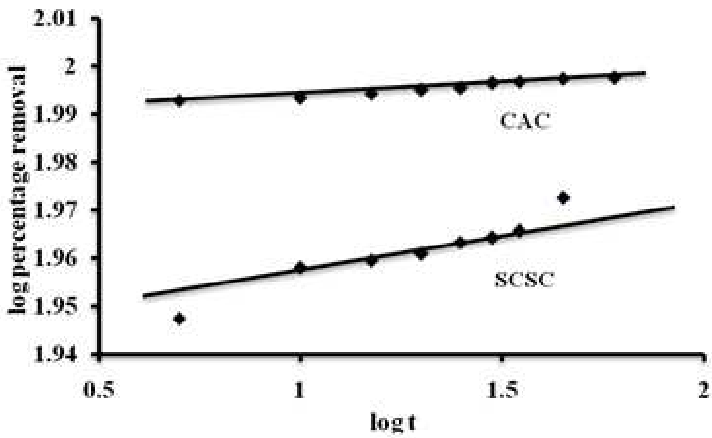


Figure 9: Effect of Contact Time Variation: Intra-Particle Diffusion model

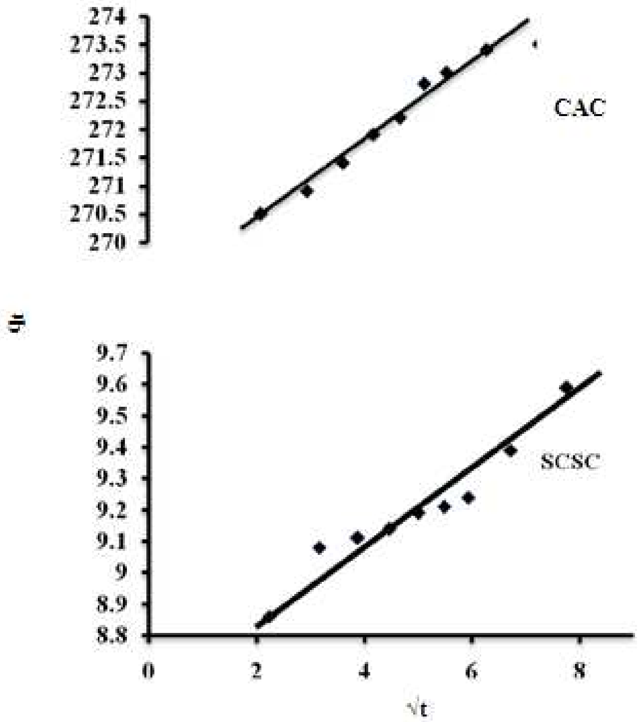


Figure 10: Effect of dose of adsorbents on the percentage removal of dye

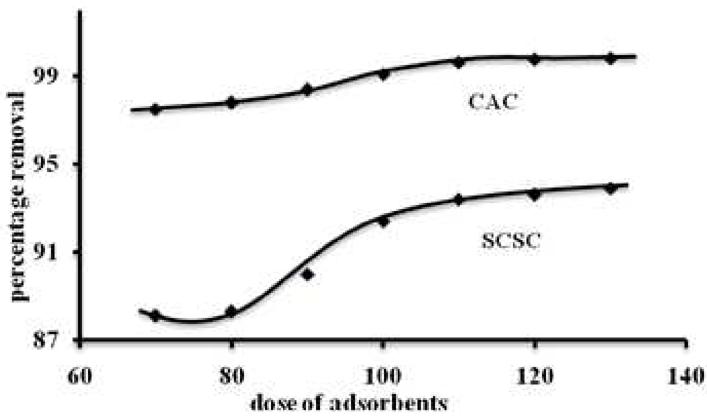


Figure 11: Effect of pH variation

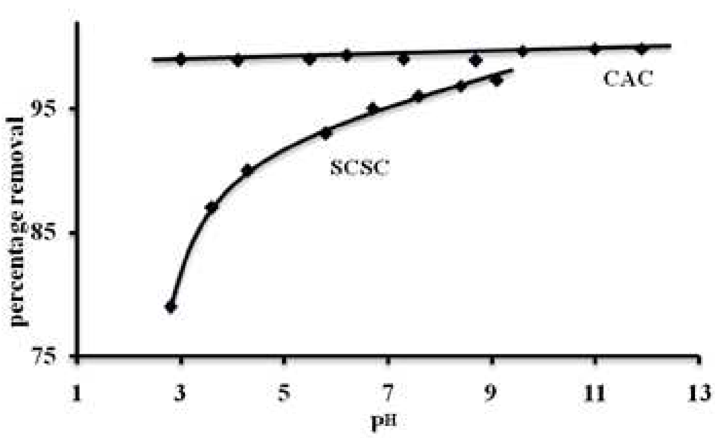
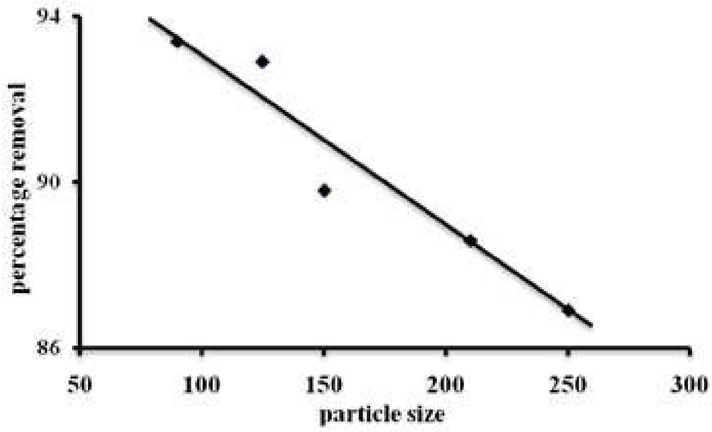


Figure 12: Effect of particle size



CONCLUSION

The removal of dye CV by adsorption process on SCSC as an adsorbent was found to decrease with increase in initial concentration of dye, increase with increase in contact time, and increase with increase in dose of adsorbent and increase with increase in P^H. The present study concludes that SCSC can be used as a better adsorbent for the effective removal of dyes from water and waste water.

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