4

RESULTS AND DISCUSSION

In the present work the feasibility of removal of selected textile dyes Crystal Violet, Acid Blue 110, Reactive Black 5 and Congo Red from aqueous solution using low-cost, eco-friendly activated carbon adsorbents (BR-SAC & BR-PAC) were carried out. The activated carbon used in this study was prepared from the fruit pods of *Bauhinia racemosa* using concentrated sulphuric acid and 60% phosphoric acid. Batch mode adsorption studies were conducted by varying the parameters such as initial dye concentration, pH, adsorbent dosage, agitation time and temperature with the low-cost adsorbents prepared. The results of the work with suitable discussions were given in this chapter.

4.1 Effect of Initial Dye Concentration and Contact Time on the Removal of Dyes from Aqueous Solution:

To evaluate the adsorption capacity of the absorbents for the dye molecules, it is essential to study the distribution of the dyestuffs between the adsorbent and adsorbate at equilibrium **(Mckay *et al*., 1999).** Batch mode experiments were executed by varying the initial concentration of the dye solution (30, 50 70 and 100mg/l) at pH 6.8 $\pm$ 0.2 and at temperature 32$\pm$2°C using the adsorbents BR-SAC and BR-PAC at various time intervals (10 to 160 minutes). The experimental results obtained for the removal of various dyes (CV, AB 110, RB5 & CR) are shown in **Tables 4-11** and **Figures 4–11.**

From the results it was observed that the percentage adsorption of dye molecules from aqueous dye solution with the adsorbent BR-SAC reduced with raise in concentration of the dye solutions and increased with increase in contact time. The percentage adsorption of dyes from aqueous solution revealed a decreasing trend from 99.36% to 83.21% for CV dye (Table 4), 97.98% to 80.90% for AB110 dye (Table 5), 93.44% to 73.64% for RB5 dye (Table 6) and 92.7% to 77.92% for CR dye (Table 7) as the initial adsorbate concentrations were changed from 30 to 100 mg/l in 160 minutes of contact time (Figures 4 to 7).

Similarly the percentage adsorption of dye molecules from aqueous solution with the adsorbent BR-PAC also decreased from 99.86% to 91.96% for CV (Table 8), from 98.88% to 87.85% for AB110 (Table 9), from 97.88% to 87.88% for RB5 (Table 10) and from 99.20% to 89.00% for CR (Table 11) as the initial dye concentrations were varied from 30 to 100 mg/l in 120 minutes of contact time (Figures 8 to11)

This may be because of the fact that a fixed adsorbent dose contains fixed number of adsorption sites. Therefore at higher initial dye concentration, lesser number of surface active adsorption sites present on the surface of the adsorbents exhibited a lower dye removal percentage **(Bharathi and Ramesh, 2013; Samarghandy *et al.,* 2011; Kannan and Sundaram, 2001).**

. Moreover the adsorption capacity (q) of adsorbents was enhanced with raise in dye concentration because the initial dye concentration gives a driving force to surmount the mass transfer resistance of the dye molecules between the aqueous and solid phase **(Ansari *et al*., 2012; Bulut and Aydin, 2006).** The q values of adsorbent BR-SAC increased from 29.81 to 83.21mg/g for CV dye, 29.39 to 80.90mg/g for AB110 dye, 28.03 to 72.12mg/g for RB5 dye and 27.83 to 76.14mg/g for CR dye. Similarly the amount of dye adsorbed by the adsorbent BR-PAC increased from 59.92 to 183.92mg/g for CV dye, 59.33 to 175.7mg/g for AB 110 dye, 58.73 to 175.76mg/g for RB5 dye and 59.52 to 178mg/g for CR dye.

The adsorption rate was prominent in the early stages of adsorption due to immediate uptake of dye molecules by the outer surface and subsequently the dye molecules goes into the interior surface of the adsorbent which is comparatively a slow process **(Ayesha wasti and Ali Awan, 2016; Ahmad and Kumar, 2010).** Also, at higher initial dye concentration, the development of subsequent layers of the dye molecules is disturbed due to the existence of repulsive interactions among the adsorbed dye molecules on the adsorbent surface and unadsorbed dye molecules exist in the solution **(Theivarasu *et al*., 2010; Venckatesh *et al.,* 2010).**

The results obtained in this study are in good agreement with the results reported on the removal of Reactive Black dye on acid treated potato peel waste **(Samarghandy *et al*., 2011)**, modified wheat straw **(Nadar Yousefi *et al*., 2011),** Congo Red dye removal using saw dust modified carbon **(Reza Ansari *et al*., 2012),** Algerian kaolin**(Meroufel *et al*., 2013),** biowaste material **(Sumanjit Kaur *et al*., 2013),** removal of Reactive Yellow dye on modified activated alumina (**Ayesha wasti and Ali Awan, 2016)** and removal of Malachite Green dye on wood apple shell **(Sartape *et al*., 2017)** and paper industry waste sludge **(Thakur *et al*., 2016).**

Table 4

Adsorption of CV Dye from Aqueous Solution with Variation of Initial Concentration of CV Dye Solution Using BR-SAC

Conditions: Adsorbent Dose: 100mg pH: 6.8 ± 0.2 Temperature: 32 ± 2°C

Time in minutes	Removal of Crystal Violet Dye (%)			
	Initial Dye Concentration			
	30mg/l	50mg/l	70mg/l	100mg/l
10	45.86	39.75	35.66	32.18
20	60.04	54.75	50.01	45.65
30	73.64	67.48	61.71	55.96
40	85.20	78.10	71.44	64.88
50	93.22	85.89	79.98	72.00
60	96.82	90.32	83.67	77.61
80	99.36	93.44	86.66	80.71
100	99.36	95.44	89.12	83.21
120	99.36	95.44	89.12	83.21
140	99.36	95.44	89.12	83.21
160	99.36	95.44	89.12	83.21

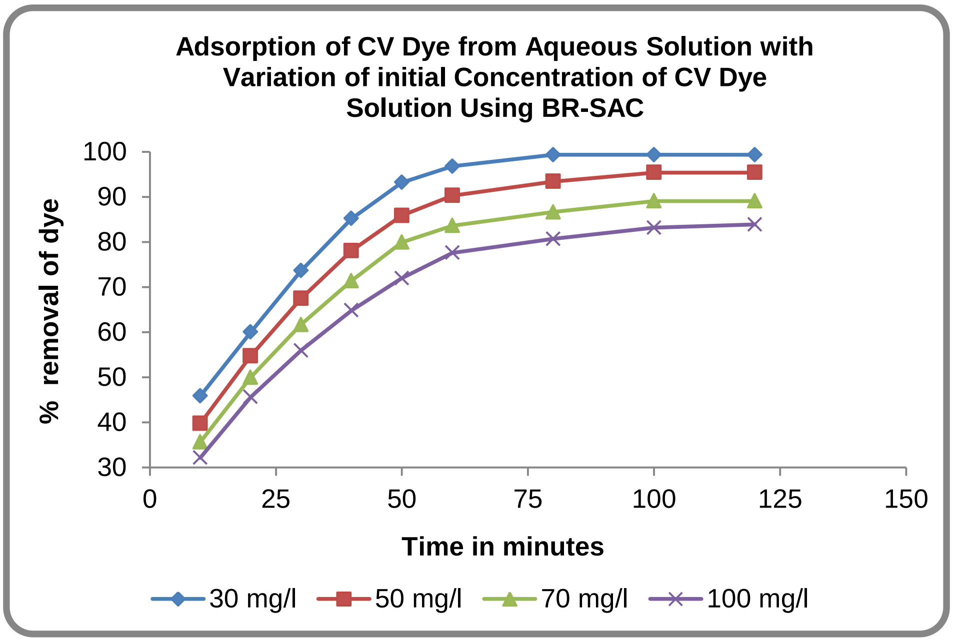


Figure 4

Table 5

Adsorption of AB110 Dye from Aqueous Solution with Variation of Initial Concentration of AB110 Dye Solution Using BR-SAC

Conditions: Adsorbent Dose: 100mg pH: 6.8 ± 0.2 Temperature: 32 ± 2°C

Time in minutes	Removal of AB 110 dye (%)			
	Initial Dye Concentration			
	30mg/l	50m/l	70mg/l	100mg/l
10	40.51	36.58	31.22	25.23
20	56.20	50.05	44.32	38.77
30	68.11	61.10	54.82	48.51
40	77.61	69.85	63.91	57.22
50	85.21	77.71	70.85	63.61
60	90.83	82.88	75.11	69.22
80	95.51	88.32	80.78	75.01
100	97.98	90.82	83.52	78.22
120	97.98	92.82	85.82	79.02
140	97.98	92.82	85.82	80.90
160	97.98	92.82	85.82	80.90

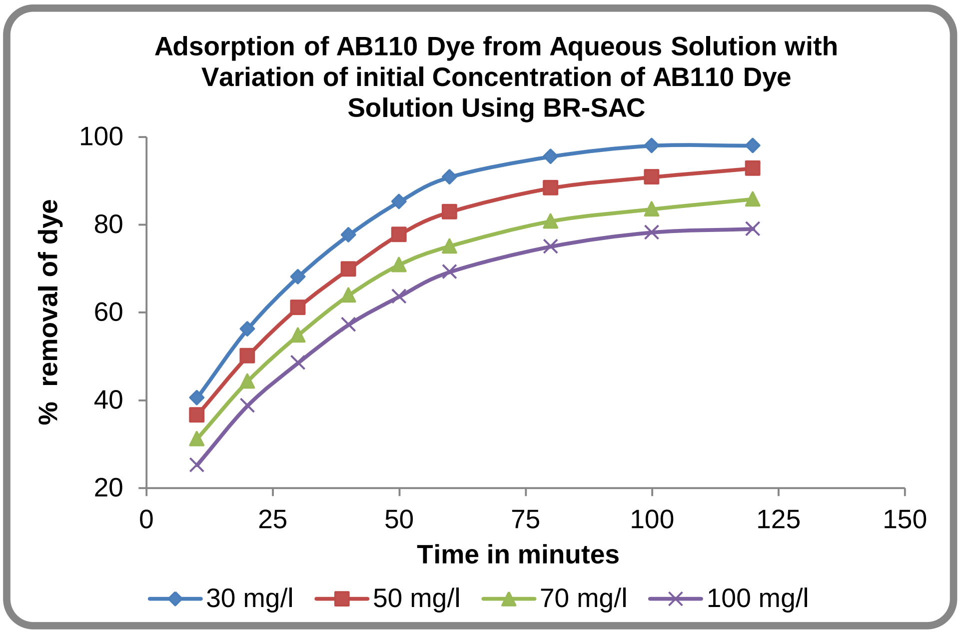


Figure 5

Table 6

Adsorption of RB5 Dye from Aqueous Solution with Variation of Initial Concentration of RB5 Dye Solution Using BR-SAC

Conditions: Adsorbent Dose: 100mg pH: 6.8 ± 0.2 Temperature: 32 ± 2°C

Time in minutes	Removal of RB5 dye (%)			
	Initial Dye Concentration			
	30mg/l	50mg/l	70mg/l	100mg/l
10	43.92	39.15	36.52	32.25
20	57.65	51.46	45.20	39.96
30	68.23	61.73	54.69	47.65
40	78.12	70.88	62.12	54.74
50	83.56	76.62	67.36	59.00
60	87.32	81.93	72.52	63.85
80	91.12	86.33	77.32	68.22
100	93.44	89.22	79.22	71.69
120	93.44	89.22	80.64	72.12
140	93.44	89.22	80.64	72.12
160	93.44	89.22	80.64	72.12

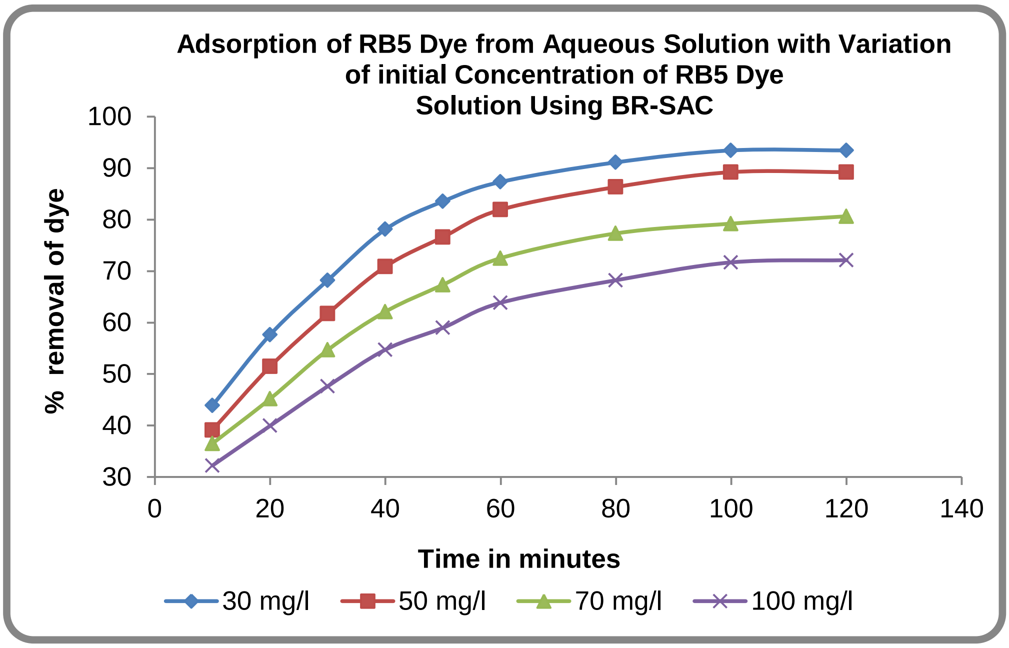


Figure 6

Table 7

Adsorption of CR Dye from Aqueous Solution with Variation of Initial Concentration of CR Dye Solution Using BR-SAC

Conditions: Adsorbent Dose: 100mg pH: 6.8 ± 0.2 Temperature: 32 ± 2°C

Time in minutes	Removal of CR dye (%)			
	Initial Dye Concentration			
	30mg/l	50mg/l	70mg/l	100mg/l
10	39.83	31.66	26.84	22.48
20	51.48	42.21	36.29	30.55
30	61.23	50.69	44.19	39.54
40	69.88	59.86	52.64	46.30
50	77.69	67.33	60.51	53.22
60	82.98	72.62	66.23	57.60
80	87.78	79.75	72.68	65.50
100	90.89	84.76	76.58	70.25
120	92.77	87.41	79.25	73.65
140	92.77	88.42	82.63	76.14
160	92.77	88.82	82.63	77.92

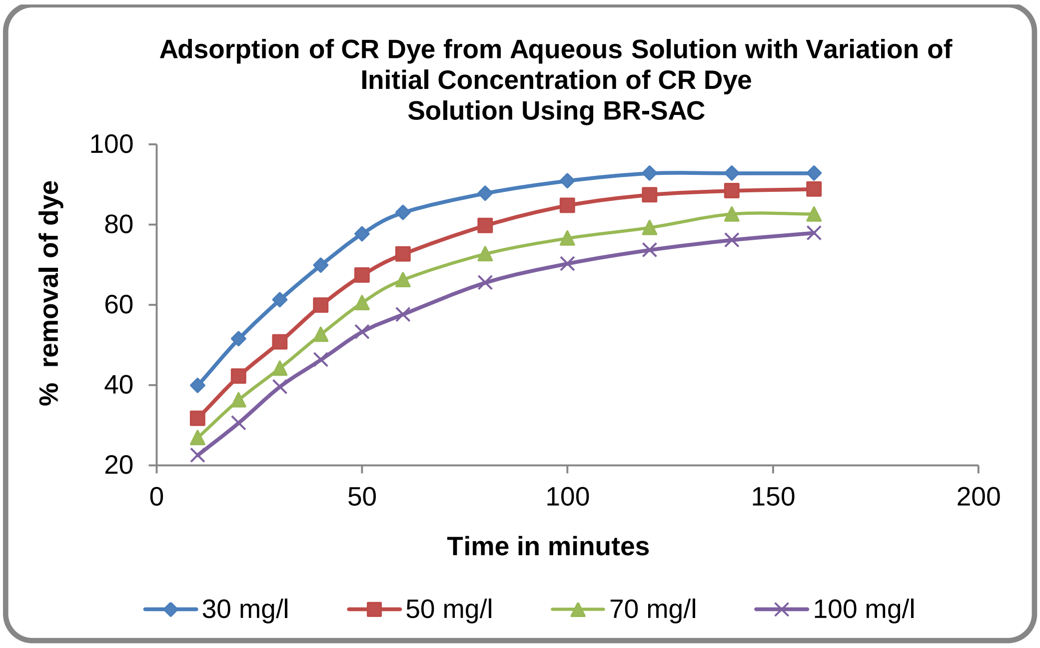


Figure 7

Table 8

Adsorption of CV Dye from Aqueous Solution with Variation of Initial Concentration of CV Dye Solution Using BR-PAC

