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FILM AND PORE DIFFUSION MODELING FOR ADSORPTION OF REACTIVE RED-4 ONTO *STERCULIA QUADRIFIDA* SEED SHELL WASTE AS ACTIVATED CARBON

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ABSTRACT
Sterculia Quadrifida seed shell waste was employed for the removal of reactive red 4 from aqueous solution under different experimental conditions was investigated. The influences of initial Reactive red 4 concentration (20, 40 and 60 mg/L), temperature (30 °C , 45 °C and 60 °C) and particle size (75-180, 180-250 and 250-355 microns) have been reported. Plausible mechanism of the on going adsorption process and thermodynamics parameters involved were obtained by carrying out kinetic measurements. To identify whether the on going process is particle diffusion or film diffusion, the treatment given by Boyd and Reichenberg was applied.
Keywords: *Sterculia Quadrifida* seed shell waste, Adsorption of reactive red 4, Adsorption kinetics, Thermodynamic parameters.

INTRODUCTION

Textile effluent is known toxicants, which inflict acute disorder in aquatic organism. Uptake of textile effluents through food chain in aquatic organisms, may causes various physiological disorders like hypertension, sporadic fever, renal damage, cramps etc. Hence the treatment of wastewater containing dye is a challenging problems[1].

Many investigators have the feasibility of using inexpensive alternative materials like Jatropha Curcus seed shell, Delomix regia seed shell, Ipomea Carnia stem, turmeric waste[2], Fly-ash[3], Wollastonite[4], Olive stones[5], almond shells[6], apricot and peach stones[7], maize cob[8], linseed straw, saw dust[9], rice hulls[10], cashew nut hull, cashew nut sheath[11], coconut shells and husks[12], eucalyptus bark[13], linseed cake, tea waste ash[14]. Beside these other source of activated carbon is sulfonated coal[15], tyre coal dust[16], activated bauxite, cement kiln dust[17], Share oil ash[18] and ground sunflower stalk[19], Feronia limonia swingle shell [20] etc., as the carbonaceous precursors for the removal of dyes from waste water.

In the present investigation the adsorption of Reactive Red 4 on activated carbon prepared from *Sterculia Quadrifida* seed shell waste by carbonization with phosphoric acid activation process. The kinetic and equilibrium adsorption data obtained ware utilized to characterize the sample prepared.

The amount and rates of adsorption of Reactive Red 4 using above activated carbon from water were then measured. Three simplified kinetic models including Pseudo first order equations, Pseudo second order equations and Elovich equations were used to describe the adsorption process.[21]

EXPERIMENTAL

Adsorbent

Sterculia Quadrifida shells were collected from various places in Erode city, Tamil Nadu, India. They were cut into small pieces, dried in sunlight until all the moisture was evaporated. The dried Material was used for the preparation of activated carbons using physical and chemical activation methods. The

materials to be carbonized were soaked with phosphoric acid for a period of 24 hours. After impregnation, the product was washed with large volume of water to remove the free acid, and then it was dried at 160 °C for 2 hours by using air oven, finally activated at 800 °C and powdered.
The Nitrogen adsorption-desorption isotherms of activated carbons were measured using a gas sorption analyzer in order to determine the surface area and the total pore volume. The surface area was calculated using the BET equation.

Batch adsorption studies
The batch adsorption studies were performed at 30 °C. A predetermined amount of adsorbent is mixed with known initial concentration of Reactive Red-4 solution and agitated for desired time. The adsorbent and the adsorbate were separated by filtration and the filtrate was analyzed for residual Reactive Red-4 concentration spectrophotometrically.
The amount of Reactive Red 4 adsorbed in mg/L at time t was computed by using the following equation.

$$q_t = \frac{C_o - C_t}{m_s} \times V \quad (1)$$

Where, C_o and C_t are the Reactive Red-4 concentration in mg/L initially and at given time t, respectively, V is the volume of the Reactive Red-4 solution in ml and m_s is the weight of the activated carbon. The percentage of removed Reactive Red-4 ions (R %) in solution was calculated using equation.

$$\% \text{ Removal} = \frac{C_o - C_t}{m_s} \times 100 \quad (2)$$

The initial concentration of Reactive Red 4, pH and temperature was investigated by varying any one parameters and keeping the other parameters constant.

Kinetic Models
In order to investigate the mechanism of adsorption and potential controlling steps such as mass transport, several kinetic models were tested including the Pseudo first order kinetic model, the Elovich model and the Pseudo second order kinetic model for a batch contact time process, where the rate of sorption of dye on to the given adsorbent is proportional to the amount of dye sorbed from the solution phase.

