CHAPTER 4

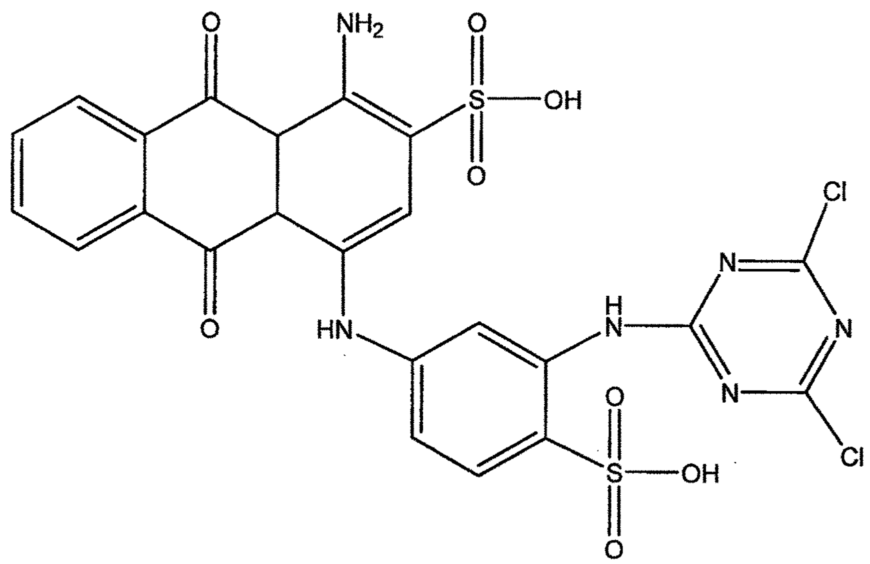
ADSORPTION STUDIES OF REACTIVE DYES WITH CHITOSAN

4.1 Introduction

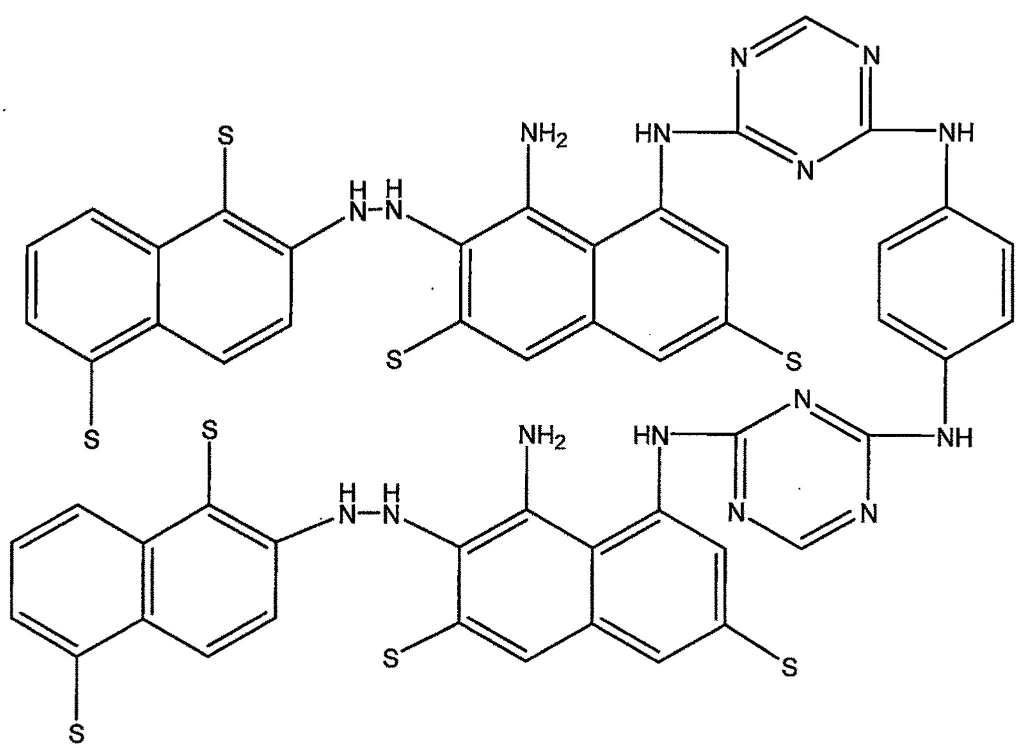
Reactive dyes are typically azo-based chromophores combined with different types of reactive groups. They differ from all other classes of dyes in that they bind to the textile fibers such as cotton to form covalent bonds [4.1-4.6]. The expanded use of reactive dyes during the last decade has made an impact on conventional methods for treating textile effluents due to the generally poor biodegradation of such dyes (especially those containing azo-groups) under aerobic conditions [4.7]. Some of the dyes are toxic and carcinogenic and require separation and advanced treatment of textile effluents before discharge into conventional systems [4.8]. Due to low biodegradability of dyes, a conventional biological wastewater treatment process is not very efficient in treating dye wastewater. Hence, investigations have been conducted on physicochemical methods of removing colour from textile effluents [4.9]. These studies include chemical oxidation [4.10], membrane filtration [4.11] and adsorption techniques [4.12]. In these techniques, adsorption has been found to be an efficient process to remove dye [4.12].

The present study involves the use of chitosan and acid activated palm shell powder (APSP) for the removal of acidic reactive dyes Reactive Blue 21 (RB-21) and Reactive Red141 (RB-141). The equilibrium isotherm and kinetic characteristics of reactive dye adsorption on the above mentioned adsorbents were investigated using bench scale batch tests.

Structures of Dyes:



Reactive Blue 21



Reactive Red 141

4.2 Preparation of Adsorbent:

Chitosan flakes (87.6 % deacetylated and molecular weight 5.5 x 10^5 g/mol) were from Sigma. The Chitosan flakes were used for further experimental studies as an adsorbent. The preparation of APSP has been described in Chapter 3 (page no. 109)

4.3 Characterization of APSP and Chitosan:

Though the FTIR spectra, SEM and BET surface area of APSP have been described in Chapter 3 we felt it would be logical to describe it again here in comparision with chitosan.