Conditions: Adsorbent Dose: 50mg pH: 6.8 ± 0.2 Temperature: 32 ± 2°C

Time in minutes	Removal of Crystal Violet Dye (%)			
	Initial Dye Concentration			
	30mg/l	50mg/l	70mg/l	100mg/l
10	72.22	68.12	64.22	60.18
20	88.54	82.46	77.36	73.42
30	96.31	92.55	87.42	83.16
40	99.12	95.32	91.53	88.33
50	99.86	96.17	93.61	90.21
60	99.86	96.96	94.00	91.24
80	99.86	96.96	94.62	91.96
100	99.86	96.96	94.62	91.96
120	99.86	96.96	94.62	91.96

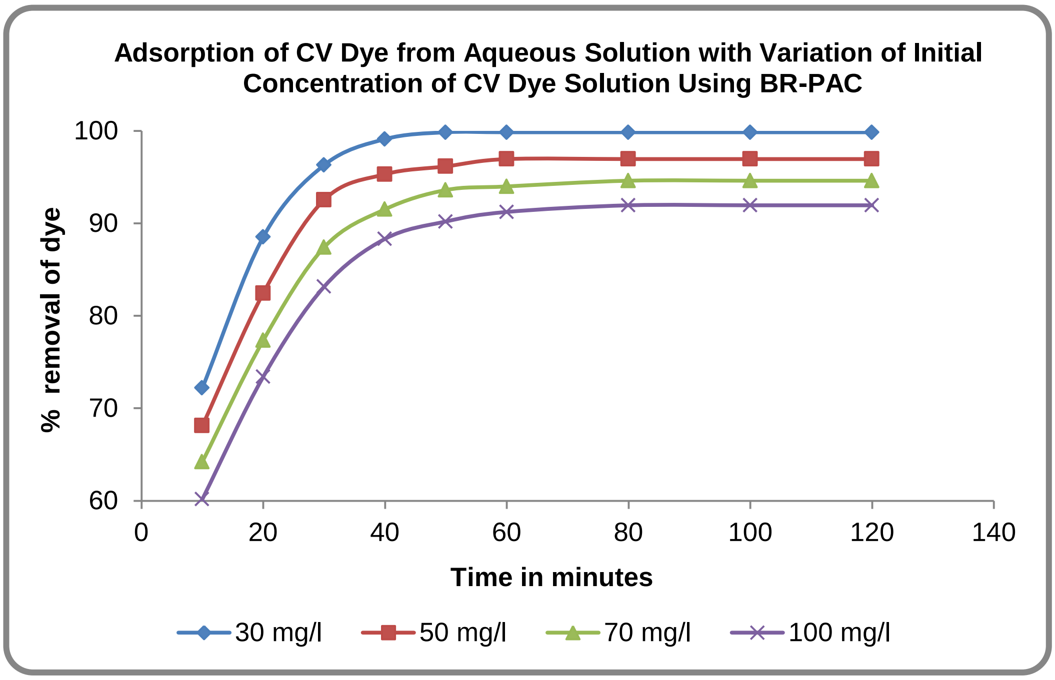


Figure 8

Table 9

Adsorption of AB110 Dye from Aqueous Solution with Variation of Initial Concentration of AB110 Dye Solution Using BR-PAC

Conditions: Adsorbent Dose: 50mg pH: 6.8 ± 0.2 Temperature: 32 ± 2°C

Time in minutes	Removal of AB110 dye (%)			
	Initial Dye Concentration			
	30mg/l	50mg/l	70mg/l	100mg/l
10	68.21	65.32	61.42	58.36
20	80.14	75.12	70.26	66.13
30	89.42	82.52	77.37	72.75
40	94.37	88.43	83.71	78.19
50	97.16	92.36	87.64	81.62
60	98.88	94.12	89.52	84.43
80	98.88	95.79	92.92	87.85
100	98.88	95.79	92.92	87.85
120	98.88	95.79	92.92	87.85

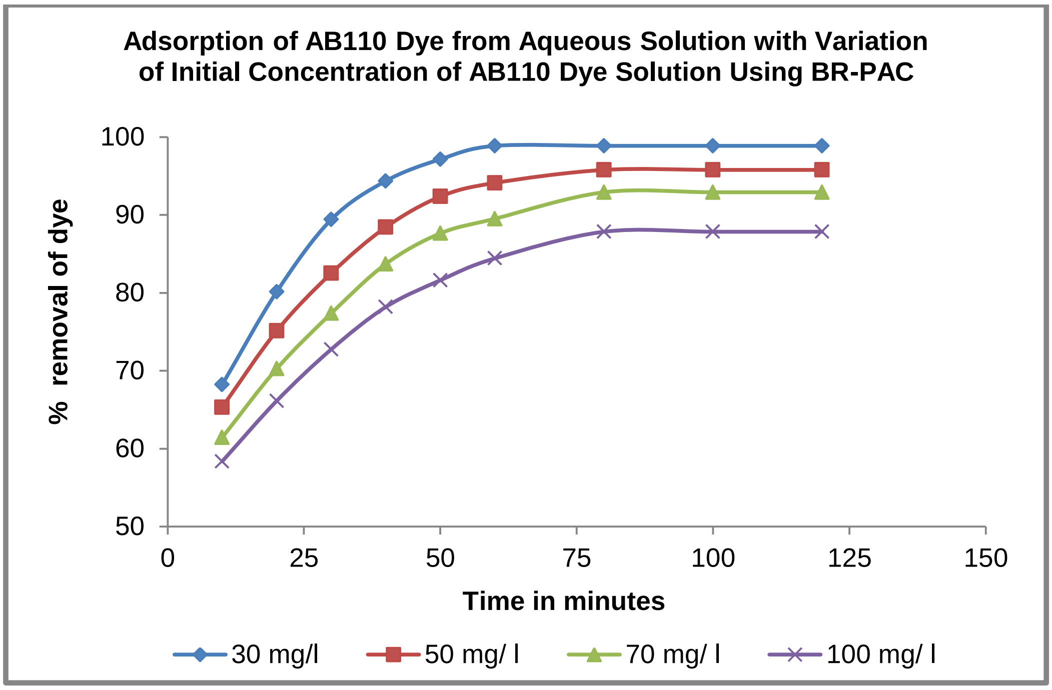


Figure 9

Table 10

Adsorption of RB5 Dye from Aqueous Solution with Variation of Initial Concentration of RB5 Dye Solution Using BR-PAC

Conditions: Adsorbent Dose: 50mg pH: 6.8 ± 0.2 Temperature: 32 ± 2°C

Time in minutes	Removal of RB5 dye (%)			
	Initial Dye Concentration			
	30mg/l	50mg/l	70mg/l	100mg/l
10	67.12	62.22	57.11	51.11
20	79.61	74.16	68.24	61.22
30	90.00	84.12	77.32	69.53
40	95.12	90.16	84.46	77.40
50	97.13	93.42	88.62	83.81
60	97.88	94.88	90.24	86.26
80	97.88	95.66	91.16	87.48
100	97.88	95.66	91.16	87.88
120	97.88	95.66	91.16	87.48

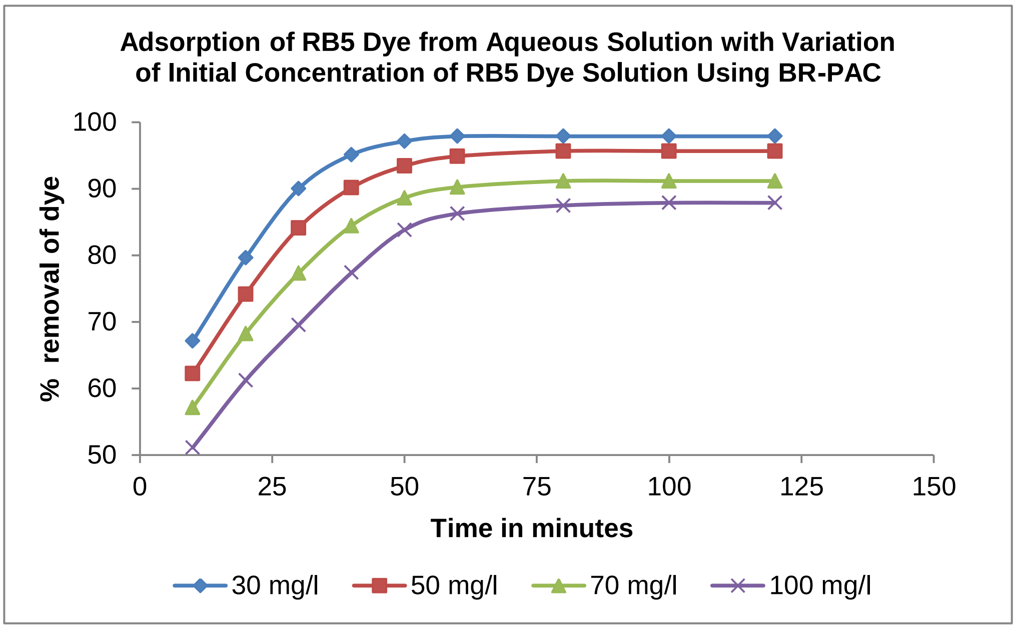


Figure 10

Table 11

Adsorption of CR Dye from Aqueous Solution with Variation of Initial Concentration of CR Dye Solution Using BR-PAC

Conditions: Adsorbent Dose: 50mg pH: 6.8 ± 0.2 Temperature: 32 ± 2°C

Time in minutes	Removal of CR dye (%)			
	Initial Dye Concentration			
	30mg/l	50mg/l	70mg/l	100mg/l
10	69.12	65.52	61.25	56.22
20	81.22	76.42	71.55	65.32
30	88.62	84.22	79.62	73.45
40	94.32	89.62	85.17	79.36
50	98.41	93.42	89.32	84.52
60	99.20	94.80	91.68	87.14
80	99.20	96.32	92.45	88.5
100	99.20	96.32	92.45	89.00
120	99.20	96.32	92.45	89.00

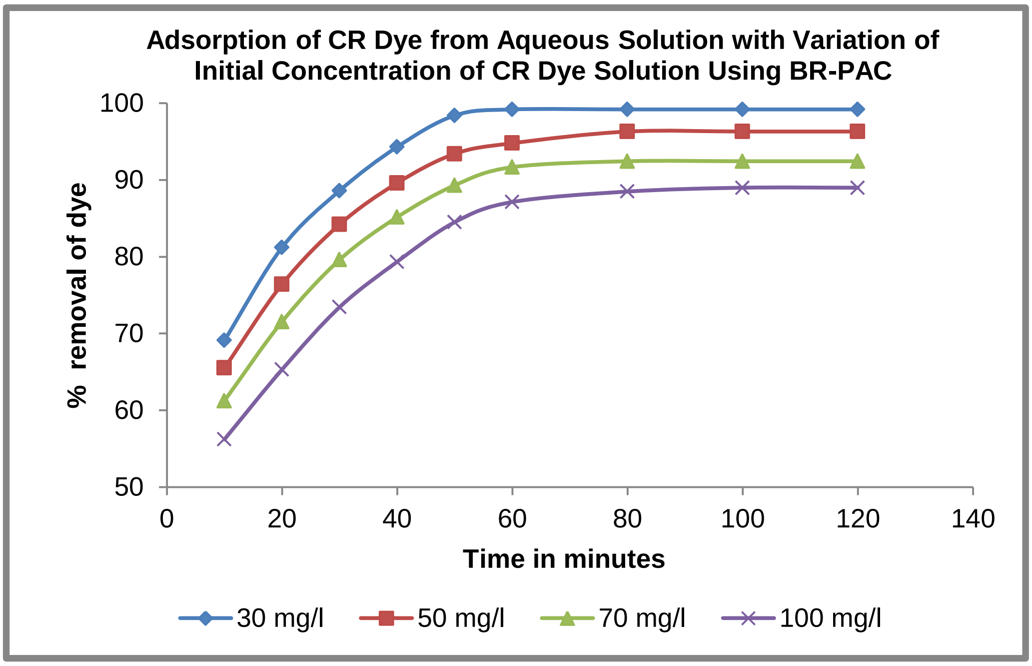


Figure 11

4.2 Effect of pH on Dye Removal

Solution pH influence both aqueous chemistry and surface adsorption sites of the adsorbents **(Bharathi and Ramesh, 2013; Alishamel *et al*., 2016; Aparna Roy *et al*., 2013).** To know the adsorption mechanism it is essential to observe the pH at which the surface charges correspond to zero known as zero point change (pHzpc) of the adsorbent. The pHzpc of the adsorbent BR-SAC is 6.8 and BR-PAC is 6.5. The carbon surface gets positive charge below its zero point charge and develops negative charge above its zero point charge. The adsorption of cationic dyes are favored at pH > pHzpc while anionic dyes are favored at pH < pHzpc **(Mall *et al*., 2006)**

In the aqueous solution the sulphonic acid group of anionic dye ($D\text{-}SO_3Na$) is dissociated and converted to anionic dye ion **(Mall *et al*., 2006; Sivakumar *et al*., 2014)**.

$$\mathbf{D\text{-}SO_3Na \xrightarrow{H2O} D\text{-}SO_3^- + Na^+}$$

The carbon surface acquires positive charge below its zero point charge (6.8 for BR-SAC and 6.5 for BR-PAC) and therefore below pH 7, a considerable electrostatic attraction exists between the positively charged surface of the adsorbent and anionic dye ions causes increase in the removal of dyes from the aqueous dye solution.

The removal of cationic dyes increases with increase in solution pH and the association of dye cations with more negatively charged sites of carbon adsorbent take place thereby increasing cationic dye removal **(Mall *et al*., 2006).**

$$M^- + Dye^+ \rightleftharpoons M\text{-}O\text{-}Dye$$

where M - stands for adsorbent surface.

In the present study 100ml dye solution of initial dye concentration of 100 mg/l was taken in pyrex bottles containing 100 mg of BR-SAC **/** 50 mg of BR-PAC adsorbents at 32 ± 2°C and batch mode adsorption experiments were performed by varying the pH of the dye solution from 2 to 10 using 0.1 N H_2SO_4 or 0.1 N NaOH. The results were depicted in **Tables 12 -13** and **Figures 12-15.**

The percentage adsorption of cationic dye CV increased from 60.32 to 89.46 % with the adsorbent BR-SAC and 61.32% to 92.46% with the adsorbent BR – PAC when the pH of the dye solution was increased from 2.0 to 10 in 120 minutes of adsorption time. Lesser adsorption of CV dye at acidic pH may be because of the electrostatic repulsion between positively charged surface and positively charged dye molecules. In addition the existence of excess H^+ ions competing with cationic dye molecules for adsorption sites

(Sartape *et al.,* 2017). At higher pH the surface of the adsorbent acquires negative charge, which attracts the positively charged dye molecules due to electrostatic attraction.

Similar results were observed for the adsorption of Crystal Violet dye on Fertiliser plant waste carbon **(Mall *et al*., 2006),** Chitosan **(Mona Shouman *et al*., 2012),** Mustard waste ash and Buffalo dung ash **(Harminder singh *et al*., 2013)** and adsorption of Malachite Green dye on Sea shell **(Ali Shamel *et al*., 2016).**

In the case of anionic dyes such as AB110, RB5 and CR the percentage removal of dyes using BR-SAC / BR-PAC adsorbents decreased with the increase in pH of the dye solution from 2.0 to 10 in 120 minutes of agitation time when the initial concentration of dye used was 100 mg/l (Tables 12 -13).

At higher pH the electrostatic repulsion between the negatively charged surface of adsorbent and the anionic dye ions (AB110, RB5 and CR) causes considerable drop in the removal of dyes from aqueous dye solutions.