Pseudo First Order Kinetic Model
A simple kinetic analysis of adsorption, the pseudo first order kinetics and its integrated form, is given by Lagergren.[22 & 23]

$$\frac{dq_t}{dt} = k_L(q_e - q_t) \quad (3)$$

$$\log(q_e - q_t) = \log q_e - \frac{k_L}{2.303} t \quad (4)$$

Where k_1 is the pseudo first order rate constant. A plot of log (q_e-q_t) V/s time enables calculation of the rate constant k_1 and q_e from the slope and intercept of the plot.

Elovich Model
The Elovich or Roginsky–Zeldovich equation is generally expressed as follows-[24,25]

$$\frac{dq_t}{dt} = \alpha \exp(\beta q_t) \quad (5)$$

On integrating this equation for the boundary conditions,

$$q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (6)$$

Where the initial dye adsorption rate (mg/g) and desorption constant (g/mg) respectively are obtained from the slope and intercept of linear plot of q_t V/s ln t.

Pseudo Second Order Kinetic Model

To describe the dye adsorption, the modified pseudo second order kinetic equation is expressed as[26]

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (7)$$

Where, k_2 is the pseudo second order rate constant. A plot of t/q_t Vs t enables calculation of the rate constant k_2 which in turn is used to calculate the initial sorption rate h as follows

$$\frac{t}{q_t} = \frac{t}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

Adsorption Thermodynamics

Any chemical system tends to attain a state of equilibrium from one of non- equilibrium. The thermodynamic parameters, which characterize the equilibrium of the system, are the Gibbs free energy change ΔG, the enthalpy change ΔH and the entropy change ΔS. These parameters were determined using the following relations[27].

$$K_c = \frac{C_{Ae}}{C_e} \quad (9)$$

$$\Delta G = RT \ln K_c \quad (10)$$

$$\log K_c = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (11)$$

Where K_c is the equilibrium constant, C_{Ae} is the solid phase concentration at equilibrium, C_e is the residual concentration at equilibrium, R is the gas constant (J/mole) and T is the temperature in Kelvin.

RESULTS AND DISCUSSION

Adsorption kinetics

Effect of initial concentration on rate parameters

Reactive Red 4 dyes were carried out by using various concentrations of 20, 40 & 60 mg/L at P^H 6.5 at reaction temperature of 30 °C. The rate constant and the rate parameters at different initial dye concentration presented in the Table-1 showed that the rate constants increase with increase in initial dye concentration.

Table-1: Rate parameters for the adsorption of Reactive Red-4 onto SQAC seed shell waste activated carbon at various initial concentrations

Concentration, mg/L	Pseudo First Order		Elovich			Pseudo Second Order			
	k_L min^{-1}	R^2	β g/ min	α, mg/g/ min	R^2	q_e mg/g	k_2 g/mg/min	h g/ mg/ min	R^2
20	0.2330	0.7298	0.1750	1.5694	0.9786	26.666	0.0382	3.681	0.9931

40	0.0177	0.9616	0.1123	2.4507	0.9869	42.016	0.0621	0.912	0.9993
0	0.0186	0.9833	0.0822	2.5439	0.9899	56.179	0.3688	0.859	0.9985

From the analysis the data reveals that the influence of the initial concentration of Reactive Red-4 was little persuade on the Pseudo first order rate constant. In the case of Elovich model the obtained data reveals that the initial sorption rate (α) was 2.067, 1.1203 & 1.7772, for 20 mg/L, 40 mg/L and 60 mg/L simultaneously. Then the (β) desorption constant ranges from 0.1570 to 0.0619.

In the case of Pseudo second order the amount of dye adsorbed at equilibrium q_e increase simultaneously for 20 mg/L, 40 mg/L and 60 mg/L concentrations. Then the rate constant k_2 was 0.0240, 0.0178 & 0.0197 for all the three concentrations. The initial adsorption rate (h) gradually decreases.

When increasing the initial dye concentration for 20 ppm, 40 ppm and 60 ppm the Reactive Red -4 the linear regression co-efficient (R^2) was very closer or equal to 1 for Pseudo second order kinetic model, where as the Pseudo first order and Elovich kinetic models the R^2 values was comparatively low than the Pseudo second order. Hence the relatively higher R^2 value indicates that the model successfully describes the kinetics of Reactive Red-4 adsorption (Fig.-1a, 2b, 2c).