4.3.1 Fourier Transform Infra-Red Spectroscopy:

FTIR was used to determine the vibrational frequencies of the functional groups in the adsorbents. The IR spectra of PSP (palm shell powder), APSP and chitosan are shown in Figure 4.1. The strong broad band in the region of (3300 to 3500) cm^{-1} is characteristic of the N-H stretching vibration although there is the possibility of overlapping between the N-H and the O-H stretching vibrations in chitosan. The absorption bands at (1630, 1590, 1381, 1080 and 1030) cm^{-1} are ascribed to the C=O of amide I, NH, amide III, C3-OH and C6-OH of chitosan respectively. APSP showed a broad frequency at ~3419.42 cm^{-1}, which can be assigned to N-H/-OH stretching. The peak at ~1625.29 cm-1 is characteristic of the N-H bond of amine or of the elongation of the aromatic -C=C- bonds. The peak at 1378.58 cm^{-1} corresponds to C-N stretching while the peak at 1200 cm^{-1} is associated with the C-O stretching of the aromatic ring. PSP has peaks at ~1739, ~1735 cm^{-1} which shows the presence of carboxylic acid groups which is not seen in APSP. The characteristic peak of carbohydrates ~1379 cm^{-1} is seen in both PSP and APSP inferring the presence of lignin.

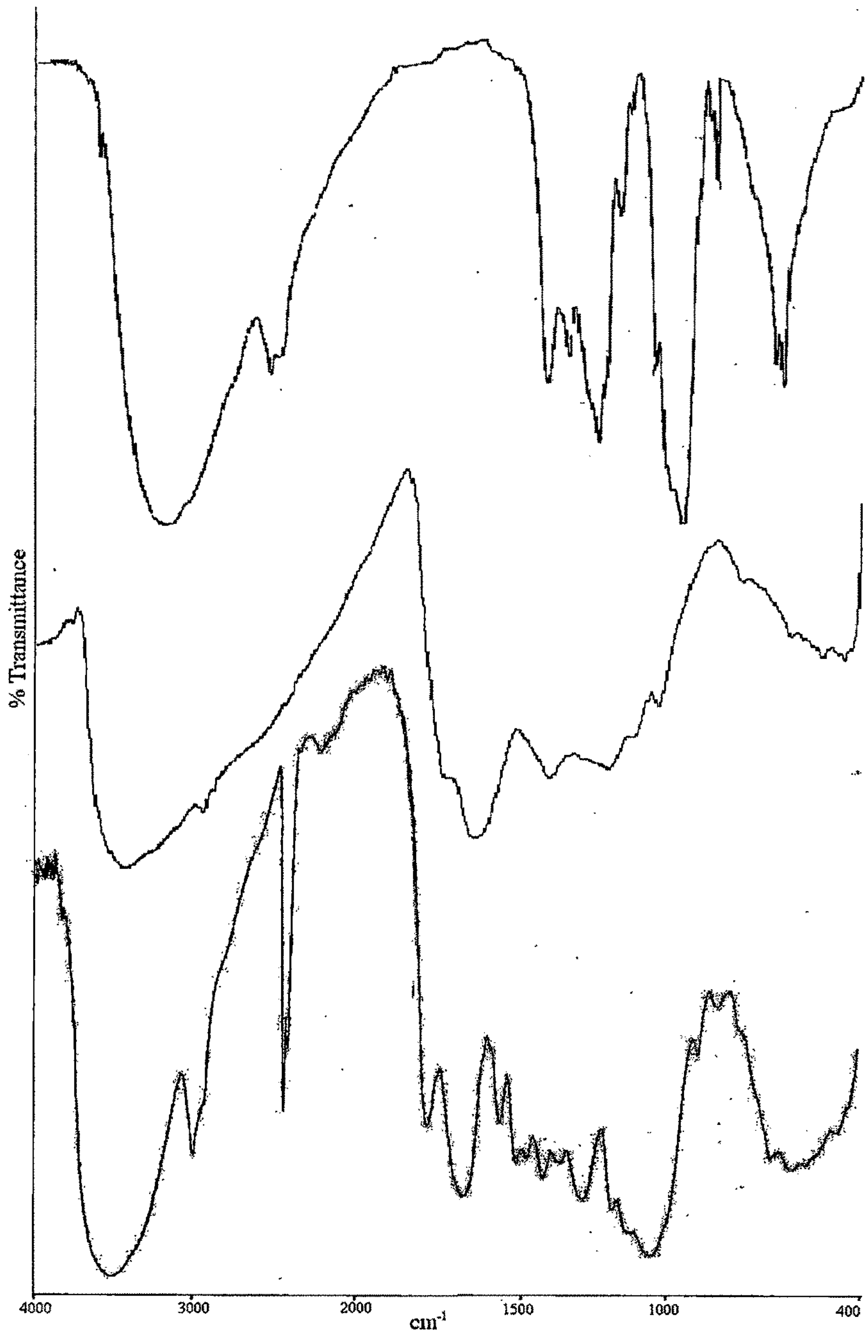


Figure 4.1: FTIR Spectra of PSP, APSP and Chitosan

4.3.2 Scanning Electron Microscopy:

The morphology of PSP, APSP and chitosan were studied using a scanning electron microscope (SEM) (Figure 4.2) The surface of APSP was found to be irregularly rough and porous with identifiable micropores and mesopores in comparision to PSP. The SEM micrograph of chitosan shows that it is has a larger number of pores connected by channels compared to APSP.

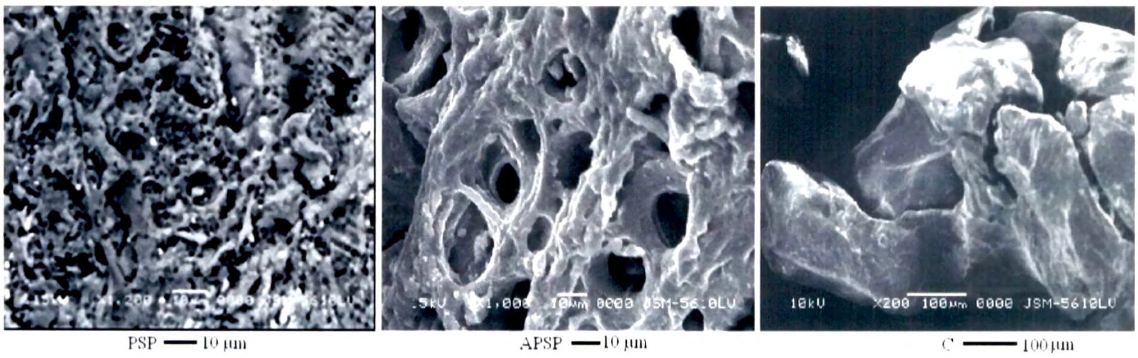


Figure 4.2: SEM of PSP, APSP and Chitosan

4.3.3 BET analysis:

The BET surface area of PSP, APSP and chitosan was measured by nitrogen adsorption isotherms using a BET surface area analyzer (Micrometrics ASAP 2020 V3.03H). The BET surface area was found to be (0.6735, 0.2979 and 1.11) m^2/g for PSP, APSP and chitosan respectively.

4.4 Preparation of dye solutions:

Stock solutions of dyes (1g/L) were prepared by dissolving accurately weighed amounts of RB-21 and RR-141 in double distilled water with subsequent dilution to the required concentration.