Similar results of pH effect were also reported for the adsorption of Acid Green 25 on Ananas comosus **(Parimalam *et al*., 2012),** Congo Red on Rice husk (**Kumaraswamy *et al.,* 2014)** and modified Jute fiber **(Aparna Roy *et al*., 2013),** Direct Red 23 on powdered Tourmaline (**Na Liu *et al*., 2016),** Remazol Black RL on Pine needles **(UCAR.C, 2014),** Direct Yellow on Coconut shell carbon **(Aseel Aljeboree *et al.,* 2017),** Reactive Red 2 and Reactive Yellow145A on wild Almond shell and Coir pith **(Thitame and Shukle, 2016) .**

Table 12

Adsorption of CV and AB110 Dyes from Aqueous Solution with Variation of pH of Dye Solution Using BR-SAC and BR-PAC adsorbents

Conditions:

Dye Concentration: 100mg/l

Adsorbent Dose: 100mg BR-SAC / 50mg BR-PAC

Time: 2 Hours

Temperature : 32 ± 2°C

pH	Removal of CV dye (%)		Removal of AB 110 dye (%)	
	BR- SAC	BR - PAC	BR- SAC	BR – PAC
2	60.32	61.32	90.11	91.11
3	68.52	70.52	89.12	90.12
4	72.86	72.86	84.16	88.16
5	77.13	78.13	83.21	87.21
6	80.05	81.05	81.40	82.84
7	83.09	91.09	79.24	80.22
8	85.88	92.88	75.12	79.21
9	87.70	93.70	72.02	78.11
10	89.46	93.46	71.12	77.63

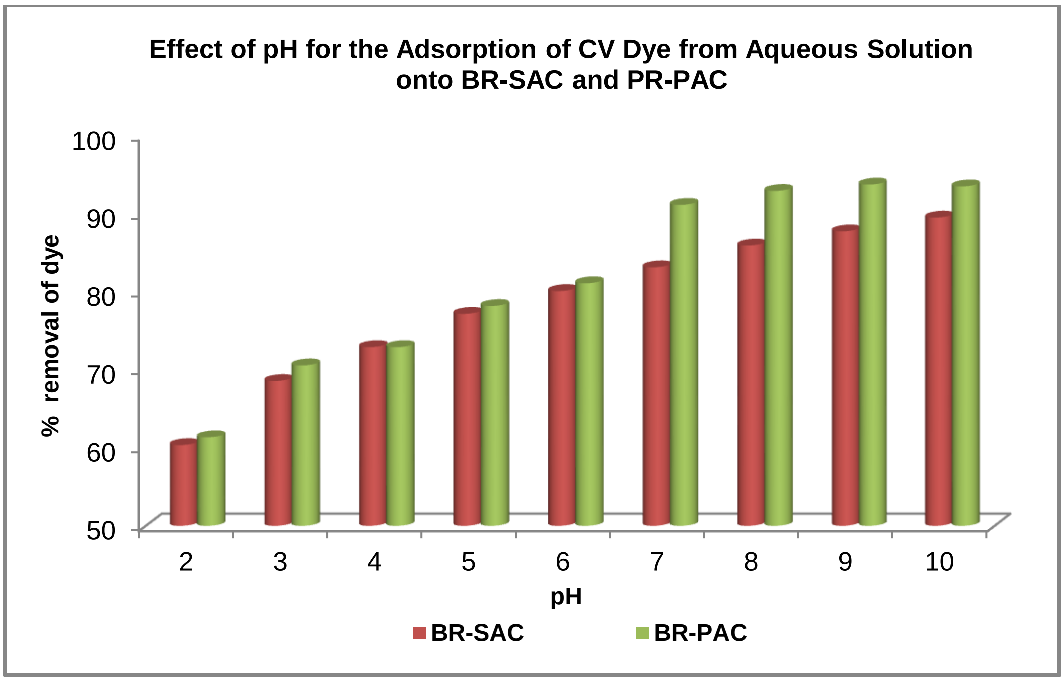


Figure 12

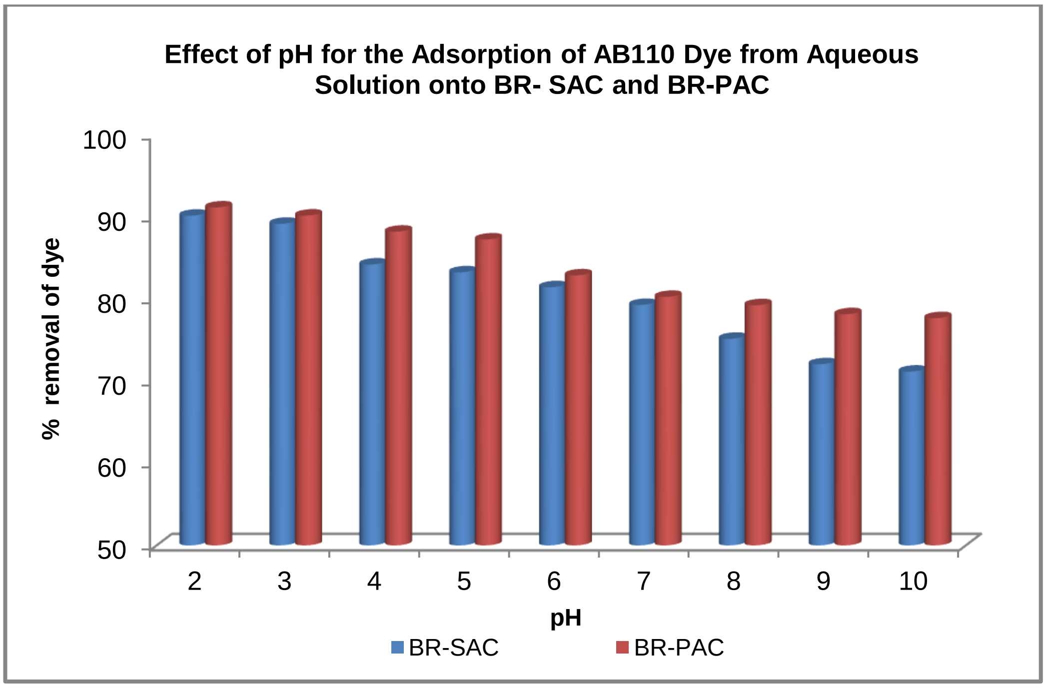


Figure 13

Table 13

Adsorption of RB5 and CR Dyes from Aqueous Solution with Variation of pH of Dye Solution Using BR-SAC and BR-PAC adsorbents

Conditions:

Dye Concentration: 100mg/l

Adsorbent Dose: 100mg BR-SAC / 50mg BR-PAC

Time: 2 Hours

Temperature : 32 ± 2°C

pH	Removal of RB5 dye (%)		Removal of CR dye (%)	
	BR- SAC	BR - PAC	BR- SAC	BR - PAC
2	89.32	90.32	82.12	90.12
3	87.62	88.62	80.88	89.88
4	85.75	85.33	77.80	88.20
5	83.14	82.00	75.92	85.00
6	78.16	81.00	73.00	83.42
7	74.31	79.31	71.62	83.95
8	72.68	78.68	69.28	82.28
9	68.25	77.25	65.66	82.66
10	60.66	77.66	61.52	81.52

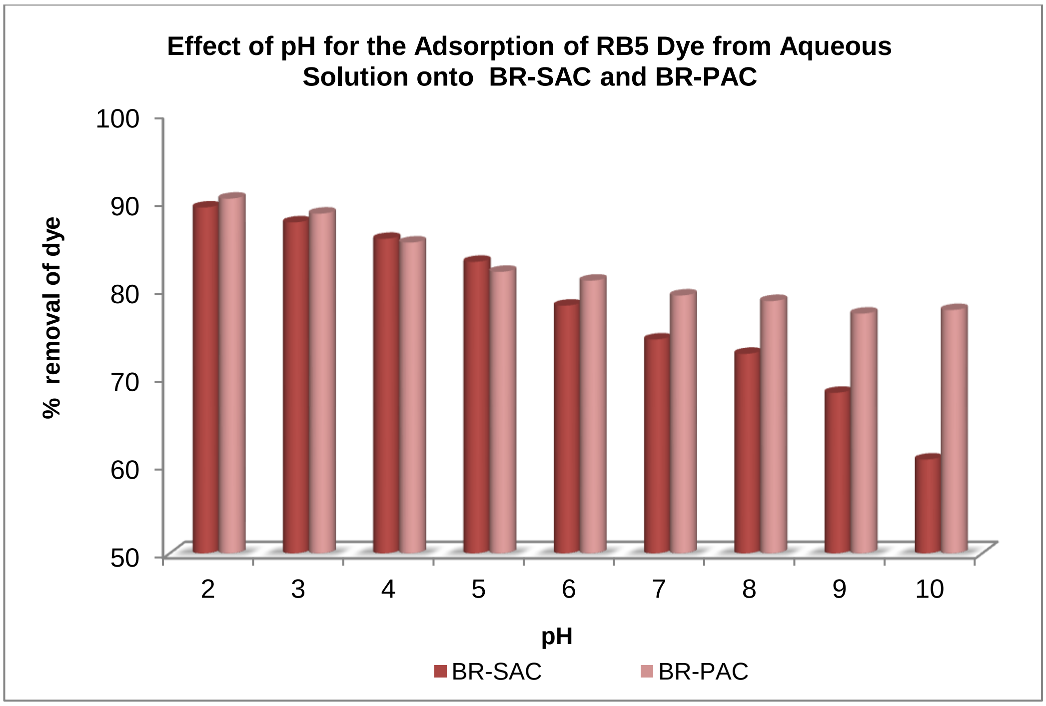


Figure 14

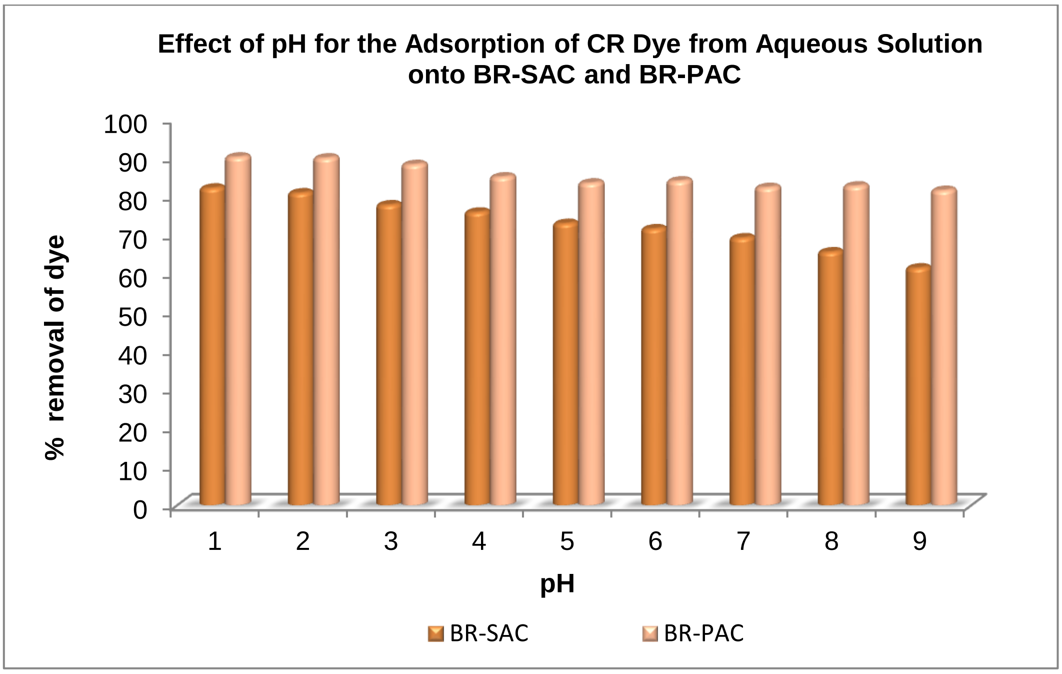


Figure 15

4.3 Effect of Temperature on Dye Removal

To study the consequence of temperature on the adsorption of Crystal Violet, Acid Blue 110, Ramazol Black 5 and Congo Red dyes, adsorption experiments were performed by varying the temperature (30℃, 40℃ and 50℃). Batch mode adsorption experiments were conducted using 100ml dye solution of initial concentration 100 mg/l, at pH 6.8±0.2 with 100mg of adsorbent BR-SAC and 50 mg of adsorbent BR-PAC.

The dye removal efficiency of BR-SAC and BR-PAC adsorbents increased as the temperature was raised from 30-50°C (**Tables 14 to 17**, **Figures 16 to 23**). The increase in temperature elevates the mobility of the dye molecules and supply adequate kinetic energy to make good interaction between the dye molecules and surface active sites of the adsorbents. Moreover the raise in temperature may impel swelling effect within the internal surface of the adsorbents and enhance the movement of dye molecules inside the pores of the adsorbents **(Lin Liu *et al.,* 2015).**

Similar results were reported for the adsorption of Crystal Violet dye on Grape fruit peel **(Saeed *et al.,* 2010),** Oak saw dust **(Abd El – Latifa *et al.,* 2010)** and Chitosan **(Mona Shouman, 2012)**, adsorption of Direct Red dye on powdered Tourmaline **(Na Liu *et al*., 2016),** adsorption of Methylene Blue dye on Bale tree bark **(Valliammai *et al*., 2013) ,** adsorption of Reactive Red and Acid Red dyes on Bio polymer resin **(Wen Song *et al*., 2016)** and adsorption of Reactive Black 5 on TiO_2 nanoparticles **(Majeed *et al*., 2014).**

Table 14

Adsorption of CV Dye from Aqueous Solution with Temperature Variation Using BR-SAC/BR-PAC

Conditions:

Dye Concentration: 100mg/l
Adsorbent Dose: 100mg BR-SAC / 50mg BR-PAC
pH: 6.8 ± 0.2

Time in minutes	Removal of CV dye (%)					
	BR-SAC			BR-PAC		
	30℃	40℃	50℃	30℃	40℃	50℃
10	30.18	34.16	36.42	59.12	61.28	62.66
20	43.77	45.24	46.86	69.04	70.16	70.88
30	54.62	56.48	57.91	77.62	78.42	79.72
40	63.82	65.36	66.76	83.46	85.38	86.42
50	70.91	72.82	74.43	86.02	91.74	92.71
60	75.42	77.94	78.21	88.24	94.16	95.00
80	78.61	80.22	81.66	89.16	94.82	95.55
100	81.88	82.66	84.42	89.52	95.36	95.65
120	82.21	84.10	85.53	90.08	95.88	95.70

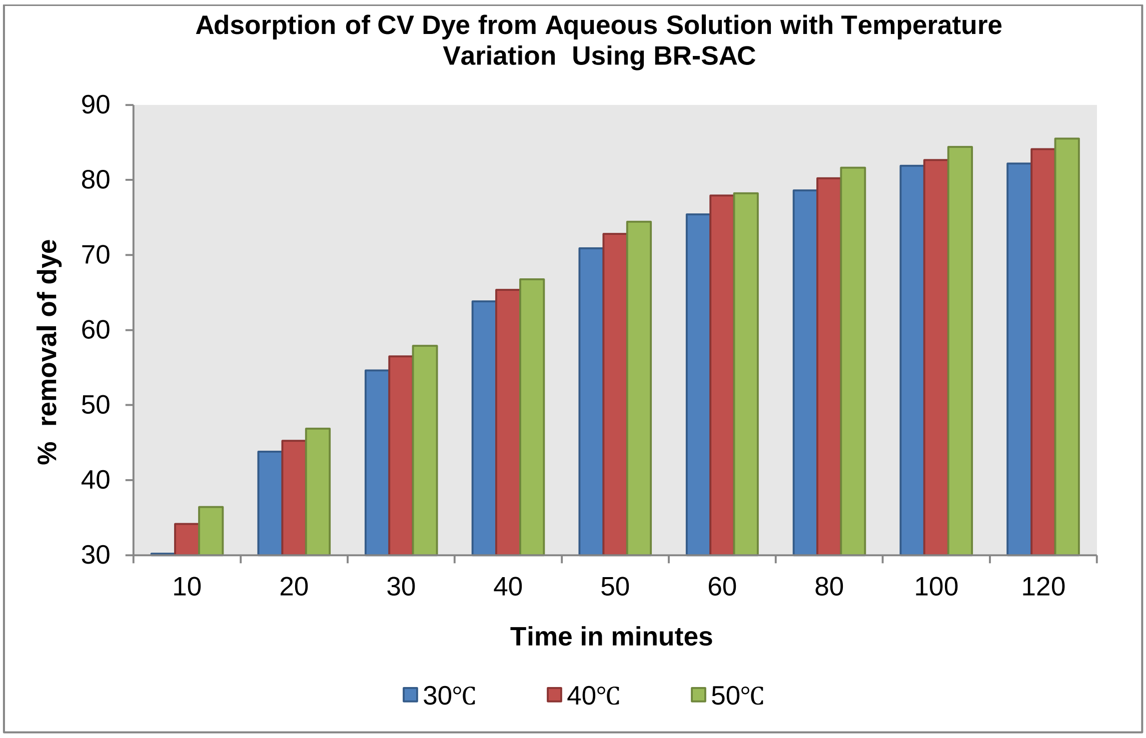


Figure 16

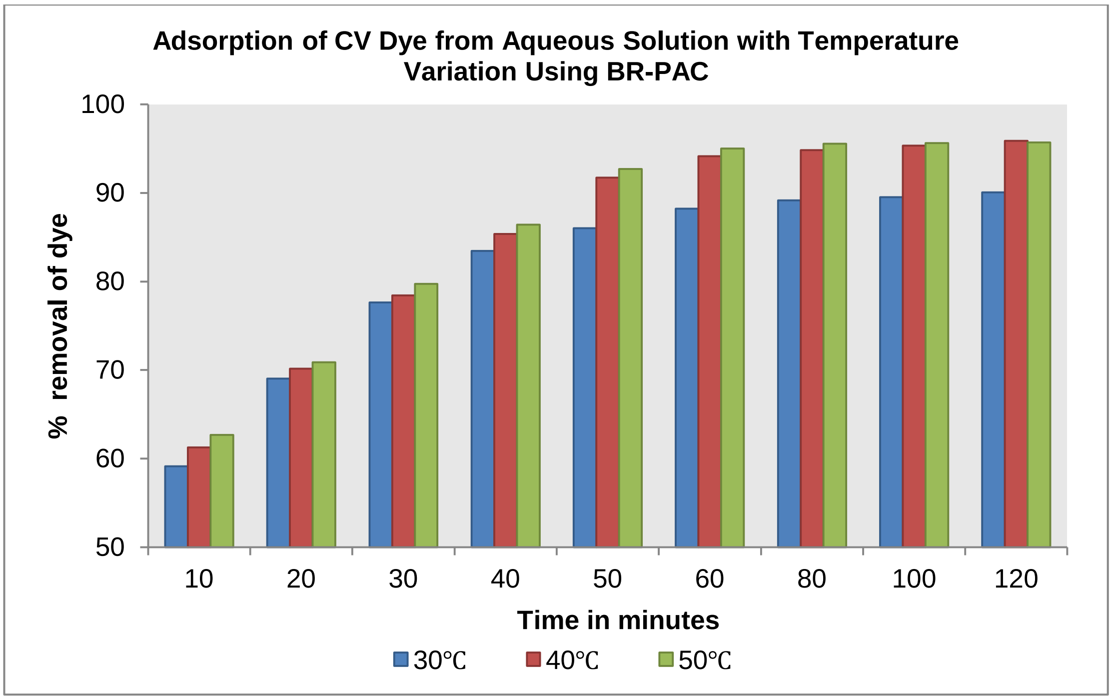


Figure 17

Table 15

Adsorption of AB110 Dye from Aqueous Solution with Temperature Variation Using BR-SAC/BR-PAC