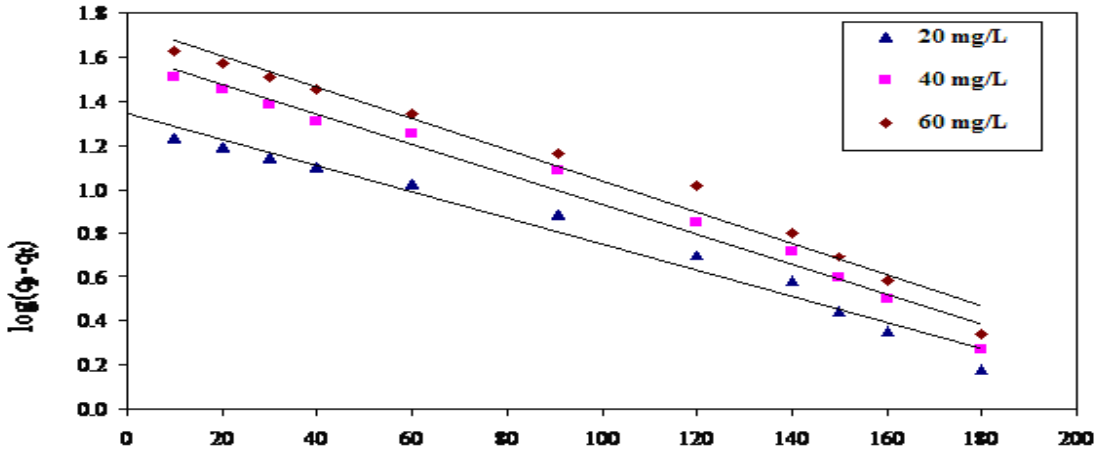

Fig.-1a: effects of initial dye concentration on Pseudo First Order Plots for Reactive Red-4 adsorption

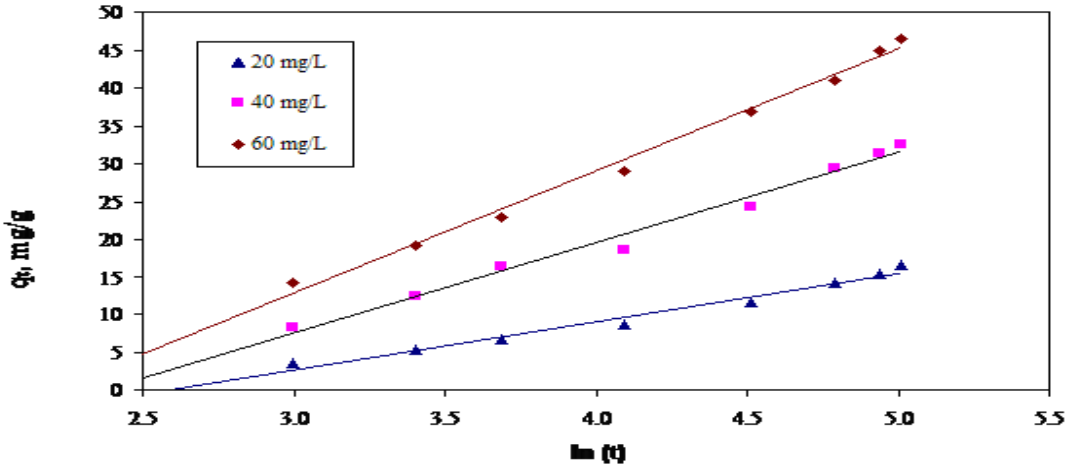

Fig.-1b: effects of initial dye concentration on Elovich Plots for Reactive Red-4 adsorption

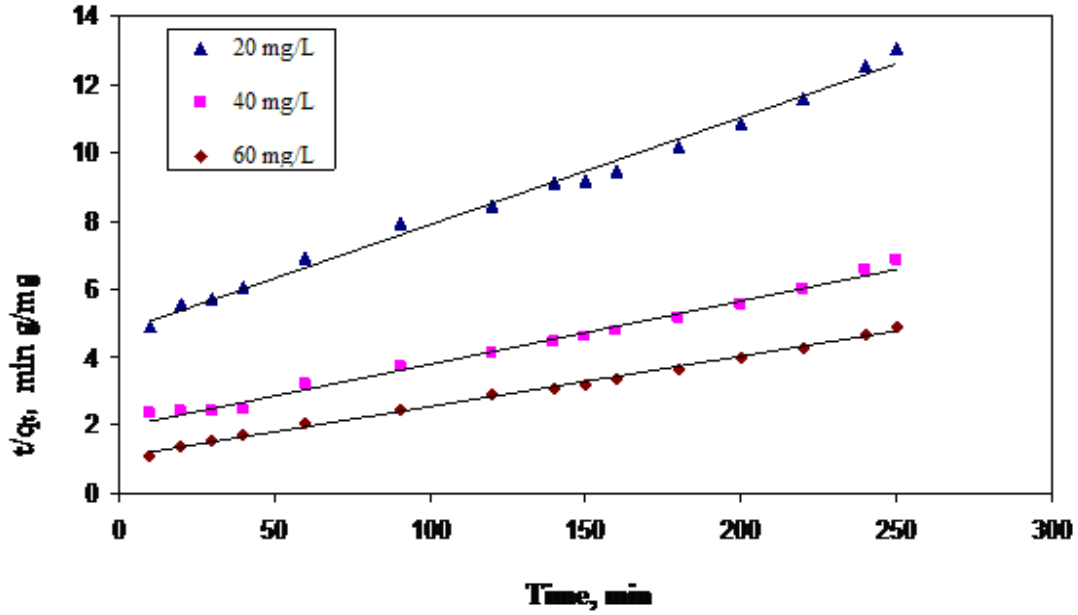

Fig.-1c: effects of initial dye concentration on Pseudo Second Order Plots for Reactive Red-4 adsorption

Effect of temperature on kinetic rate parameters

The data obtained from experiment at various temperatures viz 30, 45 and 60 °C presented in the Table 2, the rate constant values K_L for Pseudo first order decreases with increase in temperature.