4.5 Batch adsorption studies of Reactive dyes:

Adsorption studies were carried out with 100 mL Durasil Stoppered flasks containing 25 mL solution of desired adsorbate concentration. A known amount of adsorbent was introduced into each flask and the flasks were agitated at 180 rpm in a thermo regulated water bath shaker. A series of dye adsorption experiments were conducted to study the effect of pH, dose and temperature. In the adsorption experiment a 25 mL of dye solution of known initial concentration was kept in contact with a required dose of APSP and Chitosan at room temperature. The pH of solutions was adjusted using 0.1N HCl or 0.1N NaOH solution using pH meter (MFRS: TOSHNIWAL INST. MFG. PVT. LTD. AJMER, CAT. NO. CL54). After a specific time period the reaction mixture was filtered. The dye concentration in the filtrate was determined by measuring absorbance at the wavelength of maximum absorption (648nm and 540nm for RB-21 and RR-141 respectively) using a SYSTRONICS Digital 166 model visible spectrophotometer.

The percentage removal of the dye and the amount adsorbed (mg/g) were calculated by the following relationship:

$q_e = (C_i - C_e)/m$;

Where, C_i-initial concentration of dye in mg/L; C_e – Equilibrium concentration of dye in mg/L; m – Mass of adsorbent g/L; q_e – Amount of dye adsorbed per gram of adsorbent. The experiments done without adsorbent were treated as blanks and they showed no precipitation of dye occurred under the conditions selected.

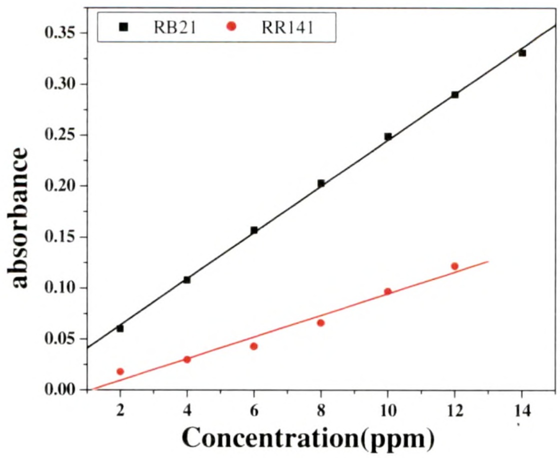


Figure 4.3: Calibration graph of RB21 and RR141

4.6 Optimization parameters for adsorption of Reactive Dyes:

4.6.1 Effect of adsorbent dose on the adsorption:

The effect of the amount of APSP and chitosan on the uptake of RR-141 and RB-21 was studied and the results have been presented in Figure 4.4 and Table.4.1. The experiments were conducted by taking different adsorbent doses from (0.01 to 0.2) g in 25 mL of dye solution. Other parameters like pH, contact time and temperature were kept constant. The removal increased from 74 % to 100 % and 30 % to 96 % for RB-21 and for RR-141 respectively with increased adsorbent dose from (0.01 to 0.08) g in the case of APSP and from 27 % to 92 % and 18.5 % to 94 % for RB-21 and RR-141 respectively with increased adsorbent dose from (0.02 to 0.18) g in the case of chitosan as adsorbent. This can be attributed to the larger availability of active sites for the same number of adsorbate molecules. The dyes are seen to require a greater dose of chitosan as compared to palm shell powder which could be attributed to a lesser number of active sites as compared to APSP.

Table 4.1: Variation in the dose on Adsorption

Initial Concentration: 50 ppm, adsorbent: APSP, Chitosan, Adsorbate: RR141 and RB21, Volume of aqueous phase: 25 mL, Contact time: 60 min (APSP), 120 min (Chitosan), Temperature: 30^{0}C, pH: 3(RB21), 4(RR141) for APSP and 4 (RR21, RB141) for Chitosan, Adsorbent Dose: 0.01-0.08 g (APSP) and 0.02-0.18g (Chitosan)

Percentage Uptake of Reactive Dyes					
APSP			Chitosan		
Dose (g)	**RB21**	**RR141**	**Dose (g)**	**RB21**	**RR141**
0.01	74.9534	30.9779	0.02	27.2917	-
0.02	96.7788	70.8239	0.04	53.4375	-
0.03	98.1677	87.9557	0.06	65.3125	18.5517
0.04	100.9454	91.4206	0.08	80.3125	52.3448
0.05	100.8462	95.2705	0.1	83.0208	63.7241
0.06	101.9375	96.4254	0.12	87.8125	80.9655
0.07	101.6399	96.4254	0.14	89.5833	85.4483
0.08	102.2351	96.4254	0.16	91.1458	92.3448
			0.18	92.1875	93.7241

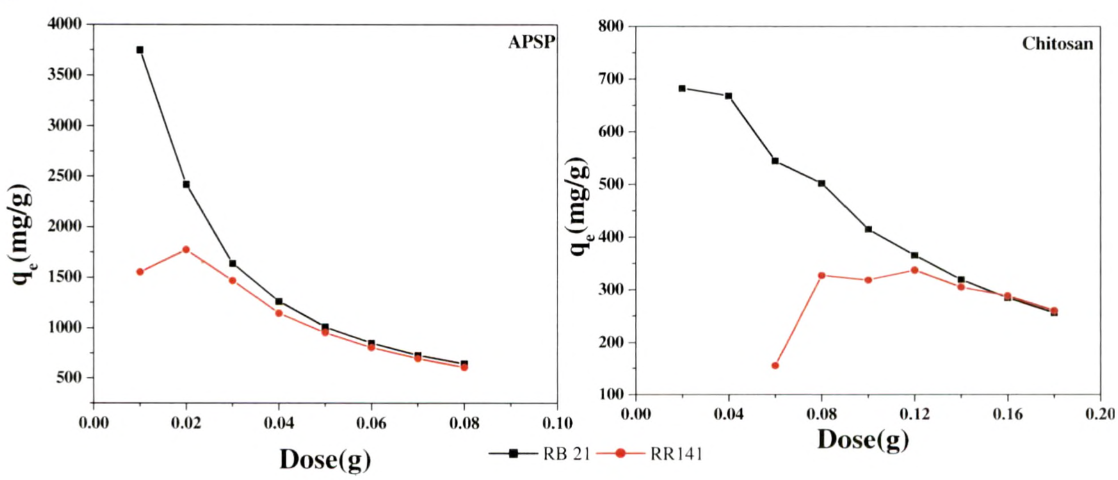


Figure 4.4: Effect of adsorbent dose on adsorption of dyes

4.6.2 Effect of Reactive Dye concentration and Agitation time:

The effect of reactive dye concentration on their uptake by APSP and chitosan were studied at a constant temperature of 30°C by taking 50-200 ppm of the respective dyes in a total volume of 25 mL, in contact with an adsorbent dose of 0.05g of APSP and 0.1g of chitosan respectively maintained at a pH of 3 for RB 21 and 4 for RR 141. The results in Figure 4.5 and Table 4.2 indicate that the increase in reactive dye concentration resulted in decrease in % uptake of the dyes in the case of both APSP and chitosan. To evaluate the effect of contact time between dyes and sorbent (APSP and chitosan) the agitation time was varied between 30-180 min. The results are shown in Table 4.2 and Figure 4.5. It is seen that adsorption is fast and equilibrium is achieved within 60 min for APSP and ~ 120 min for chitosan. Chitosan requires a greater contact time to achieve equilibrium. The solutions were equilibrated for 60 min for APSP and 120 min for Chitosan.