Conditions:

Dye Concentration: 100mg/l
Adsorbent Dose: 100mg BR-SAC / 50mg BR-PAC
pH : 6.8 ± 0.2

Time in minutes	Removal of AB110 dye (%)					
	BR-SAC			BR-PAC		
	30℃	40℃	50℃	30℃	40℃	50℃
10	23.12	27.16	29.42	57.02	59.44	60.7
20	36.28	38.42	39.11	66.24	68.58	69.52
30	48.62	50.72	51.64	73.38	74.32	75.36
40	58.54	61.91	63.72	78.49	79.10	80.48
50	67.42	69.64	70.83	82.72	83.26	84.16
60	72.38	74.53	76.22	83.53	85.71	86.82
80	75.71	77.00	78.66	85.52	86.58	88
100	77.54	80.88	81.42	86.42	87.42	88.65
120	78.88	81.66	83.12	86.66	87.77	88.98

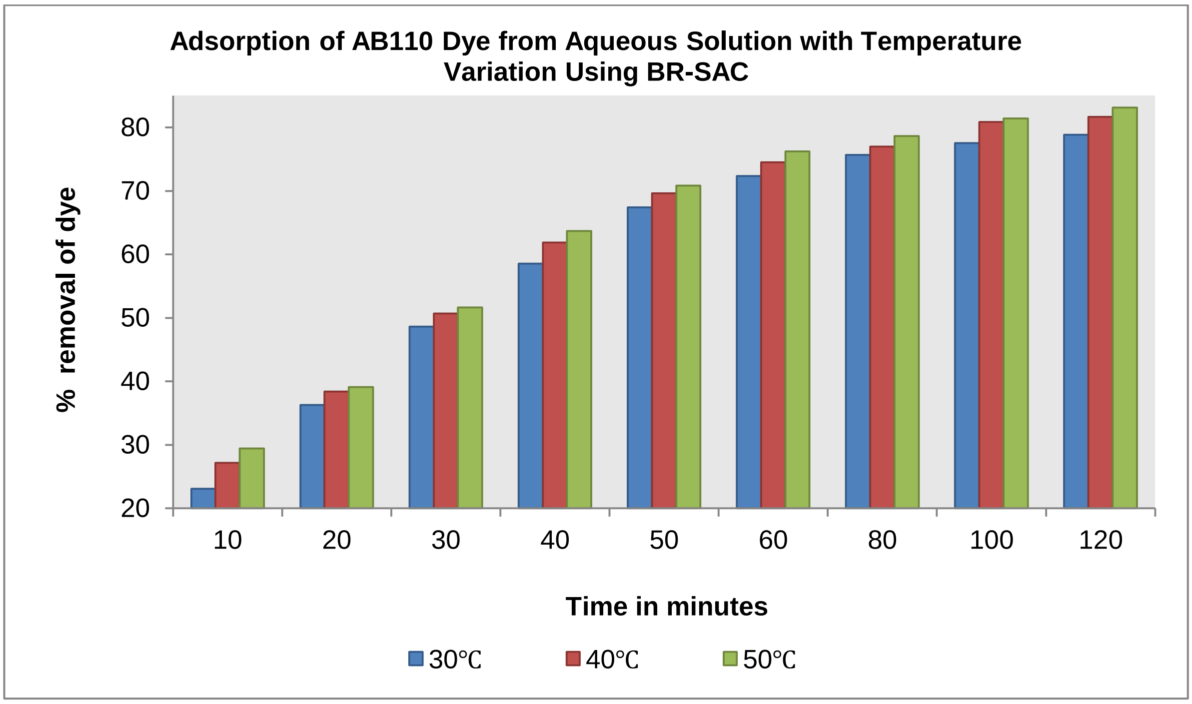


Figure 18

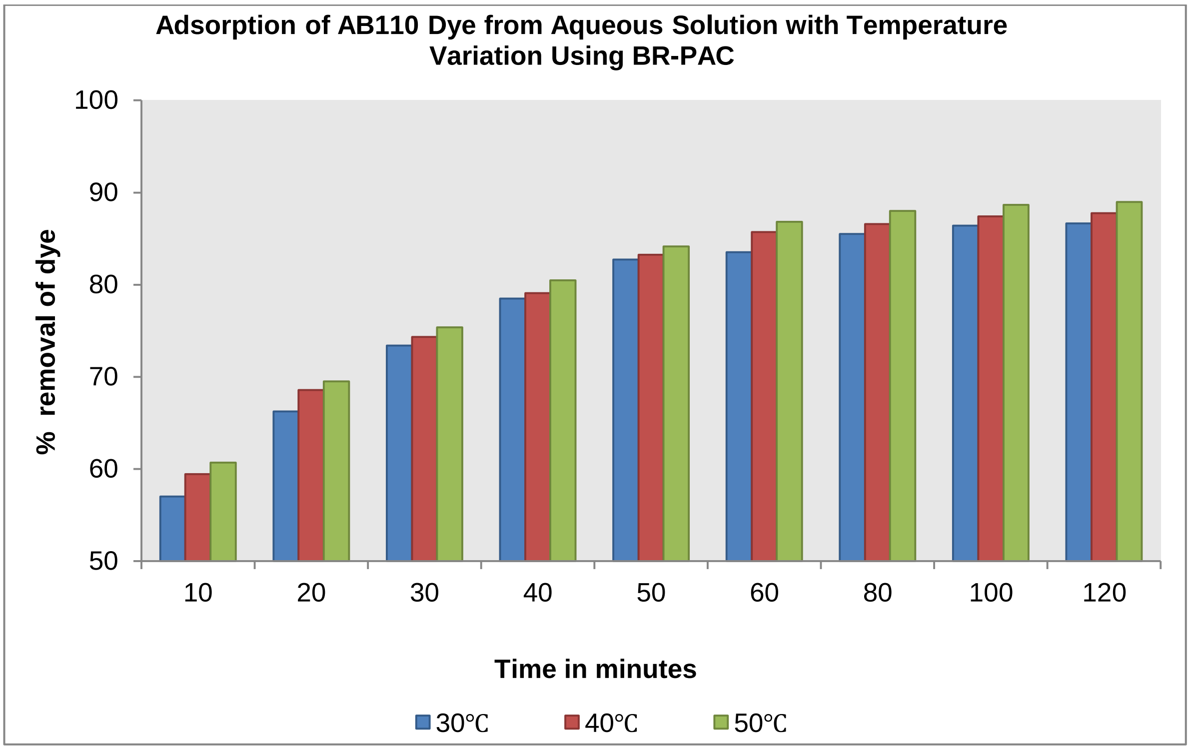


Figure 19

Table 16

Adsorption of RB5 Dye from Aqueous Solution with Temperature Variation Using BR-SAC/BR-PAC

Conditions:
Dye Concentration: 100mg/l
Adsorbent Dose: 100mg BR-SAC / 50mg BR-PAC
pH : 6.8 ± 0.2

Time in minutes	Removal of RB5 dye (%)					
	BR-SAC			BR-PAC		
	30℃	40℃	50℃	30℃	40℃	50℃
10	31.12	35.72	37.12	50.64	52	53.26
20	41.42	42.66	43.82	62.12	63.66	64.14
30	48.36	49.74	50.66	72.41	73.14	74.22
40	55.71	56.61	57.72	78.64	79.24	80.61
50	60.21	62.76	63.86	82.72	84.42	85.78
60	65.42	67.34	68.46	85.22	87.61	88.61
80	69.32	71.22	72.43	85.86	88.9	89.82
100	71.64	74.26	76.02	86.00	89.76	90.24
120	72.48	76.41	77.88	86.12	89.84	90.31

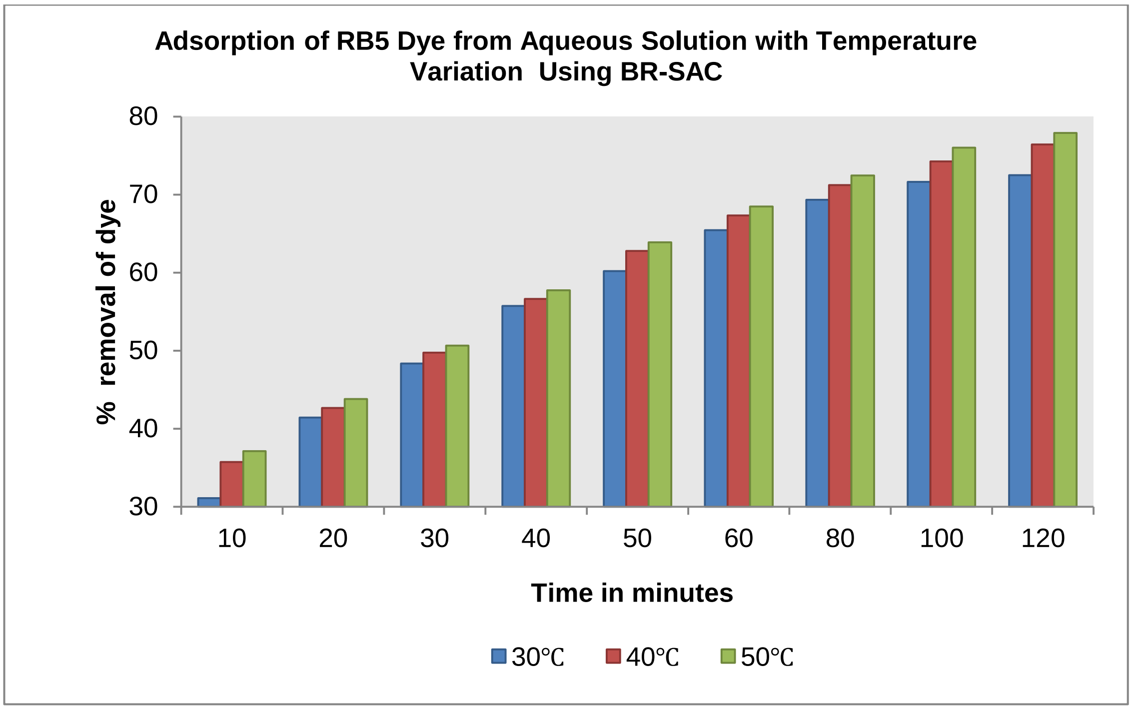


Figure 20

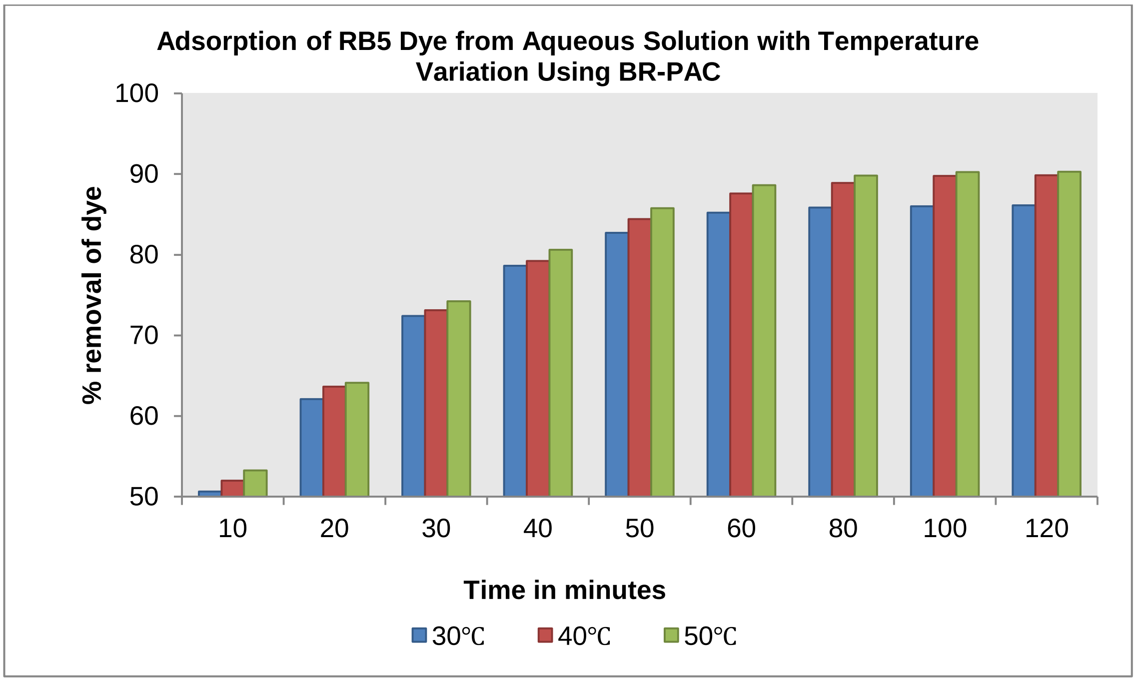


Figure 21

Table 17

Adsorption of CR Dye from Aqueous Solution with Temperature Variation Using BR-SAC/BR-PAC

Conditions:
Dye Concentration: 100mg/l
Adsorbent Dose: 100mg BR-SAC / 50mg BR-PAC
pH : 6.8 ± 0.2

Time in minutes	Removal of CR dye (%)					
	BR-SAC			BR-PAC		
	30℃	40℃	50℃	30℃	40℃	50℃
10	21.12	25.14	28.16	55.12	57.71	58.42
20	32.26	33.42	35.72	65.46	66.62	67.16
30	42.48	44.68	46.19	73.64	74.41	76.16
40	50.76	51.82	53.67	78.81	79.53	81.42
50	57.92	59.26	61.54	81.76	82.71	83.74
60	63.61	65.43	67.82	83.52	84.86	86.32
80	67.86	69.26	71.22	85.36	86.02	87.46
100	70.24	71.61	72.41	86.14	87.14	88.24
120	71.62	72.54	74.02	86.92	87.66	89.66