The initial sorption rate (α) values decreases at the desorption constant (β) ranges from 0.237 to 0.3929. In the case of Pseudo second order kinetic modal at the different temperature 30 °C, 45 °C and 60 °C, the amount of dyes adsorbed at equilibrium (q_e) increases with decrease in rate constant (k_2).Then the initial adsorption rate (h) increases with increase in amount of dyes adsorbed at equilibrium (q_e).

When increasing the temperature 30 °C, 45 °C and 60 °C the adsorption of Reactive Red-4 on to SQAC, comparing the R^2 value obtained for Pseudo first order, Elovich and Pseudo second order, the relatively higher R^2 values obtained only for the Pseudo second order. Hence the Pseudo second order equation fits good correlation co-efficient (Fig.-2a, 2b, 2c).

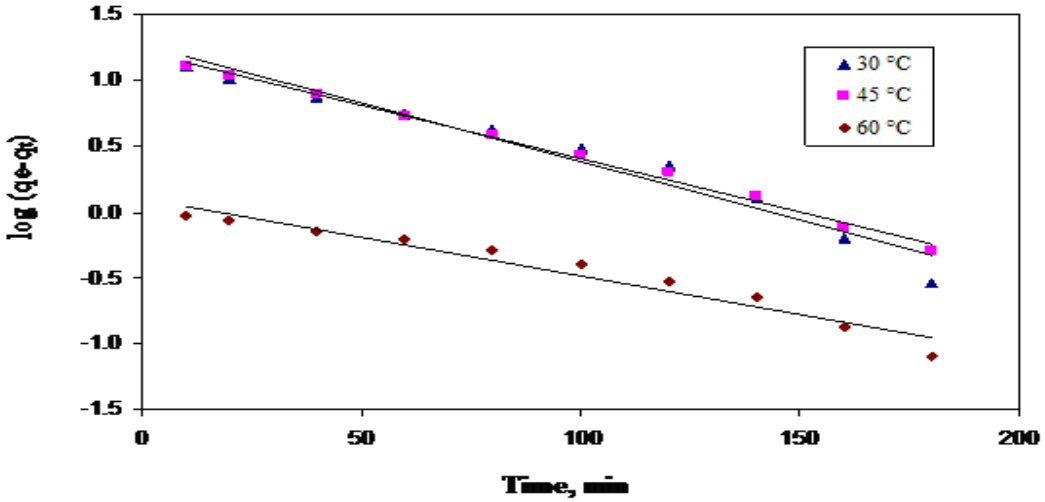

Fig.-2a: Effects of Temperature on Pseudo first Order Lagergren Plot for Reactive Red-4 adsorption