The adsorption of dyes was rapid during the initial stages of the sorption process, followed by a gradual process. The dye molecules have to first encounter the boundary layer effect, then adsorb from the surface and finally they have to diffuse into the porous structure of the adsorbent which takes a longer time[4.29].

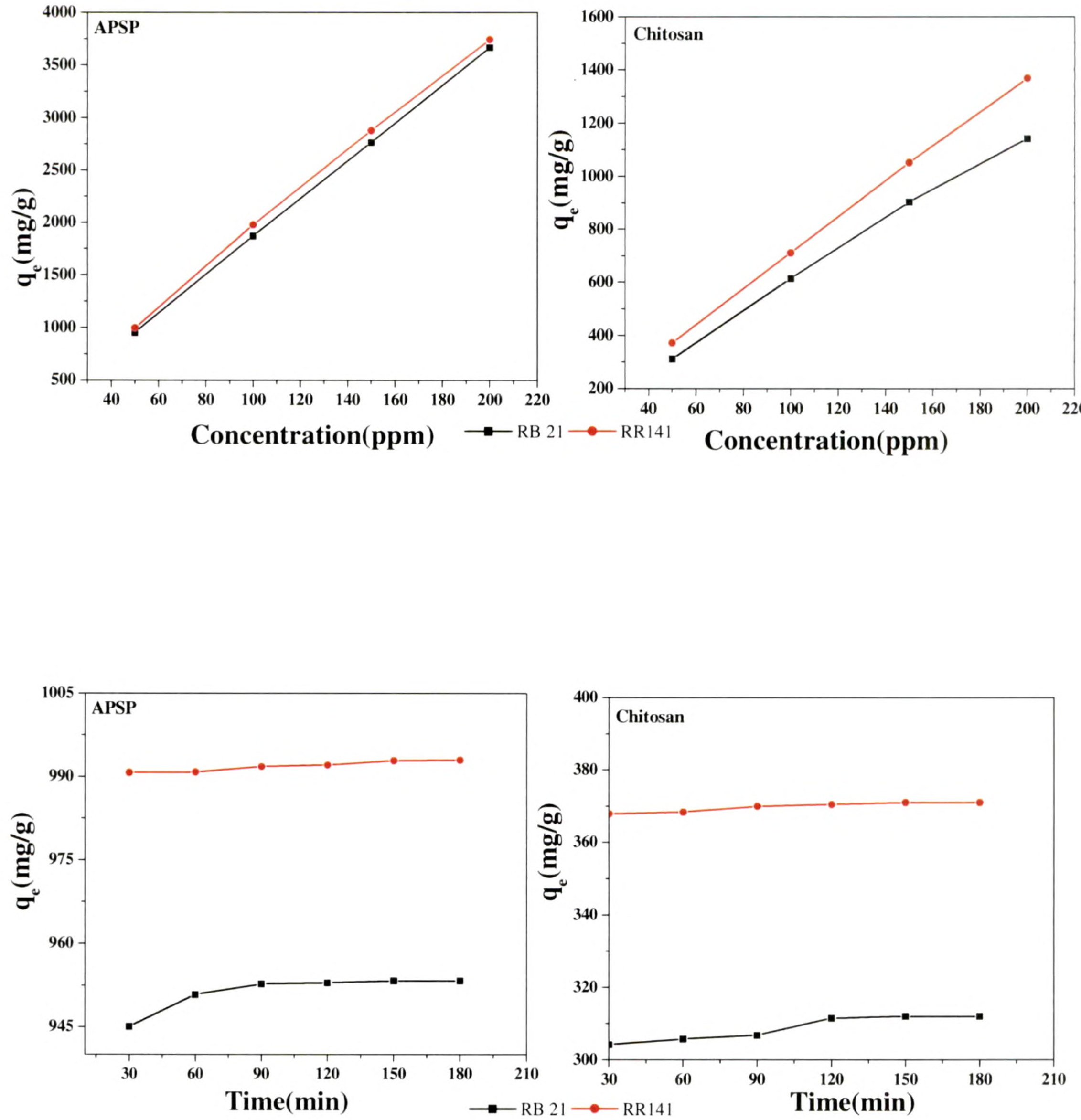


Figure 4.5: Effect of Concentration and agitation time on amount of dye adsorbed on APSP and Chitosan

Table 4.2: Percentage uptake of reactive dyes with variation in time and concentration

Initial Concentration: 50-200 ppm, adsorbent: APSP, Chitosan, Adsorbate: RR141 and RB21, Volume of aqueous phase: 25 mL, Contact time: 30-180 min, Temperature: 30^0C, pH: 3(RB21), 4(RR141) for APSP and 4 (RR21, RB141) for Chitosan, Adsorbent Dose: 0.05 g (APSP) and 0.1 g (Chitosan)

Time (min)	Percentage Uptake of Reactive dyes on APSP							
	Concentration (ppm)							
	Reactive Blue 21				Reactive Red 141			
	50	100	150	200	50	100	150	200
30	94.5005	93.3455	91.9981	91.4206	99.0605	98.7629	95.6875	93.5050
60	95.0780	93.5380	92.0943	91.6131	99.0704	98.6835	95.7470	93.4355
90	95.2705	93.7305	92.2483	91.5938	99.1696	98.7034	95.7550	93.4454
120	95.2900	93.7305	92.4601	91.8056	99.1994	98.7728	95.8363	93.4752
150	95.3282	93.8268	92.4986	91.6708	99.2788	98.7827	95.8562	93.4752
180	95.3282	93.8075	92.5371	91.7093	99.2887	98.8125	95.8661	93.4851
	Percentage Uptake of Reactive dyes on Chitosan							
30	60.8333	59.4792	58.9583	55.3125	73.5417	69.8958	68.8854	66.7708
60	61.1458	60.0000	59.4792	55.7292	73.6458	70.3125	68.9063	67.0833
90	61.3542	61.0417	60.0000	56.4583	73.9583	70.5208	68.9792	67.9167
120	62.2917	61.3542	60.2083	57.0833	74.0625	70.9375	70.0208	68.3333
150	62.3958	61.4792	60.3125	58.1250	74.1667	71.3542	70.0417	68.4375
180	62.3958	61.4896	60.3125	58.1250	74.1667	71.4583	70.0417	68.4375