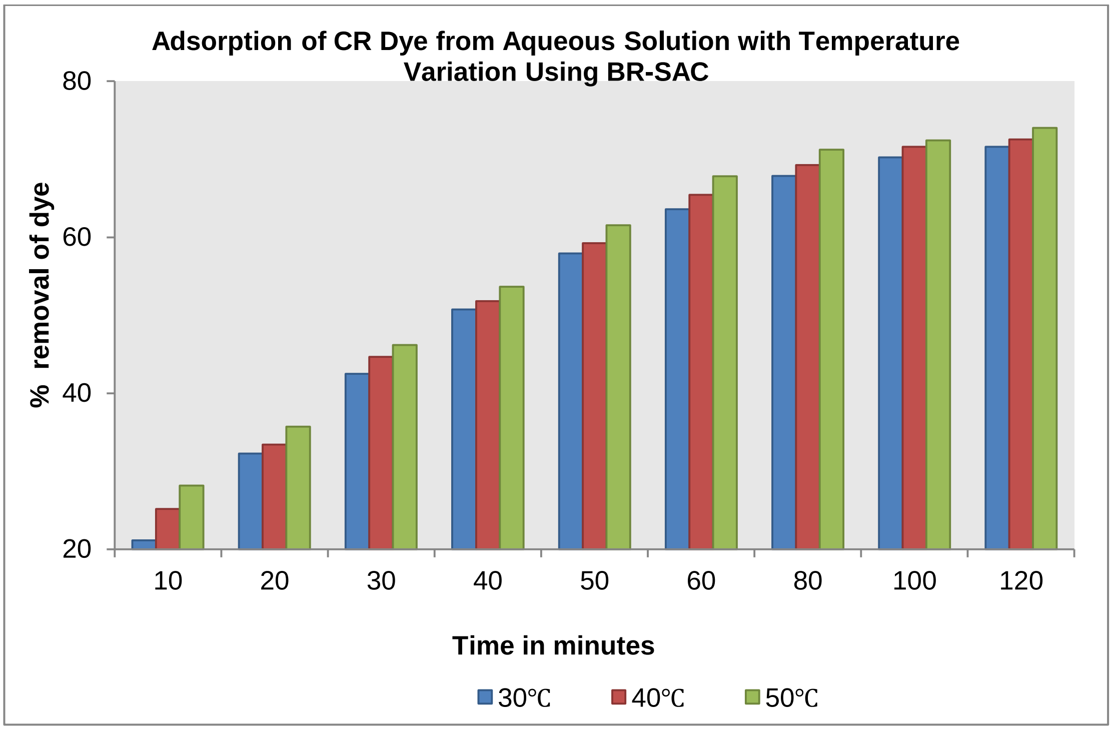


Figure 22

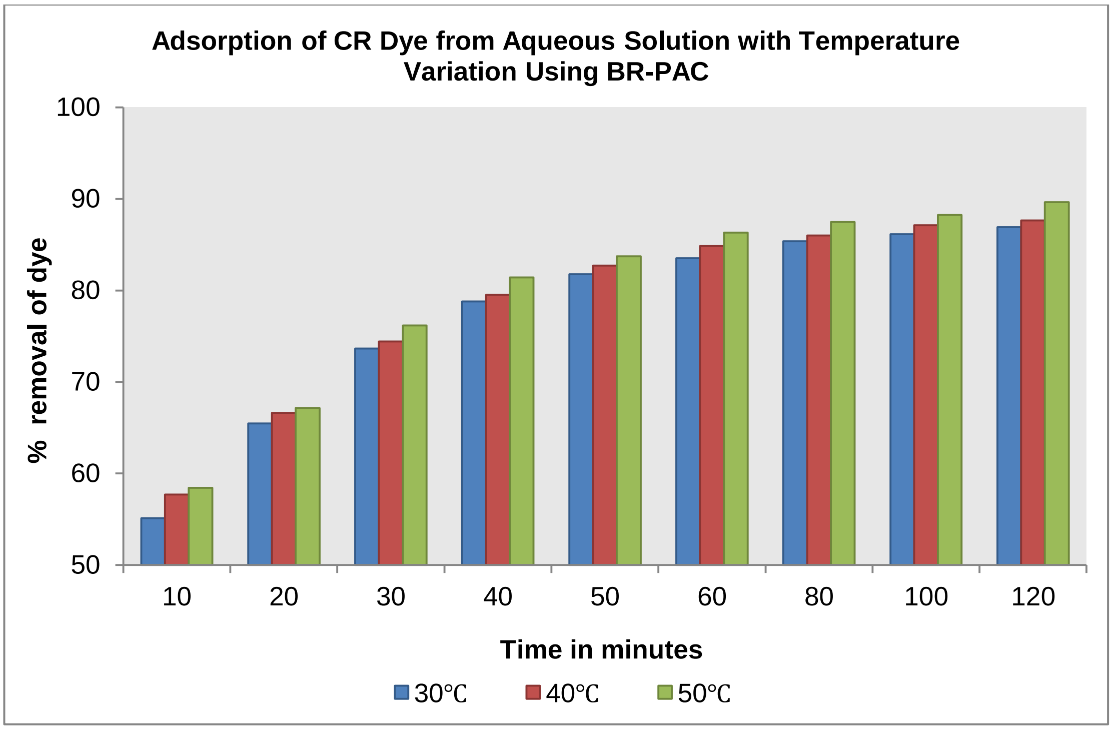


Figure 23

4.4 Effect of Adsorbent Dosage on Dye Removal

The influence of adsorbent dosage on the removal of CV, AB110, RB5 and CR dyes from aqueous solution were studied by changing the dosage of the adsorbents (BR-SAC 50 to 200mg and BR-PAC 25 to 100mg). Batch mode adsorption studies were conducted by varying the adsorbent dosage using 100ml dye solution of initial concentration 100mg/l at temperature 32±2℃ and at pH 6.8 ± 0.2 (**Tables 18 to 21 and Figures 24 to 31**). The enhanced dye removal efficiency with the increase in amount of adsorbent material was caused by enhanced surface area and more number of adsorption sites obtained on the surface of the adsorbents.

Similar results were observed for the adsorption of Methylene Blue dye on Bael tree bark **(Valliammai *et al*., 2013)**, Acid Blue on Cellulose based biosorbent **(Lin Liu *et al*., 2015)**, adsorption of Cibacron Reactive Yellow dye on modified Alumina **(Ayesha Wasti and Ali Awan, 2016)**,Congo Red dye on Lignocellulosic jute fiber **(Aparna Roy, 2013)** and Acid Orange dye on Coconut shell and Coal ash **(Ramakrishnaian and Arpitha 2014).**

Table 18

Adsorption of CV Dye from Aqueous Solution with Adsorbent Dosage Variation (BR-SAC/BR-PAC)

Conditions:
Dye Concentration: 100mg/l
pH : 6.8 ± 0.2
Temperature 32±2℃

Time in minutes	Removal of CV Dye (%)							
	BR-SAC				BR-PAC			
	Adsorbent Dosage				Adsorbent Dosage			
	50mg	100mg	150mg	200mg	25mg	50mg	75mg	100mg
10	32.78	41.88	49.63	56.00	42.78	48.88	50.63	57.85
20	40.02	50.22	58.02	67.38	45.02	53.22	57.02	68.38
30	46.66	57.56	66.66	75.44	47.66	58.56	65.66	76.44
40	52.73	63.72	73.82	82.54	53.73	65.72	74.82	83.54
50	57.89	69.89	82.93	89.32	58.89	71.89	83.93	88.32
60	62.09	76.34	88.42	94.16	63.09	77.34	87.42	93.16
90	68.66	85.23	96.62	99.06	68.66	86.23	95.62	99.46
120	72.86	92.88	99.22	100	75.86	90.88	98.22	100
150	73.00	93.22	100	100	78.42	91.22	100	100

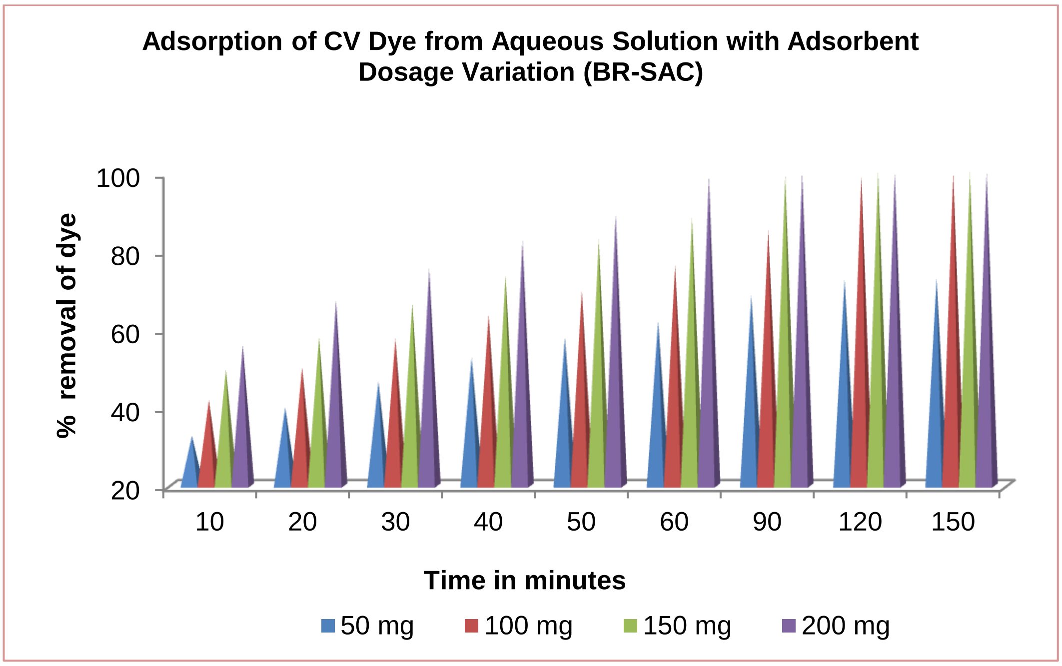


Figure 24

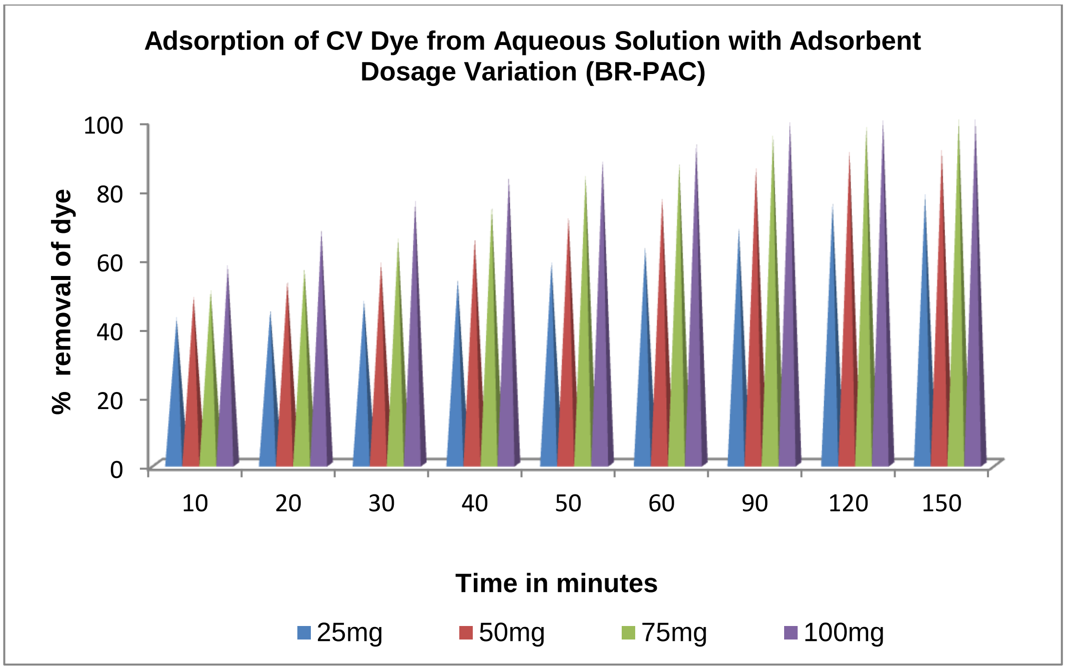


Figure 25

Table 19

Adsorption of AB110 Dye from Aqueous Solution with Adsorbent Dosage Variation (BR-SAC/BR-PAC)

Conditions:
Dye Concentration: 100mg/l
pH : 6.8 ± 0.2
Temperature 32±2℃

Time in minutes	Removal of AB110 Dye (%)							
	BR-SAC				BR-PAC			
	Adsorbent Dosage				Adsorbent Dosage			
	50 mg	100 mg	150 mg	200 mg	25 mg	50 mg	75 mg	100 mg
10	30.48	39.25	48.33	54.22	35.48	40.25	50.33	58.22
20	37.21	44.86	54.26	63.02	38.21	45.86	55.26	64.02
30	40.23	49.32	59.47	68.00	41.23	48.32	58.47	68.58
40	44.12	54.22	63.82	70.95	45.12	53.22	64.82	71.95
50	47.35	59.22	68.32	75.52	48.35	60.22	69.32	76.52
60	51.88	63.63	72.88	80.14	54.88	64.63	73.88	82.14
90	61.56	73.88	81.88	91.42	62.56	72.88	82.88	93.42
120	71.26	80.22	88.52	99.00	70.26	81.22	87.52	99.05
150	71.66	83.24	92.41	100	71.66	85.24	94.41	100

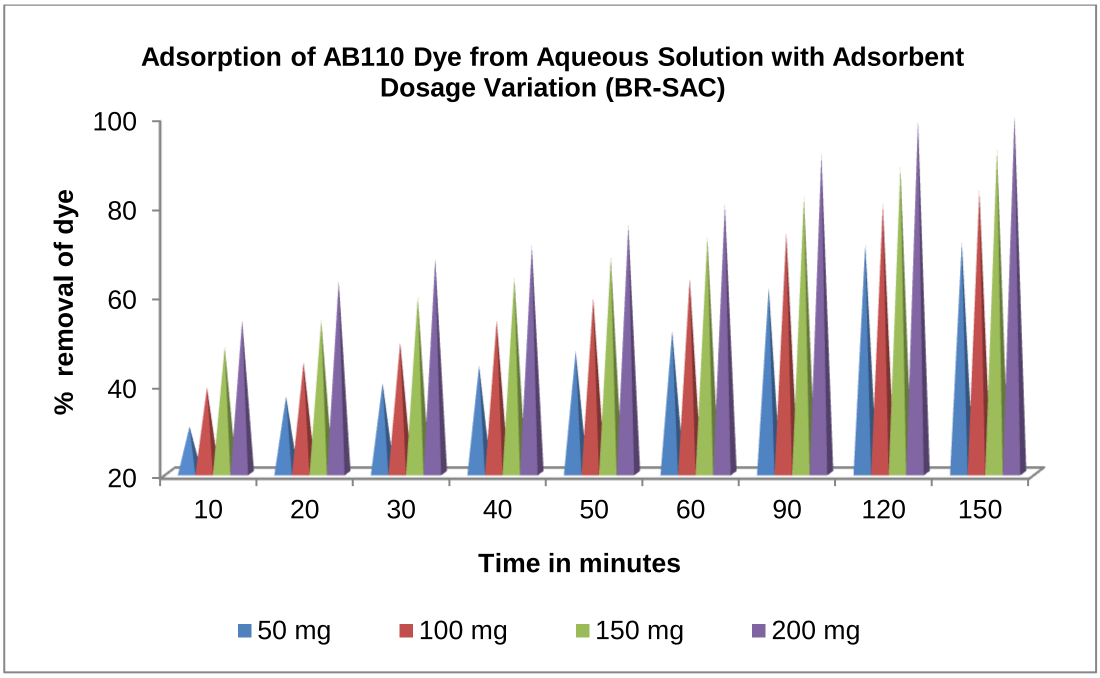


Figure 26

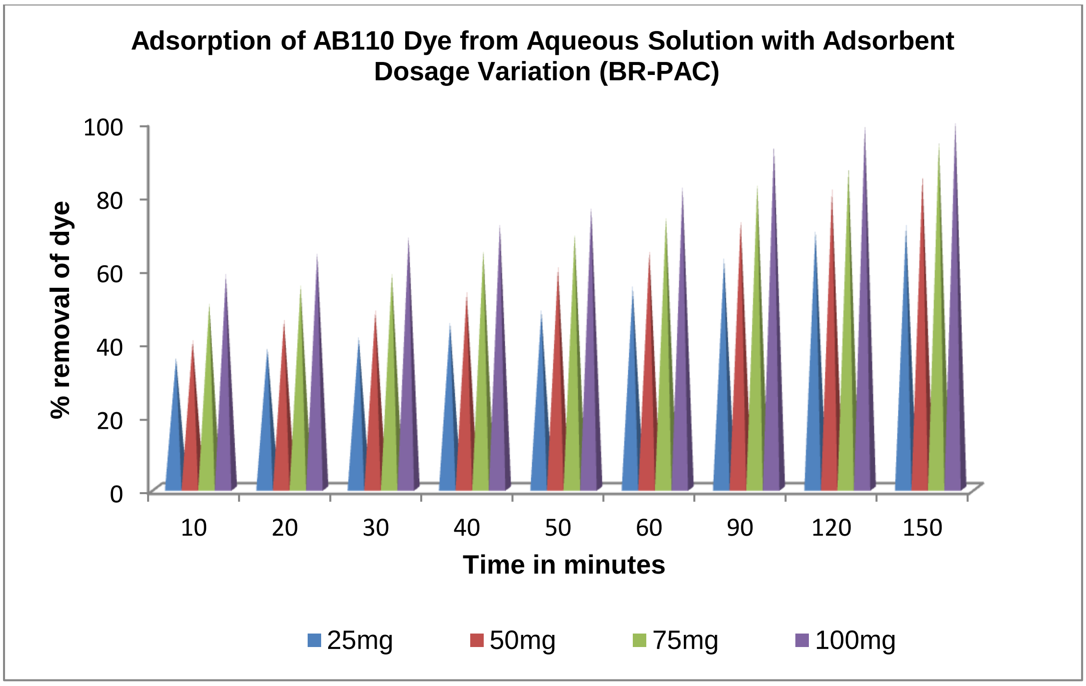


Figure 27

Table 20

Adsorption of RB5 Dye from Aqueous Solution with Adsorbent Dosage Variation (BR-SAC/BR-PAC)