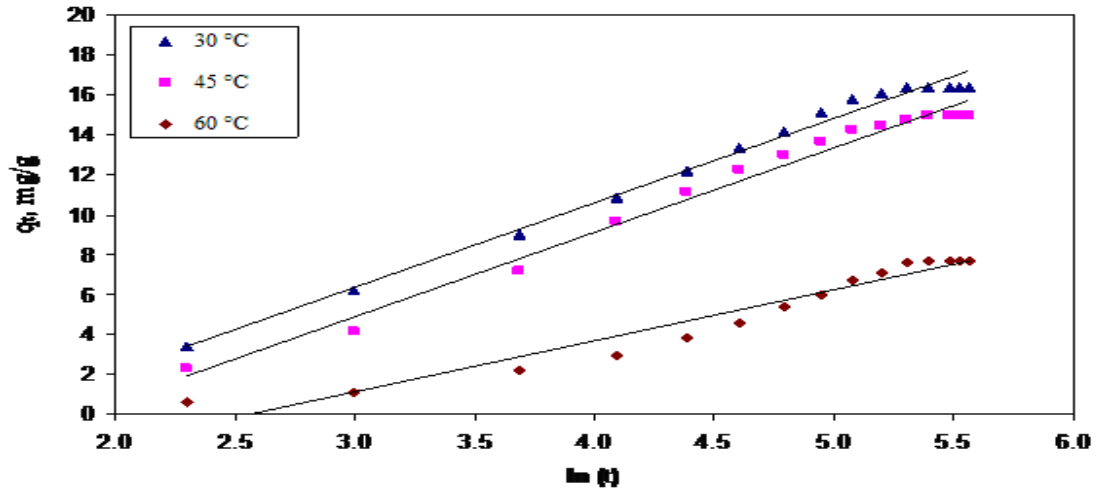

Fig.-2b: Effects of Temperature on Elovich Plot for Reactive Red-4 adsorption

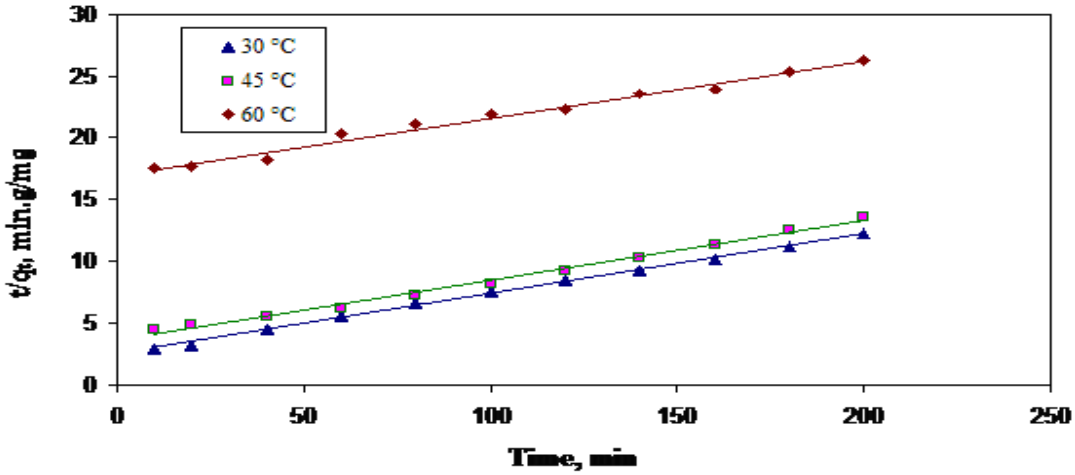

Fig.-2c: Effects of Temperature on Pseudo Second Order Plot for Reactive Red-4 adsorption

Table-2: Rate parameters for the adsorption of Reactive Red 4 onto SQAC at various Temperatures

Temp °C	Pseudo First Order		Elovich			Pseudo Second Order			
	k_L min^{-1}	R^2	B g/ min	A mg/ g/ min	R^2	q_e mg/g	k_2 g/ mg/ min	h g/ mg/ min	R^2
30	0.0204	0.9600	0.237	1.053	0.9898	20.576	0.0942	2.513	0.9982
45	0.0181	0.9765	0.2354	1.5163	0.9863	20.876	0.0621	3.700	0.9950
60	0.0135	0.9494	0.3929	5.0611	0.9456	21.459	0.0128	16.97	0.9884

Effect of particle size on kinetic rate parameters

The experiments were conducted at different particle size viz 75-180, 180-280 and 280-355 microns, the rate constant were calculated and the results are presented in the Table-3.

Table-3: Rate parameters for the adsorption of Reactive Red 4 onto SQAC at various Particle sizes

Particle size microns	Pseudo First Order		Elovich			Pseudo Second Order			
	k_L min^{-1}	R^2	β g/ min	A mg/g/ min	R^2	q_e mg/g	k_2 g/ mg/ min	h g/ mg/min	R^2
75-180	0.0207	0.9239	0.1811	1.2528	0.9756	25.5754	0.0532	2.8851	0.9904
180-250	0.0198	0.9143	0.1972	1.5193	0.9693	25.1256	0.0400	3.9603	0.9897
250-355	0.0177	0.9169	0.2065	4.119	0.9696	23.8095	0.0368	4.9019	0.9871

Pseudo first order and Pseudo second order kinetic models, the rate constant values decreases with increase in particle size simultaneously. The amount of dyes adsorbed at equilibrium (q_e) for the Pseudo second order decreases with increase in practical size as well as the initial adsorption rate (h) increases with increase in practical size. For the Elovich kinetic modals the initial sorption rate (α) increases with increase in particle size and the desorption constant (β) increases with increase in particle size.

The results of the sorption of Reactive Red-4 on to SQAC at various particle size, from the obtained data's the linear regression co-efficient values R^2 obtained for the Pseudo first order, Elovich and Pseudo second order, The relatively higher R^2 values obtained only in the Pseudo second order kinetic model. Hence the Pseudo second order fits good correlation (Fig.-3a, 3b, 3c).