4.6.3 Effect of pH on the adsorption:

The effect of pH on the adsorption of RB-21 and RR-141 by chitosan and APSP was studied by varying the solution pH over a range of 1-11 using 0.1 N NaOH /HCl. The results in Figure 4.6 and Table 4.3 reveal that when APSP was used as adsorbent the removal was at a maximum at the initial pH of 3 and 4 for RB-21 and RR-141 respectively and remained constant with (97 to 100) % removal up to pH 9.0. This suggests that two possible mechanisms of the adsorption of reactive dyes on APSP may be operating. At acidic pH an electrostatic attraction exists between the protonated surface of APSP and the negatively charged acidic dyes. The removal of anionic dyes at alkaline pH, where the adsorbent is negatively charged cannot be explained based on electrostatic attraction. There might be another mechanism of adsorption like ion exchange or chemisorption might be operative. A similar trend was observed for the adsorption of Congo red on activated carbon prepared from coir pith [4.30], adsorption of Congo Red [4.15], Acid Brilliant Blue [4.13] and Acid Violet [4.14] on a biogas residual slurry and adsorption of Congo Red on waste orange peel [4.20] and banana pith [4.16].

Figure 4.6 and Table 4.3 represent the RB-21 and RR-141 removal efficiency at equilibrium for varying pH in the range of 1 to 10 using chitosan as adsorbent. The optimum pH is 4 for both RB-21 and RR-141 using chitosan. When the pH is lower than the pK_a of chitosan, the nitrogen containing functional groups of chitosan are protonated and the positive charge would be expected to attract anions. At neutral pH the electrostatic balance between anionic and cationic groups on chitosan would make it less favourable for dye binding.

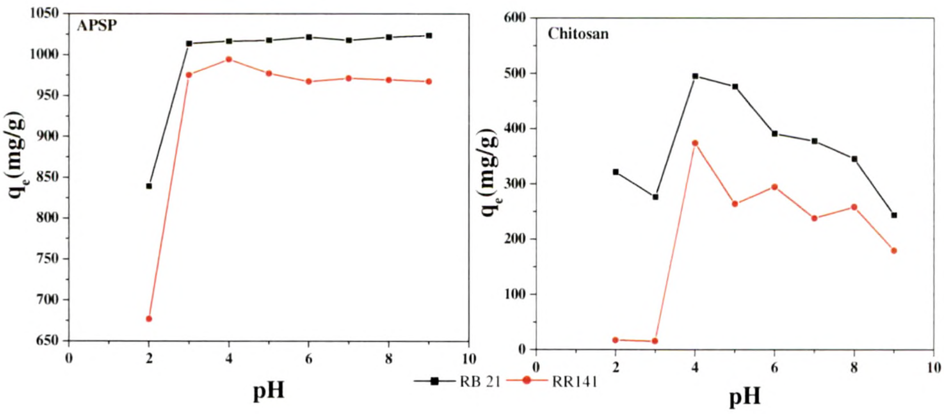


Figure 4.6: Effect of pH on the adsorption of Reactive dyes on APSP and Chitosan

Table 4.3: Percentage Uptake of Reactive dyes at pH vatiation

Initial Concentration: 50ppm, adsorbent: APSP, Chitosan, adsorbate: RR141 and RB21, Volume of aqueous phase: 25 mL, Contact time: 120 min for chitosan and 60 min for APSP, Temperature: 30^{0}C, pH: 2-9, Adsorbent Dose: 0.05g (APSP) and 0.1g (Chitosan)

pH	Percentage Uptake of Reactive dyes			
	APSP		Chitosan	
	RB21	RR	RB121	RR
2	83.8819	67.5515	64.2708	3.0345
3	101.3423	97.3879	55.2083	2.6897
4	101.6399	99.3128	98.9583	74.4138
5	101.7391	97.5804	95.2083	52.3448
6	102.1359	96.6179	78.1250	58.5517
7	101.7391	97.0029	75.5208	47.1724
8	102.1359	96.8104	69.0625	51.3103
9	102.3343	96.6179	48.6458	35.4483

4.6.4 Effect of temperature:

The removal of RR-141 and RB-21 was investigated as a function of temperature and results are given in Figure 4.7 and Table 4.4. The removal increased from 77 % to 95 % and 92 % to 100 % respectively using APSP as adsorbent by increasing the temperature from (30 to 70) °C and 21 % to 94 %, and 66 % to 91 % respectively using chitosan as adsorbent for RR141 and RB21. The extent of adsorption of both dyes using both the adsorbents was found to increase with temperature indicating the endothermic nature of the process. The increase in dye adsorption with increasing temperature might be due to an increase in the number of active surfaces available for adsorption with an increase in temperature and due to an enhanced rate of intra-particle diffusion of the adsorbate as diffusion is an endothermic process. [4.31]

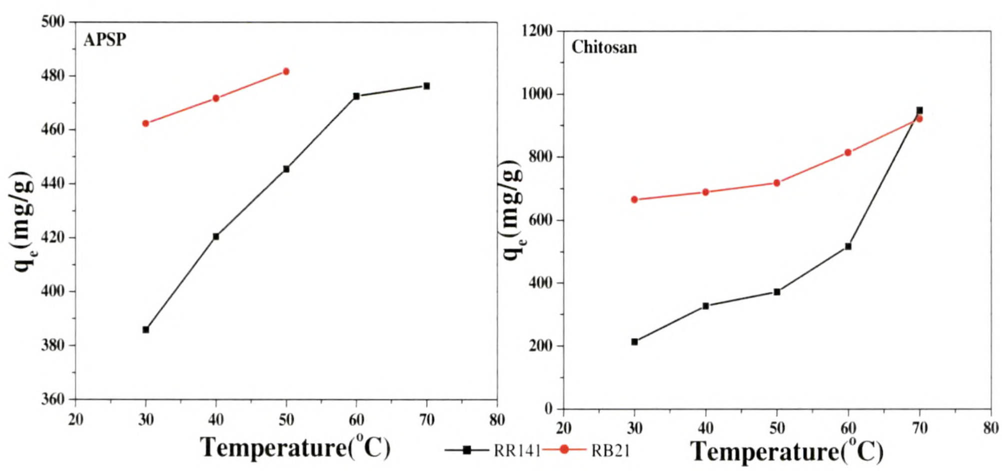


Figure 4.7: Effect of Temperature on amount of dye adsorbed on APSP and Chitosan

Table 4.4: Variation in the temperature on adsorption of reactive dyes

Initial Concentration: 50 ppm, adsorbent: APSP, Chitosan, adsorbate: RR141 and RB21, Volume of aqueous phase: 25 mL, Contact time: 60 min APSP and 120 min Chitosan, Temperature: 30^{0}C, pH: 1-11, Adsorbent Dose: 0.05g (APSP) and 0.1g (Chitosan)