Conditions:
Dye Concentration: 100mg/l
pH : 6.8 ± 0.2
Temperature 32±2℃

Time in minutes	Removal of RB5 Dye (%)							
	BR-SAC				BR-PAC			
	Adsorbent Dosage				Adsorbent Dosage			
	50 mg	100 mg	150 mg	200 mg	25 mg	50 mg	75 mg	100 mg
10	31.48	40.25	49.33	55.36	34.48	42.25	50.33	57.36
20	38.25	45.62	55.00	63.98	39.25	46.62	56.00	62.98
30	41.32	50.22	60.22	69.98	42.32	52.22	61.22	70.22
40	45.21	55.12	64.32	71.84	46.21	55.12	65.32	72.58
50	48.53	60.02	69.02	76.25	49.53	61.02	70.02	78.25
60	52.66	64.34	73.64	81.06	53.66	66.34	74.64	84.06
90	62.65	74.66	82.46	92.42	63.65	72.66	83.46	93.42
120	72.62	81.54	89.23	99.42	71.62	83.54	88.23	96.25
150	72.84	84.42	93.22	100	73.84	86.42	94.22	100

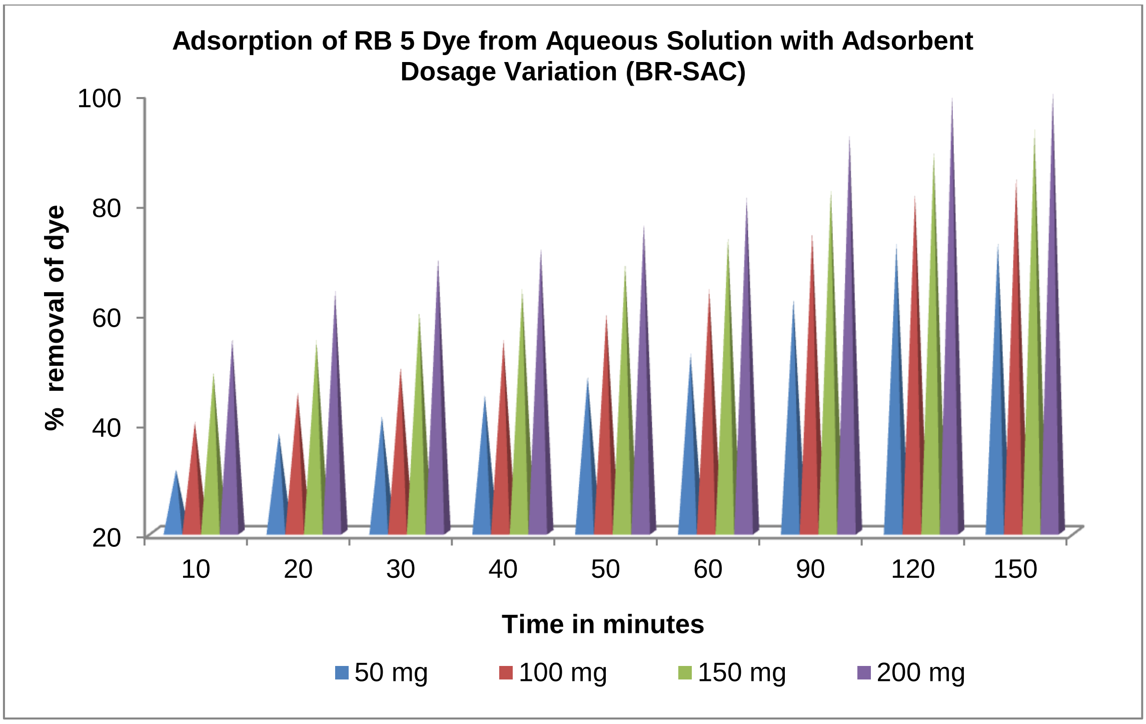


Figure 28

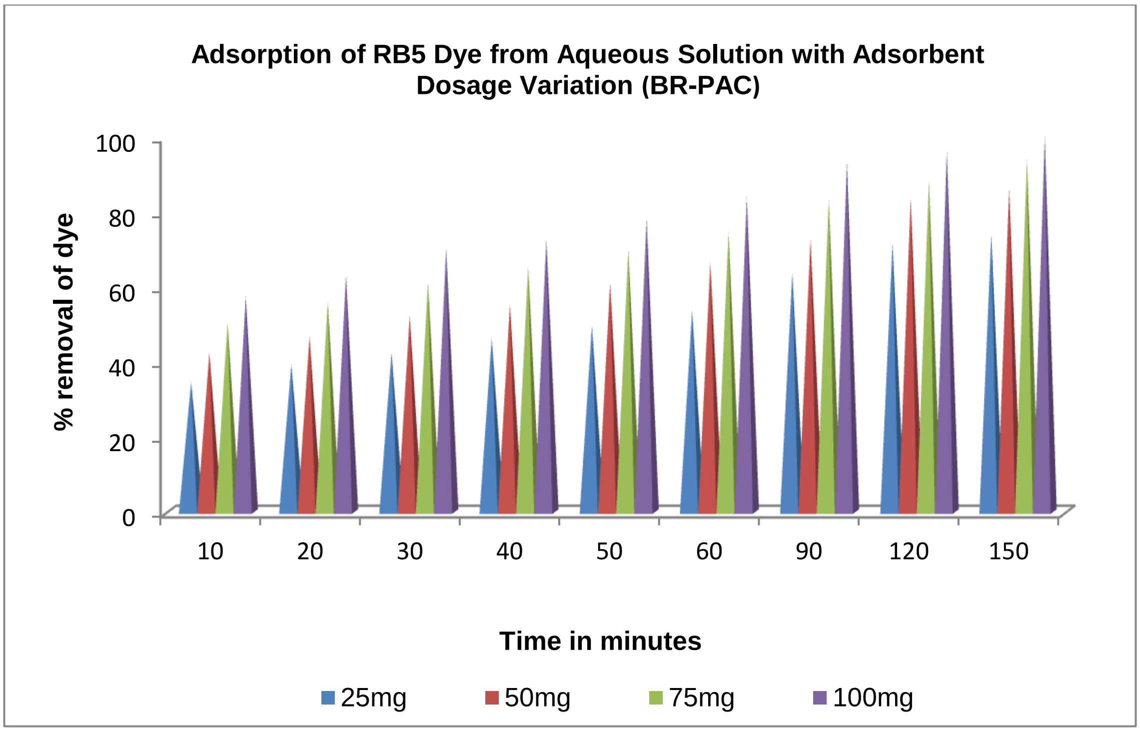


Figure 29

Table 21

Adsorption of CR Dye from Aqueous Solution with Adsorbent Dosage Variation (BR-SAC/BR-PAC)

Conditions:
Dye Concentration: 100 mg/
pH: 6.8 ± 0.2
Temperature 32±2℃

Time in minutes	Removal of CR Dye (%)							
	BR-SAC				BR-PAC			
	Adsorbent Dosage				Adsorbent Dosage			
	50 mg	100 mg	150 mg	200 mg	25 mg	50 mg	75 mg	100 mg
10	29.88	38.52	47.30	53.63	30.88	40.52	49.30	54.63
20	37.52	43.26	52.78	61.89	36.52	42.26	54.78	61.89
30	39.32	48.22	58.42	67.89	38.32	47.22	60.42	69.89
40	43.21	53.21	62.23	69.88	42.21	54.21	63.23	70.88
50	46.53	58.20	68.54	74.92	45.53	59.20	69.54	75.92
60	51.62	62.88	71.46	79.86	52.62	63.88	72.46	80.86
90	61.22	72.86	81.64	90.24	60.22	76.86	85.64	92.24
120	71.26	79.45	88.02	96.28	70.26	80.45	87.02	97.28
150	71.48	82.24	91.00	99.02	72.48	82.24	91.52	99.02

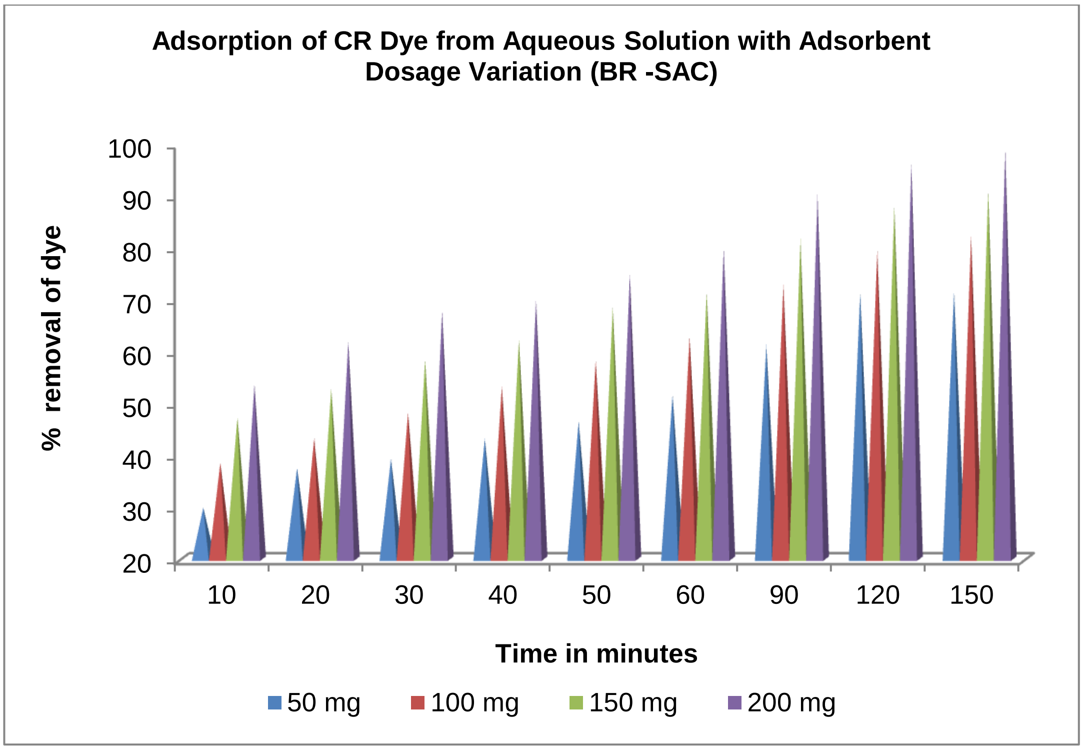


Figure 30

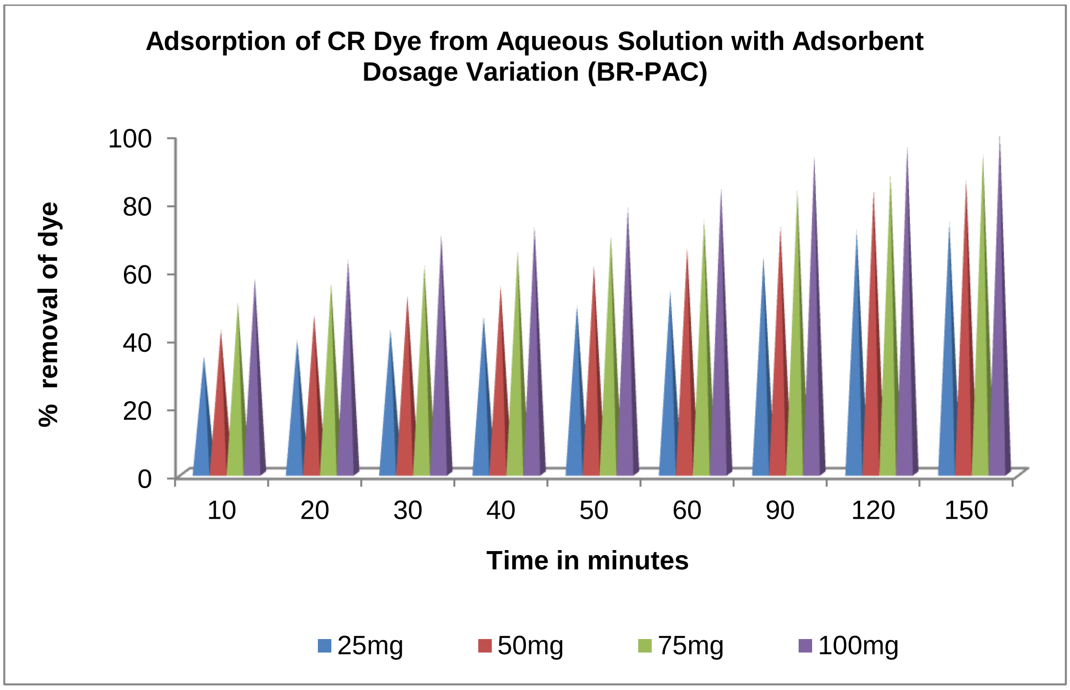


Figure 31

4.5 Adsorption Kinetics

Adsorption is a time dependent process and the study of adsorption kinetics is highly significant in the evaluation of adsorbents for removal of dyes from industrial effluent **(Mona shouman *et al*., 2012).** In the adsorption experiments, kinetics provides valuable information about the adsorption rate and reaction path ways which controls the mechanism of the adsorption. The kinetics of adsorption of CV, AB110, RB5 and CR dyes were studied using Lagergren pseudo-first order rate equation, Elovich rate equation and Intraparticle diffusion rate equation.

4.5.1 Lagergren Pseudo-First Order Rate Equation

. The linearized form of the Lagergren pseudo-first order rate equation is expressed as **(Lagergren, 1898, Aparna Roy *et al*., 2013)**

$$\log (q_e - q_t) = \log q_e - (k_1/2.303) \times t$$

where

q_t - amount of dye adsorbed at time 't'(mg g^{-1})

q_e - amount of dye adsorbed at equilibrium time(mg g^{-1})

k_1 - the rate constant of pseudo first order kinetics (min^{-1})

t - agitation time in minutes

Batch mode adsorption experiments were conducted for all the four dyes used in this study by changing the concentration of the adsorbate solutions at 32±2°C and at pH 6.8 ± 0.2. The data obtained from Lagergren rate equation and the corresponding adsorption plots of log (q_e – q_t) versus t at different initial dye concentrations were shown in **Tables 22 to 25** and in **Figures 32 - 39.** The rate constant k_1 values were calculated from the slope of the linear plots.