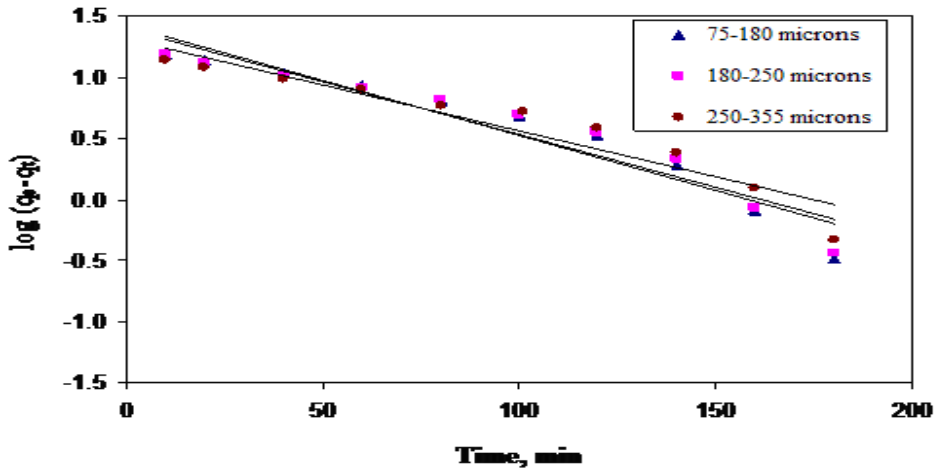

Fig.-3a: Effects of Partcle size variation on Pseudo First order Lagergren plot for Reactive Red-4 adsorption

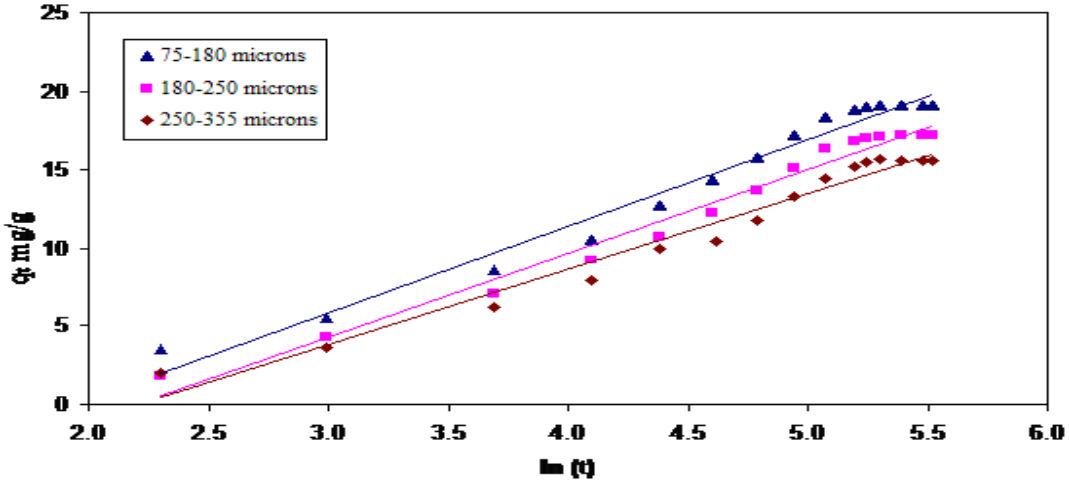

Fig.-3b: Effects of Partcle size variation on Elovich plot for Reactive Red-4 adsorption

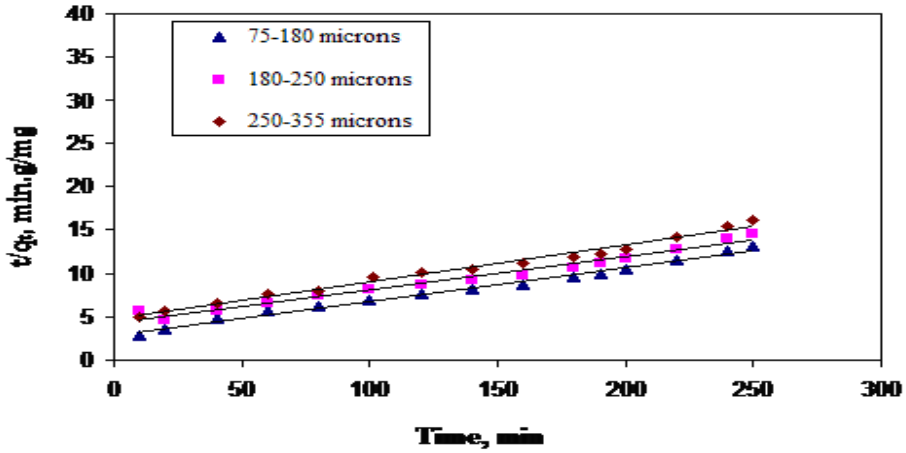

Fig.-3c: Effects of Partcle size variation on Pseudo Second order Lagergren plot for Reactive Red-4 adsorption

Mechanism for sorption of Reactive Red 4 on to *Sterculia Quadrifida* Seed Shell Waste