Temperature (^{o}C)	Percentage uptake of reactive dyes			
	APSP		Chitosan	
	RR 141	RB 21	RR 141	RB 21
30	77.1761	92.4137	21.3103	66.25
40	84.1059	94.2986	32.6896	68.6458
50	89.1107	96.2827	37.1724	71.5625
60	94.5005	100	51.6551	81.1458
70	95.2705	100	94.7586	91.875

4.6.5 Adsorption Isotherms:

The adsorption isotherms were obtained for RB-21, RR-141 onto chitosan and APSP adsorbent systems. The Langmuir and Freundlich isotherm constants at different temperatures for the adsorption of RR-141 and RB-21 onto chitosan and APSP are reported in Table 4.5. Equilibirium adsorption data of RR-141 and RB-21 onto APSP and chitosan fitted both the Langmuir and Freundlich equations. Similar observations were made by Sarkar et.al [4.32-4.34]. Comparing the parameters K_f and q_m values indicates that increasing temperature increased the adsorption capacities of the reactive dyes. With increasing temperature from 30 ^{0}C to 50 ^{0}C the values of q_m increased for RR-141 (5.0499 and 22.480 to 7.713 and 13.592) mg/g and RB-21 (16.548 and 70.028 to 19.040 and 24.866) mg/g onto chitosan and APSP respectively indicating the endothermic nature of adsorption.

Table 4.5: Isotherm parameters

Initial Concentration: 50ppm, adsorbent: APSP, Chitosan, adsorbate: RR141 and RB21, Volume of aqueous phase: 25 mL, Contact time: 60 min APSP and 120 min Chitosan, Temperature: 30-50^{0}C, pH: 3(RB21), 4(RR141) for APSP and 4 (RR21, RB141) for Chitosan, Adsorbent Dose: 0.05g (APSP) and 0.1g (Chitosan)

Isotherms	Parameters	APSP		Chitosan	
		RR-141	RB-21	RR-141	RB-21
Freundlich					
30^{0}C	K_f (mg/g)(dm^3/mg)$^{1/n}$	24.8307	25.3472	24.2141	24.7320
	N	-18.1400	-11.9900	-0.4830	-9.5474
	r^2	0.9490	0.9380	0.9630	0.9120
40^{0}C	K_f (mg/g)(dm^3/mg)$^{1/n}$	25.5470	25.2600	28.1916	24.7320
	N	-11.3200	-14.9340	-11.3410.	-20.0120
	r^2	0.9310	0.9406	0.8970	0.9250
50^{0}C	K_f (mg/g)(dm^3/mg)$^{1/n}$	28.6767	25.5517	24.9910	22.9910
	N	-6.2984	-20.3046	1.0000	8.4170
	r^2	0.96631	0.9580	1.0000	0.9380
Langmuir					
30^{0}C	q_e (exp)	19.2940	23.5740	18.6035	19.0820
	q_m (mg/g)	7.7130	19.0400	5.04990	16.5480
	K_a (L/mg)	-0.3920	11.9900	-0.0738	-0.6110
	r^2	0.9500	0.9760	0.9160	0.9670
40^{0}C		22.8090	25.3600	13.9428	17.8960
	q_m (mg/g)	18.6200	13.1670	19.1570	22.3910
	K_a (L/mg)	-2.0210	16.4320	-4.7880	-8.4740
	r^2	0.9370	0.9970	0.9120	0.9970
50^{0}C	q_m (mg/g)	13.9540	24.8660	22.4800	70.0280
	K_a (L/mg)	-0.73354	34.079	4.455	0.384
	r^2	0.974	0.9998	0.921	0.977

From Figure 4.8 it was observed that the n value lesser than one indicates the better removal efficiency of reactive dyes and the Freundlich isotherm is good fit in the case of both the dyes on APSP and Chitosan and the negative values of Ka indicates Langmuir is not such a better fit for RR141 on APSP and RR141 and RB 21 on Chitosan at 30 and 40°C.

Table 4.6 compares the adsorption capacity of different types of adsorbents used for reactive dye adsorption. It is seen that the adsorbents used have comparable adsorption capacity to many of those reported in the literature.