The results indicated that as the initial concentration of the dye solution increases, the Lagergren rate constant k_1 values decreased due to greater competition of adsorbate molecules for the surface binding sites of the adsorbents used in this study. The straight line plots with high correlation co-efficient (r^2) values revealed that the adsorption of dyes (CV, AB110, RB5 and CR) onto the adsorbents BR-SAC and BR-PAC was effectively described by this model **(Sen *et al*., 2011).**

Similar results were reported for removal of malachite green dye onto Wood apple **(Sartape *et al*., 2017),** adsorption of Direct Red 23 dye onto powdered Tourmaline **(Na Liu *et al*., 2016)**, adsorption of light green anionic dye on cationic surfactant modified peanut husk **(Zhao *et al*., 2014)** and removal of Methylene blue dye onto pine cone biomass **(Sen *et al*., 2011).**

Table 22

Lagergren Rate Equation for the Adsorption of CV Dye from Aqueous Solution onto BR-SAC/BR-PAC

Conditions:
Adsorbent Dosage: 100mg BR-SAC / 50mg BR-PAC
pH : 6.8 ± 0.2
Temperature: 32 ±2°C

Time in minutes	$\log(q_e-q_t)$							
	BR-SAC				BR-PAC			
	Dye Concentration				Dye Concentration			
	30mg/l	50mg/l	70mg/l	100 mg/l	30mg/l	50mg/l	70mg/l	100 mg/l
10	1.21	1.44	1.57	1.71	1.22	1.46	1.63	1.80
20	1.07	1.31	1.44	1.57	0.83	1.16	1.38	1.57
30	0.89	1.15	1.28	1.44	0.33	0.64	1.00	1.24
40	0.63	0.94	1.09	1.26	-0.36	0.21	0.63	0.86
50	0.26	0.68	0.81	1.05	-	-0.10	0.15	0.54
60	-0.11	0.41	0.60	0.75	-	-	-0.06	0.16
80	-	-	0.24	0.39	-	-	-	-
Slope ($-k_1/2.303$)	**-0.026**	**-0.020**	**-0.024**	**-0.022**	**-0.052**	**-0.041**	**-0.035**	**-0.033**
Intercept ($\log q_e$)	**1.285**	**1.414**	**1.656**	**1.769**	**1.815**	**1.895**	**2.039**	**2.195**
$k_1 \times 10^{-2}$ (min^{-1})	**5.9878**	**4.6061**	**5.5272**	**5.066**	**11.981**	**9.2101**	**8.0612**	**7.6032**
Correlation Coefficient (r^2)	**0.9634**	**0.9825**	**0.9722**	**0.969**	**0.983**	**0.9922**	**0.9917**	**0.9952**

Table 23

Lagergren Rate Equation for the Adsorption of AB110 Dye from Aqueous Solution onto BR-SAC/BR-PAC

Conditions:
Adsorbent Dosage: 100mg BR-SAC / 50mg BR-PAC
pH : 6.8 ± 0.2
Temperature: 32 ±2°C

Time in minutes	**$\log(q_e-q_t)$**							
	BR-SAC				**BR-PAC**			
	Dye Concentration				**Dye Concentration**			
	30mg/l	**50mg/l**	**70mg/l**	**100 mg/l**	**30 mg/l**	**50 mg/l**	**70mg/l**	**100 mg/l**
10	1.24	1.45	1.58	1.75	1.26	1.48	1.64	1.77
20	1.10	1.33	1.46	1.63	1.05	1.31	1.50	1.64
30	0.95	1.20	1.34	1.51	0.75	1.12	1.34	1.48
40	0.79	1.06	1.19	1.37	0.43	0.87	1.10	1.29
50	0.58	0.88	1.02	1.24	0.01	0.53	0.87	1.09
60	0.33	0.70	0.87	1.07	-	0.22	0.68	0.83
80	-0.13	0.35	0.55	1.04	-	-	-	-
100	-	0.11	0.21	0.43	-	-	-	-
120	-	-	-	0.27	-	-	-	-
Slope ($-k_1/2.303$)	**-0.022**	**-0.015**	**-0.014**	**-0.011**	**-0.031**	**-0.025**	**-0.019**	**-0.018**
Intercept ($\log q_e$)	**1.274**	**1.357**	**1.464**	**1.527**	**1.636**	**1.811**	**1.881**	**2.004**
$k_1 \times 10^{-2}$ (min^{-1})	**5.0621**	**3.4533**	**3.2214**	**2.5327**	**7.1432**	**5.7611**	**4.3732**	**4.1541**
Correlation Coefficient (r^2)	**0.9597**	**0.9934**	**0.9971**	**0.9521**	**0.9852**	**0.9811**	**0.9912**	**0.9873**

Table 24

Lagergren Rate Equation for the Adsorption of RB5 Dye from Aqueous Solution onto BR-SAC/BR-PAC

Conditions:
Adsorbent Dosage: 100mg BR-SAC / 50mg BR-PAC
pH : 6.8 ± 0.2
Temperature: 32 ±2°C

Time in minutes	$\log(q_e-q_t)$							
	BR-SAC				BR-PAC			
	Dye Concentration				Dye Concentration			
	30mg/l	50mg/l	70mg/l	100 mg/l	30 mg/l	50 mg/l	70mg/l	100 mg/l
10	1.17	1.40	1.49	1.62	1.27	1.52	1.68	1.87
20	1.03	1.28	1.39	1.53	1.04	1.33	1.50	1.72
30	0.88	1.14	1.26	1.41	0.67	1.06	1.29	1.56
40	0.66	0.96	1.11	1.28	0.22	0.74	0.97	1.32
50	0.47	0.80	0.97	1.17	-0.35	0.35	0.55	0.91
60	0.26	0.56	0.75	0.99	-	-0.10	0.11	0.51
80	-0.16	0.16	0.37	0.73	-	-	-	-0.09
100	-	-	0.09	0.29	-	-	-	-
120	-	-	-	0.18	-	-	-	-
Slope ($-k_1/2.303$)	**-0.019**	**-0.017**	**-0.016**	**-0.014**	**-0.042**	**-0.032**	**-0.031**	**-0.029**
Intercept ($\log q_e$)	**1.116**	**1.336**	**1.438**	**1.531**	**1.788**	**1.952**	**2.118**	**2.321**
$k_1 \times 10^{-2}$ (min^{-1})	**4.3821**	**3.9236**	**3.6851**	**3.2252**	**9.2121**	**7.3723**	**7.1441**	**6.6814**
Correlation Coefficient (r^2)	**0.9942**	**0.9910**	**0.9880**	**0.9831**	**0.9750**	**0.9792**	**0.9692**	**0.9743**

Table 25

Lagergren Rate Equation for the Adsorption of CR Dye from Aqueous Solution onto BR-SAC/BR-PAC

Conditions:
Adsorbent Dosage: 100mg BR-SAC / 50mg BR-PAC
pH : 6.8 ± 0.2
Temperature: 32 ±2°C

Time in minutes	**log(q_e-q_t)**							
	BR-SAC				**BR-PAC**			
	Dye Concentration				**Dye Concentration**			
	30mg/l	**50mg/l**	**70mg/l**	**100 mg/l**	**30 mg/l**	**50 mg/l**	**70mg/l**	**100 mg/l**
10	1.20	1.45	1.59	1.74	1.26	1.49	1.64	1.82
20	1.09	1.36	1.51	1.68	1.03	1.30	1.46	1.67
30	0.98	1.28	1.43	1.58	0.80	1.08	1.25	1.49
40	0.84	1.15	1.32	1.50	0.46	0.83	1.00	1.28
50	0.66	1.02	1.19	1.39	-0.32	0.46	0.64	0.95
60	0.47	0.90	1.06	1.31	-	0.18	0.30	0.57
80	0.18	0.64	0.84	1.09	-	-	-	0.01
100	-0.25	0.26	0.63	0.88	-	-	-	-
120	-	-0.29	0.37	0.63	-	-	-	-
140	-	-	-	0.25	-	-	-	-
Slope (-k_1/2.303)	**-0.016**	**-0.012**	**-0.011**	**-0.011**	**-0.037**	**-0.026**	**-0.026**	**-0.026**
Intercept (log q_e)	**1.131**	**1.309**	**1.440**	**1.619**	**1.765**	**1.822**	**1.989**	**2.215**
$k_1 \times 10^{-2}$ (min^{-1})	**3.6847**	**2.7654**	**2.5312**	**2.5323**	**8.5221**	**5.9900**	**5.9902**	**5.9905**
Correlation Coefficient (r^2)	**0.9917**	**0.9828**	**0.9974**	**0.9835**	**0.9172**	**0.9873**	**0.9813**	**0.9790**