Because of the high correlation coefficients obtained using pseudo first order and pseudo second order models, it was impossible to concludes which adsorption mechanism actually occurred and was responsible for the ability of adsorbent to review other sources of information in an attempt to identify the specific adsorption mechanism.In adsorption process of dye ion on the solid surface, the dye species migrate towards the surface of the adsorbent. This type of migration proceeds till the concentration of the adsorbate species, adsorbed, on to the surface of the adsorbent. Once equilibrium is attained, the migration of the solute species from the solution stops. Under this situation, it is possible to measure the magnitude of the distribution of the solute species between the liquid and solid phases. The magnitude of this kind of distribution is a measure of the efficiency of the chosen adsorbent in the adsorbate species.

When a powdered solid adsorbent material is made in contact with a solution containing dyes, the dyes first migrate from the bulk solution to the surface of the liquid film. This surface exerts a diffusion barrier. This barrier may be very significant or less significant[28]. The involvement of a significant quantum of diffusion barrier indicates the dominant role taken up by the film diffusion in the adsorption process. Furthermore, the rate of an adsorption process is controlled either by external diffusion, internal diffusion or by both types of diffusions. The external diffusion controls the migration of the solute species from the solution to the boundary layer of the liquid phase. However, the internal diffusion controls the transfer of the solute species from the external surface of the adsorbent to the internal surface of the pores of the

adsorbent material[29]. It is now well established, that during the adsorption of dye over a porous adsorbent, the following three consecutive steps were taken place[30].

i. Transport of the ingoing adsorbate ions to external surface of the adsorbent (film diffusion),
ii. Transport of the adsorbate ions within the pores of the adsorbent except for a small amount of adsorption, which occurs on the external surface (particle diffusion) and
iii. Adsorption of the ingoing adsorbate ions on the interior surface of the adsorbent[32]

Out of these three processes, the third process is considered to be very fast and is not the rate limiting step in the uptake of organic compounds[31]. The remaining two steps impart the following three possibilities-

Case 1: External transport > internal transport, where rate is governed by particle diffusion.
Case 2: External transport < internal transport, where the rate is governed by film diffusion.
Case 3: External transport ≈ internal transport, which accounts for the transport of the adsorbate ions to the boundary and may not be possible within a significant rate, which later on gives rise to the formation of a liquid film surrounded by the adsorbent particles with a proper concentration gradient.

In the batch-mode contact time adsorption experiments, rapid stirring was maintained. This Reactive Red 4 to the transport of the adsorbed species from the solution to the pores of the adsorbent material and this step may control the rate of the adsorption process.
According to Michelson et al[31] for film diffusion to be rate-determining step, the value of the film diffusion coefficient, D_f, should be in the range 10^{-6} - 10^{-8} cm^2/ sec [32]. If pore diffusion were to the rate limiting, the pore diffusion coefficient, D_p, should be in the range 10^{-11}- 10^{-13} cm^2/ sec. In order to find out the nature of the process responsible for adsorption on to chosen adsorbent, attempts were made to calculate the diffusion co-efficient of the process. Assuming spherical geometry of the sorbents[33], the overall rate constant of the process can be correlated to the pore diffusion coefficient in accordance with the expression, $t_{½} = 0.03 \frac{r_o^2}{D_p}$ or to the film diffusion coefficient in accordance with $t_{½} = 0.23 \frac{r_o \partial}{D_p} \times \frac{\overline{C}}{C}$ Where r_o is radius of the sorbent (cm), D_p and D_f are pore diffusion coefficient (cm^2/sec) and film diffusion coefficient (cm^2/sec) respectively, $\overline{C}/C$ is equilibrium loading of the adsorbent , ∂ is the film thickness (cm) and $t_{1/2}$ is the time for half change (sec).
Since the carbon particles used were of the size range (180-250 μm), the average diameter of the particle was taken as 0.0215 x 10^{-4} cm using these values, the film diffusion coefficients and pore diffusion coefficients were calculated.Then considering the pseudo first order rate constant k_L, for the adsorption of Reactive Red-4. The values of D_p and D_f were calculated under the given set of operating conditions, and are presented in the Table-4.

Table-4: D_p and D_f values for the chosen adsorbent - adsorbate system

Dye	Particle size, microns	$t^{1/2}$, s	D_p, cm^2	D_f, cm^2
Reactive Red 4	75-180	2008.69	6.0697×10^{-10}	6.5695×10^{-9}
	180-250	2100	1.6508×10^{-9}	1.05964×10^{-8}
	250-355	2349.15	2.9214×10^{-9}	1.3327×10^{-8}

The values of D_p and D_f for all Reactive Red-4 in the present study are found to be in the order of 10^{-10} to 10^{-11} and 10^{-9} to 10^{-10} cm / sec which indicates that pore diffusion has some amount of influence in the rate determining step.