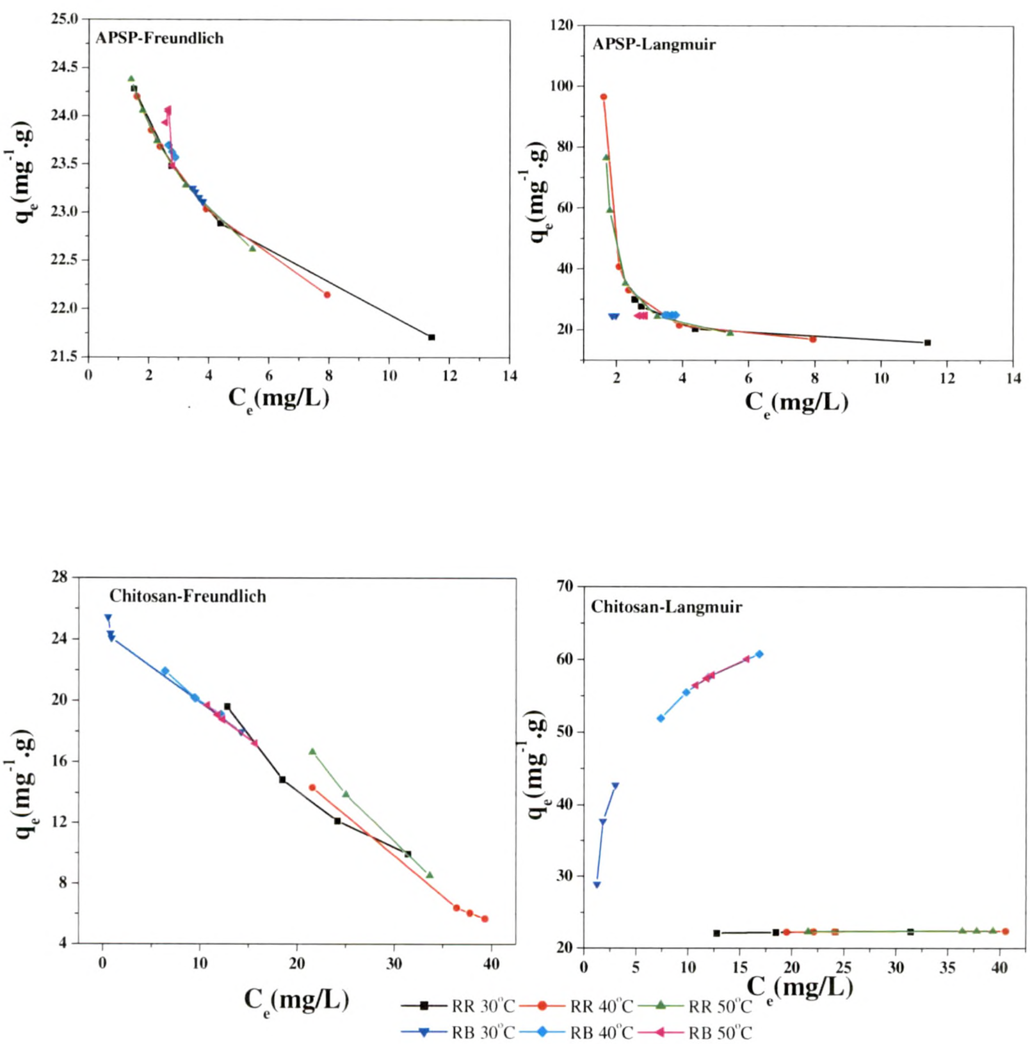


Figure 4.8: Isotherm for RR141 and RB21

Table 4.6: Comparison of adsorption capacities of agro-based adsorbents

Adsorbent	Dye	Adsorption capacity mg/g	References
Activated carbon from coir pith	Congo red	6.7 mg/g	[4.30]
Carbon slurry waste	Congo Red	272 mg/g	[4.35]
Sun flower stalk	Congo Red	26.8 mg/g	[4.17]
Waste metal hydroxide sludge	Reactive Red2, Reactive Red 120, and Reactive Red 141	(48 to 62) mg/g	[4.36]
Preprotonated chitosan	Reactive Black 5	(750 to 1000) mg/g	[4.37]
Commercial activated carbon	Reactive orange	714 mg/g	[4.38]
Ethylenediamine modified rice hull	Reactive orange 16	24.88 mg/g	[4.39]
Surfactant modified Activated Carbon	Reactive Black 5	0.11 mmol/g	[4.40]
APSP, chitosan	Reactive Red	(13.94 and 22.48) mg/g	Present study
APSP, chitosan	Reactive Blue	(24.866 and 70.02) mg/g	Present study

4.6.6 Adsorption Dynamics:

The kinetics of sorption of anionic dyes was investigated using the pseudo-first order, pseudo-second order and intra-particle diffusion reaction models.

In order to investigate the adsorption process of the dyes on APSP and chitosan, the pseudo first order, pseudo second order and intra-particle diffusion models were used. The rate of RR-141 and RB-21 adsorption by chitosan and APSP has been investigated under optimum pH and temperature conditions using four different concentrations. The coefficients of determination were found to be higher for the second order (> 0.95) than the first order (> 0.81) for both RR-141 and RB-21 onto chitosan and APSP. The calculated q_e values increased with an increase in the initial dye concentration. The rate constants of both dyes varied over a wide range suggesting that limiting steps may be chemisorption involving valency forces through the sharing and exchange of electrons between the sorbent and substrate [4.41]. The experimental data were also evaluated by the intra-particle diffusion kinetic model in order to investigate whether intra-particle diffusion is rate limiting. The coefficients of determination r^2 for the intra-particle diffusion are not lower than that of the pseudo – second order model (Table 4.7) and the plots do not pass through the origin as seen from Figure 4.9 indicating some degree of boundary layer control and also that intra-particle diffusion is not the only rate-limiting step, but also other kinetic processes may control the rate of adsorption, all of which may be operating simultaneously [4.42].