Gupta *et al.*[34] have reported a D_p value in the order of 10^{-10} cm/sec for the removal of Chrome Red 2 by a mixture of two adsorbents and these authors suggested that the adsorption process was governed by pore diffusion even though it could not be ascertained that pore diffusion was the only rate determining step.
The present study indicates the D_p values in the order of 10^{-11} to 10^{-10} cm/sec and the D_f values in the order of 10^{-10} to 10^{-9} for the respective Lagergren plots for Reactive Red 4 and hence, the investigator concludes that the mechanism of the removal of Reactive Red-4 in the present study by chosen adsorbent is complex.
Since both external Mass transfer and intra-particle diffusion constants varied with initial Reactive Red 4 concentration indicating the occurrence of both surface adsorption and intra particle diffusion, the sorption data were further analyzed by the kinetic expression given by Boyd *et al*[35]

$$F = 1 - \frac{6}{\pi}\sum_{N-1}^{\alpha}\frac{1}{n^2}\exp\left[\frac{-Dit\pi^2 n^2}{r^2}\right]$$

$$F = 1 - \frac{6}{\pi^2}\sum_{N-1}^{\alpha}\frac{1}{n^2}\exp\left[-n^2\beta_t\right]$$

Where F is the fractional attainment of equilibrium at time t and is obtained by using following equation and n. is the Freundlich constant of the adsorbate.

$$F = \frac{q_t}{q_e}$$

Where q_t and q_e are the amounts adsorbed at time t and at equilibrium respectively. On the basis of F values, corresponding values of B_t were obtained from Reichenberg's table[36] and the linearity test was carried out by plotting Bt with respect to time for both the solutions at different time intervals and at 30 °C, 45 °C and 60 °C. The linearity test of B_t versus time plot drawn for different concentrations is employed to distinguish between film diffusion and particle diffusion. From the slop of the straight line obtained from time versus B_t graph, the B value (time constant) were calculated. The values of effective diffusion coefficient (D_i) were calculated at different temperatures using the following Equation, $B = \frac{\pi^2 D_i}{r^2}$ where 'r' is the radius of the absorbent particle. The D_i values are given in the Table-5.

Table -5: Values of energy of activation E_a, entropy of activation ΔS and pre-exponential constant D_o for the present study

S.No.	Particle size, microns	D_i, cm^2s^{-1}	E_a, KJ/mol	ΔS, KJ/mol	D_o, cm^2s^{-1}
1	75-180	$5.463X10^{-6}$	-3.6756	-166.96	$2.93X10^{-12}$
2	180-250	$1.098X10^{-5}$			
3	250-355	$2.033X10^{-5}$			

The plot of 1/T versus log Di was found linear with negative slope indicating thereby the increase in the mobility of ions. This is due to the fact that with the rise in temperature the mobility of ions. This is due to the fact that with the rise in temperature the mobility of ions increases, which consequently decreases the retarding force acting on the diffusing ions. The Values of energy of activation E_a, entropy of activation $\Delta S^{\#}$ and pre-exponential constant D_o were calculated using following Equations.

$$D_i = D_o \exp\left[-\frac{E_a}{RT}\right],$$

$$D_o = 2.72d^2 \frac{kT}{h}.\exp\left[\frac{\Delta S}{R}\right]$$

Where d is the average distance between the successive exchange sites and is taken as 5 A°. R, h and k are the Gas, Planck and Boltzmann constants, respectively. The values of E_a, D_i, D_o, ΔS and other parameters are given in Table-5. The negative value of ΔS reflects that no significant change occurs in the internal structure of chosen adsorbent during the adsorption process.

Thermodynamic parameters

ΔH and ΔS was obtained from the slope on the intercept of Vant Hoff plot (1/t Vs ln K_c). ǀTable 5 gives the value of ΔG, ΔS and ΔH for the adsorption of SQAC. The negative values of free energy change ΔG indicate the feasibility and spontaneous nature of adsorption of SQAC. The negative value of ΔS is due to the increased randomness during the adsorption of adsorbent.

CONCLUSION

In the present study adsorption of Reactive Red-4 on activated *Sterculia Quadrifida* seed shell waste carbon have been investigated. The data obtained through supports that the *Sterculia Quadrifida* seed shell waste carbon is an effective low cost adsorbent for the removal of Reactive Red 4 from aqueous solution.

The Pseudo second order provides a best fit description for the sorption of the Reactive Red-4 on two *Sterculia Quadrifida* relative to Elovich and Pseudo first order equations. The Pseudo second order was consider the most appropriate due to high correlation co-efficient when compared to Pseudo first order and Elovich equations. The adsorption of Reactive Red-4 on to activated *Sterculia Quadrifida* seed shell waste carbon is an exothermic reaction based on enthalpy change values.

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