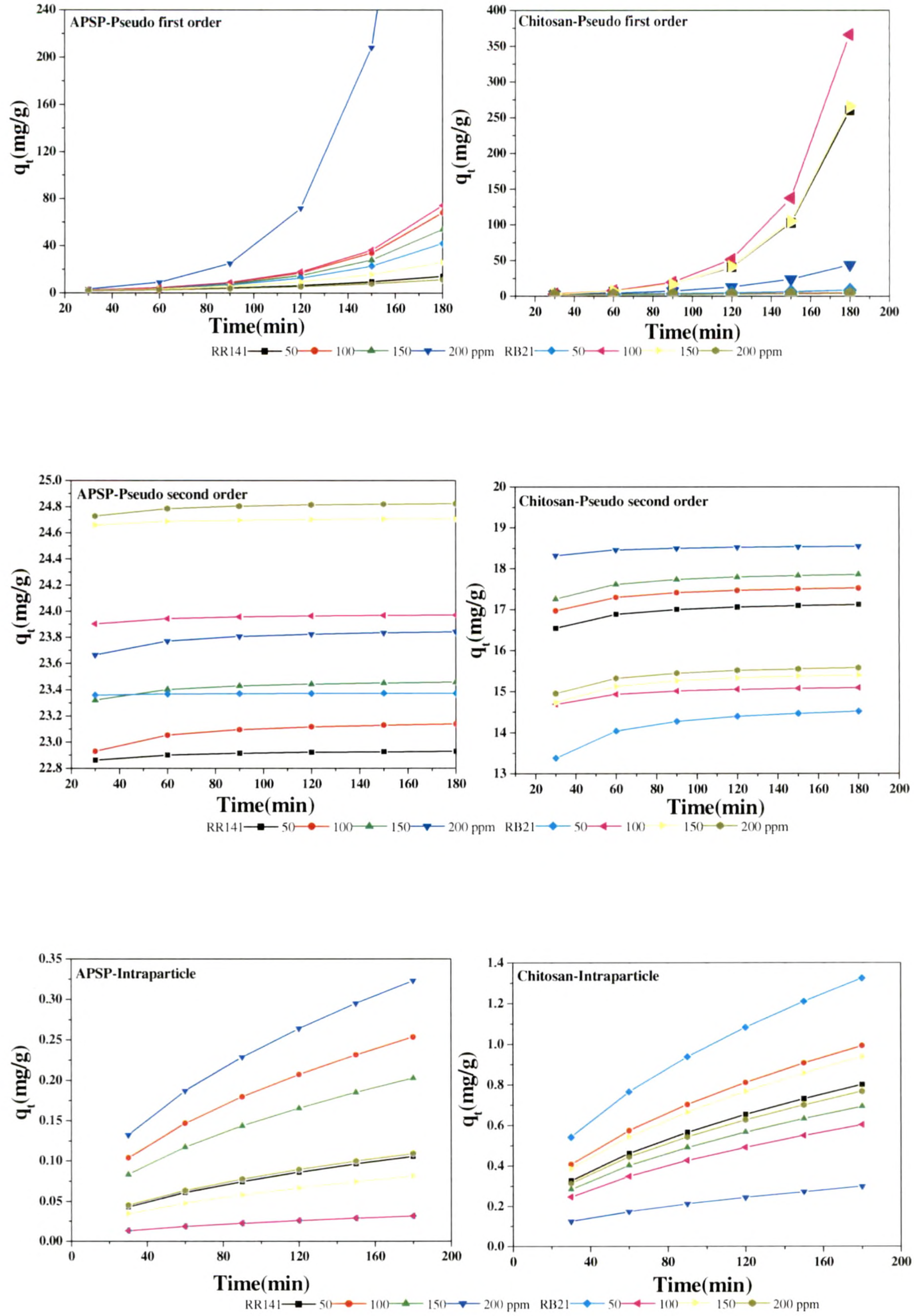


Figure 4.9: Kinetics for RR141 and RB21

Table 4.7: Kinetic parameters

Initial Concentration: 50-200 mg/L, adsorbent: APSP, Chitosan, adorbate: RR141 and RB21, Volume of aqueous phase: 25 mL, Contact time: 60 min APSP and 120 min Chitosan, Temperature: 30^{0}C, pH: 3(RB21), 4(RR141) for APSP and 4 (RR21, RB141) for Chitosan, Adsorbent Dose: 0.05g (APSP) and 0.1g (Chitosan)

Kinetics	Parameters	APSP		Chitosan	
		RR-141	RB-21	RR-141	RB-21
Pseudo 1st order					
50 (mg/L)	q_e (mg/g)	12.4420	2.5027	17.416	28.7070
	K (min^{-1})	0.0213	0.0434	9.8798	0.0330
	r^2	0.9830	0.9900	0.9900	0.8130
Pseudo 2nd order					
50 (mg/L)	q_e (exp)(mg/g)	23.6251	24.7676	18.3854	15.2864
	q_e (mg/g)	26.9170	25.6800	27.9560	27.9480
	K (g/mgmin)	0.0371	0.0565	2.750308 $\times10^{-4}$	1.3352642 $\times10^{-3}$
	r^2	0.9964	1	0.9800	0.9900
Intra-particle Diffusion					
50 (mg/L)	K_i (mg/gmin$^{0.5}$)	1.35402	0.9590	1.1926	0.0395
	r^2	0.1899	0.9250	0.9990	0.9576

4.6.7 Adsorption Thermodynamics:

The studies of temperature influence on adsorption of reactive dyes on Chitosan and APSP is following the trend of endothermic reaction. The thermodynamic parameters of the adsorption process could be determined from the experimental data obtained at various temperatures using the equations:

$\Delta G^{\circ} = - RT\ln K_d$

$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$

Where, ΔG° is gibbs free energy, ΔH° is enthalpy of the reaction, ΔS° is entropy of the reaction, R is gas constant, T is temperature in °K, K_d is distribution coefficient. The positive values of ΔH^0 reported in Table 4.8 indicate the endothermic nature of RR141 and RB21 adsorption on APSP and Chitosan respectively and reveal that the mechanism of adsorption is chemisorption. From the Table 4.8 the positive ΔG^0 values suggest a non spontaneous adsorption process for reactive dyes.

Table 4.8: Adsorption Thermodynamics of Reactive dyes adsorption on APSP and Chitosan

Parameter	APSP		Chitosan	
	RR	RB	RR	RB
ΔG°KJ/mol	8.5321	5.3034	13.1458	8.1559
ΔH°KJ/mol	41.0236	52.1074	80.8770	36.7367
ΔS°J/mol/K	-0.1070	-0.1529	-0.2190	-0.0916

4.6.8 Banghams equation:

The double logarithmic plot according to Bangham equation yielded non-linear curves showing that the diffusion of the adsorbate into the pores of the sorbent does not perfectly control the sorption process. From the Figure 4.10 it is showing that the non-linearity of these plots confirms the non-applicability of Banghams equation and indicated that the adsorption of the reactive dyes RB 21 and RR 141 is not a pore diffusion controlled.

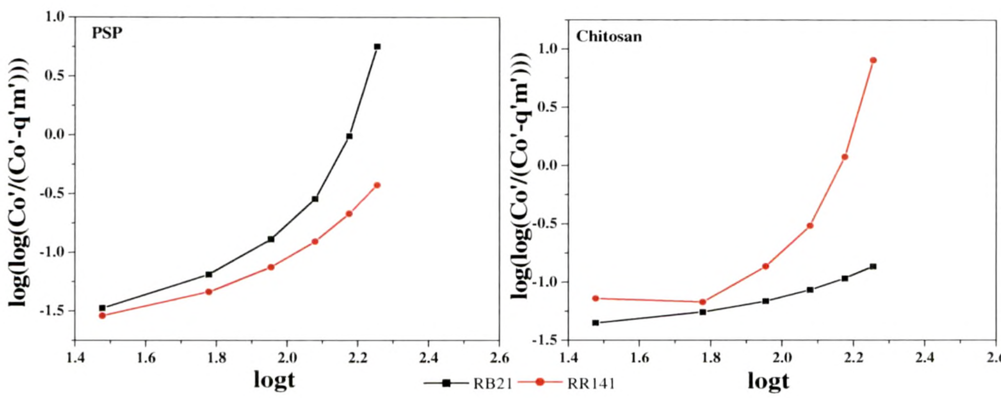


Figure 4.10: Banghams plots of RB 21 and RR 141 on the adsorption of APSP and Chitosan

4.7 Conclusion:

Acid treated palm shell powder and chitosan were used as low cost adsorbents for the removal of Reactive Red and Reactive Blue from aqueous solution. Equilibrium adsorption is achieved in about 60 min for APSP and 120 min for chitosan. The adsorption of the two dyes increase with an increase in temperature using both chitosan and APSP suggesting that the process is endothermic. The results indicate that the data fit both the Freundlich model and Langmuir model for RR-141 and RB-21 onto APSP as well as chitosan. Kinetic data tended to fit well the second order kinetic model. The reactive dyes are bound to chitosan through electrostatic attraction, between the anionic groups of the dyes and the protonated amine groups of the chitosan below the pK_a value of chitosan. Chitosan was found to have higher adsorption capacity as compared to APSP. The study can be useful in the design of treatment plants for dye containing effluents.

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