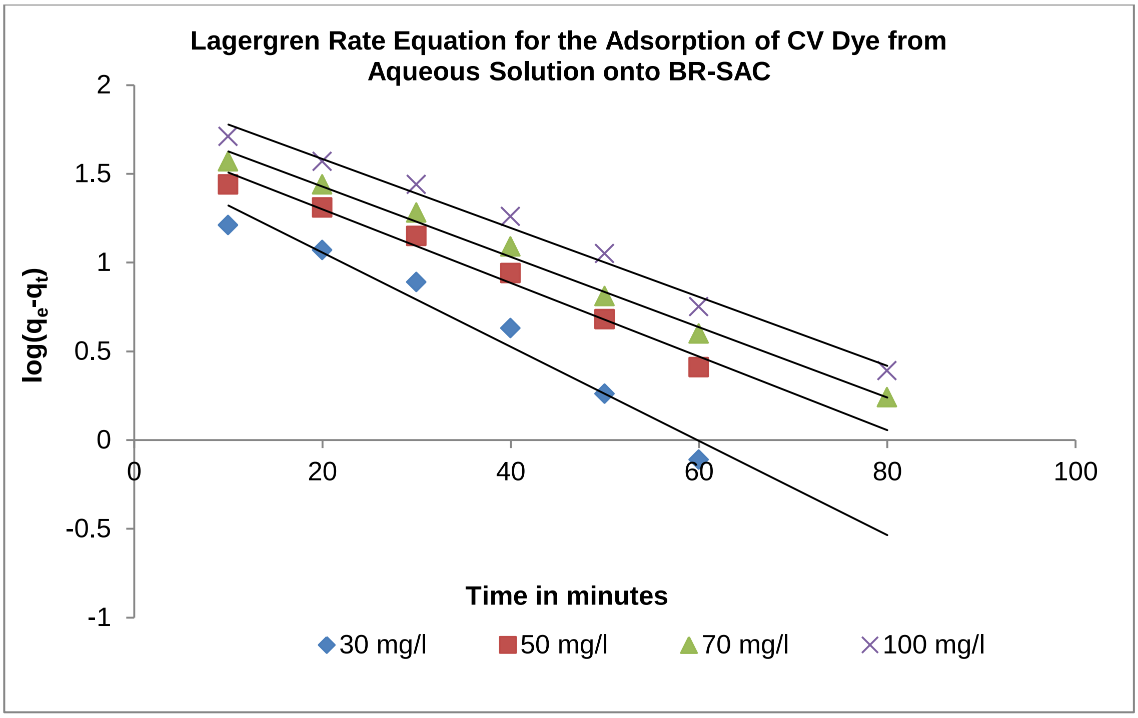


Figure 32

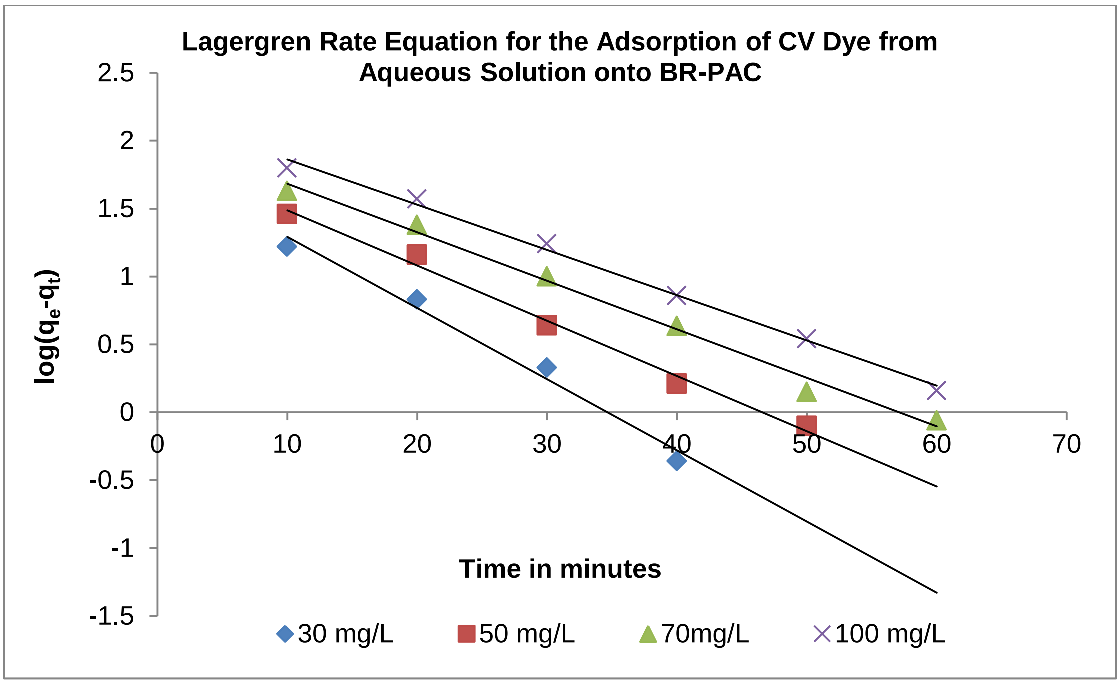


Figure 33

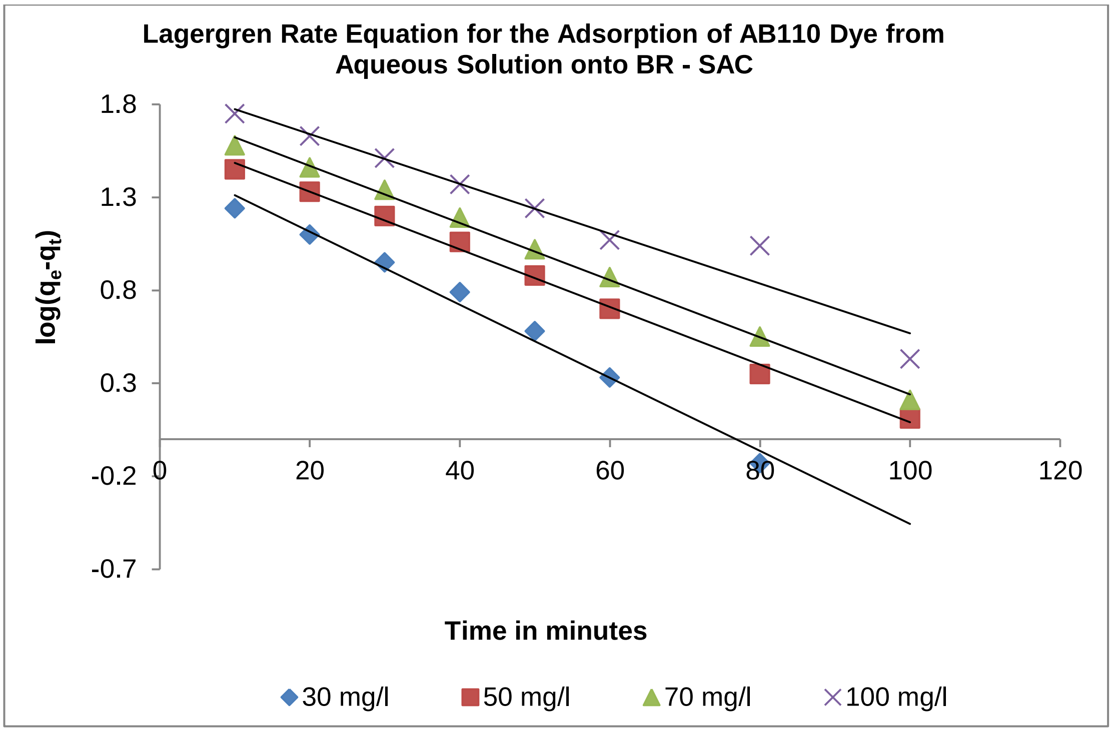


Figure 34

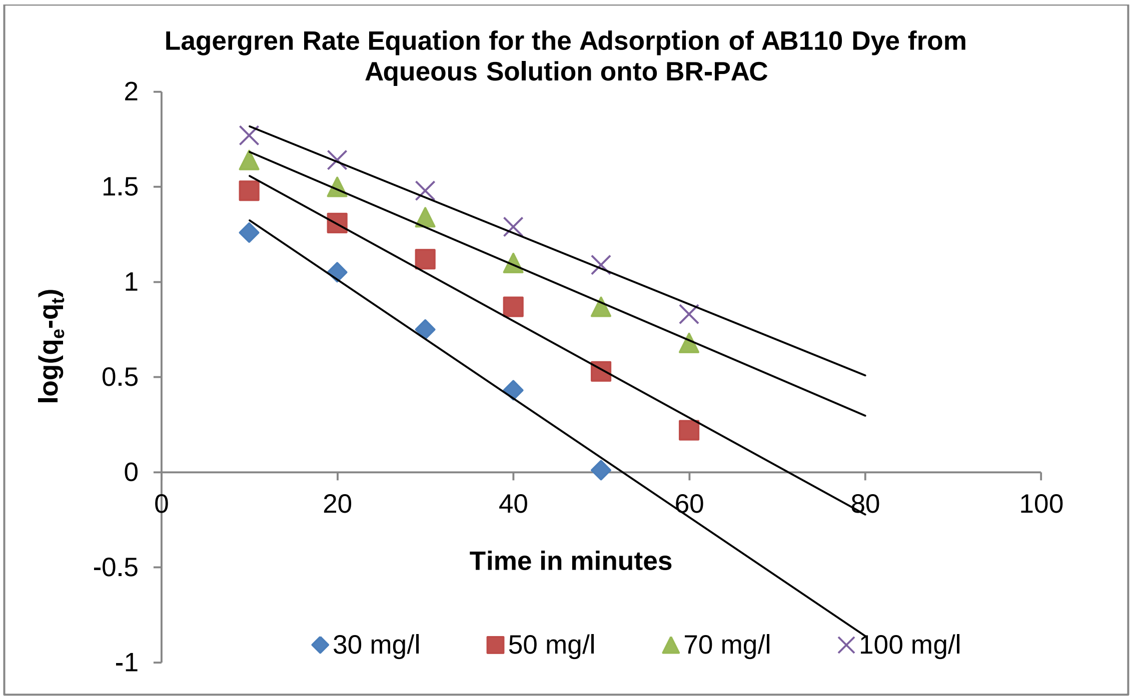


Figure 35

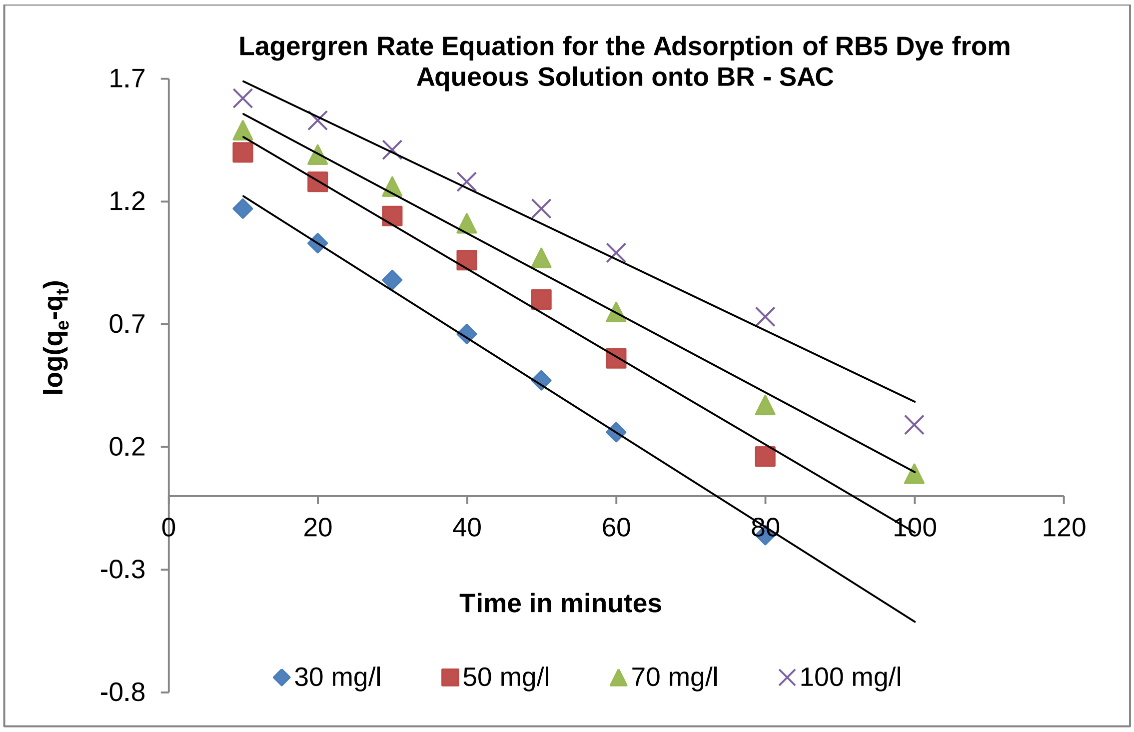


Figure 36

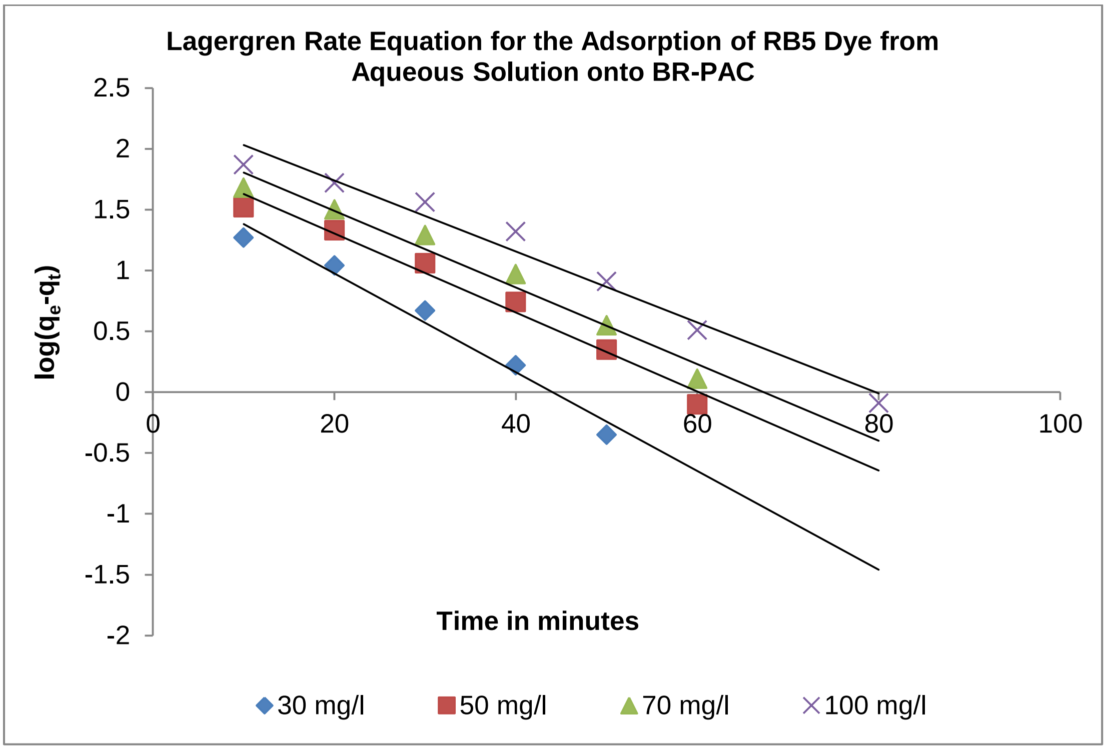


Figure 37

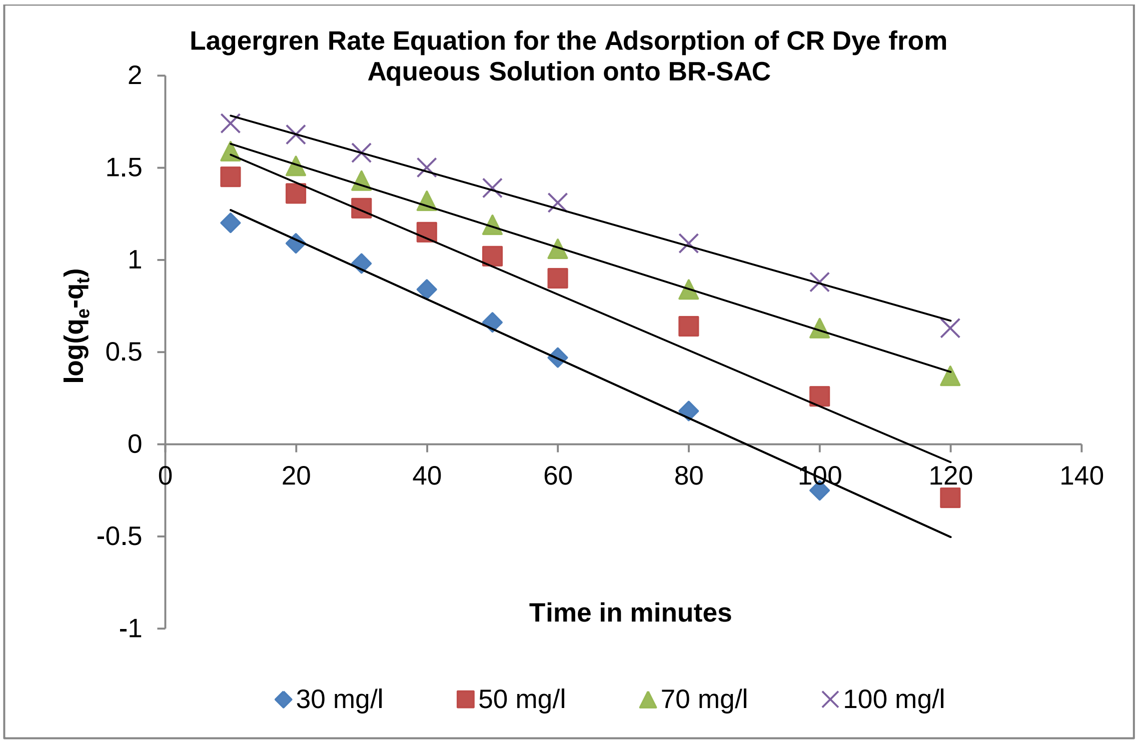


Figure 38

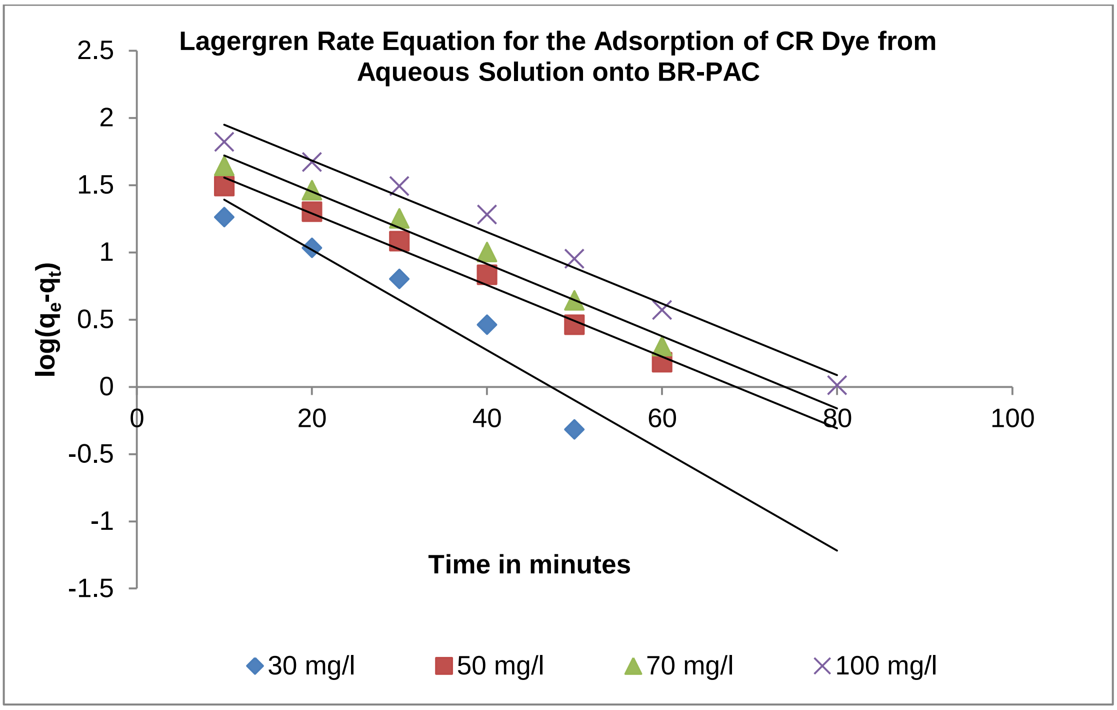


Figure 39

4.5.2 Intraparticle Diffusion Model

The adsorption process of a chemical substance over a porous adsorbent is explained by the following four successive steps **(Bharathi and Ramesh, 2013)**

(1) Transport of adsorbate from bulk solution to the liquid film or boundary layer surrounding the adsorbent
(2) Transport of adsorbate from the boundary film to the external surface of the adsorbent (surface or film diffusion)
(3) Transport of adsorbate from the surface of the adsorbent to the interior pores of adsorbent (pore diffusion or intra particle diffusion)
(4) Adsorption of dyes by the interior surface of the adsorbent.

The overall rate of the adsorption process will be controlled by the slowest step.

Step (1) and step (2) does not control the rate of adsorption since the first step is not involved with adsorbent and the fourth step is a very rapid process. Therefore the rate limiting steps mainly depend on step two (film diffusion) and step three (intra particle diffusion). Since they act in succession, the slower of the two will be the rate determining ste **(Dawood and Sen, 2012).** The chance of the adsorbate species to diffuse into the inner sites of the adsorbent particles was tested with Weber-Morris equation **(Weber and Morris., 1963; Haochun Shi *et al*., 2013)**

$$q = k_{id}\, t^{1/2} + C$$

where

k_{id} = intraparticle diffusion constant (mg $g^{-1}min^{-0.5}$)

C = intercept

To study the intra particle diffusion process, adsorption experiments (batch mode) were conducted by changing the initial concentration of dye solutions with the adsorbents BR-SAC and BR-PAC at 32±2°C and at pH 6.8 ± 0.2. The results were shown in **Tables 26 - 29 and Figures 40 - 47.**

The intra particle diffusion rate constant (k_{id}) was obtained from the slope of the straight line plots of q_t versus $t^{1/2}$. The high correlation co-efficient (r^2) values agreed well for intra particle diffusion model. The values of k_{id} increased with raise in dye concentration which indicates that the adsorption rate is controlled by the transmission of the dye molecules within the stoma of the adsorbents. Generally if the plots are straight line and passing through the origin then the rate of the reaction is controlled only by particle diffusion mechanism. The results of this study showed that the plots were linear but not passing through the origin revealed that the intra particle diffusion was not the only rate limiting step and other kinetic models concurrently limits the adsorption rate **(Theydan *et al*, 2012; Mona. A. Shouman *et al*., 2012).**

From the tables 26 - 29 it was found that the values of the intercept (C) increased with increase in initial concentration of adsorbate molecules. The values of intercept give an idea about the thickness of boundary layer. Greater the intercept, larger is the boundary layer effect. This may be due to instantaneous utilization of the most readily obtainable active sites on the adsorbent surface **(Sumansit Kaur *et al*., 2013).**

A similar phenomenon has been observed in the literature for the adsorption of Crystal Violet dye onto Opal **(Ma *et al*., 2012),** adsorption of Congo Red on Jute fiber **(Aparna roy *et al*, 2013),** removal of Crystal Violet using Water hyacinth **(Rajeswari *et al*., 2017)** and adsorption of Acid Blue 92 on agricultural wastes **(Ram prasath *et al*., 2014).**

Table 26

Intraparticle Diffusion Rate Equation for the Adsorption of CV Dye from Aqueous Solution onto BR-SAC / BR-PAC

Conditions:
Adsorbent Dosage: 100mg BR-SAC / 50mg BR-PAC
pH : 6.8 ± 0.2
Temperature: 32 ± 2°C

$t^{1/2}$ (minutes)	Amount of dye adsorbed q (mg/g)							
	BR-SAC				BR-PAC			
	30 mg/l	50 mg/l	70mg/l	100 mg/l	30 mg/l	50 mg/l	70mg/l	100 mg/l
3.1623	13.76	19.87	24.96	32.18	43.32	68.12	89.90	120.36
4.4721	18.01	27.37	35.01	45.65	53.12	82.46	108.30	146.84
5.4772	22.09	33.74	43.19	55.96	57.78	92.54	122.38	166.32
6.3245	25.56	39.05	50.01	64.88	59.48	95.32	128.14	176.66
7.0711	27.97	42.94	55.99	72.00	59.92	96.16	131.06	180.42
7.7459	29.04	45.16	58.57	77.61	-	96.96	131.60	182.48
8.944	29.81	46.72	60.66	80.71	-	-	132.46	183.92
10.00	-	47.72	62.38	83.21	-	-	-	-
Slope (k_{id})	**2.495**	**4.235**	**5.676**	**7.752**	**4.256**	**6.248**	**7.377**	**11.091**
Intercept (C)	**7.909**	**9.659**	**11.091**	**12.475**	**32.152**	**52.923**	**75.020**	**96.812**
Correlation coefficient (r^2)	**0.8902**	**0.9192**	**0.9225**	**0.9448**	**0.8959**	**0.8747**	**0.8364**	**0.8580**

Table 27

Intraparticle Diffusion Rate Equation for the Adsorption of AB110 Dye from Aqueous Solution onto BR-SAC / BR-PAC

Conditions:
Adsorbent Dosage: 100mg BR-SAC / 50mg BR-PAC
pH : 6.8 ± 0.2
Temperature: 32 ± 2°C

$t^{1/2}$ (minutes)	Amount of dye adsorbed q (mg/g)							
	BR-SAC				BR-PAC			
	30mg/l	50mg/l	70mg/l	100 mg/l	30mg/l	50mg/l	70mg/l	100 mg/l
3.1623	12.15	18.29	21.85	25.23	40.93	65.32	85.99	116.72
4.4721	16.86	25.02	31.02	38.71	48.08	75.12	98.36	132.26
5.4772	20.43	30.55	38.37	48.51	53.65	82.52	108.32	145.50
6.3245	23.28	34.92	44.74	57.22	56.62	88.43	117.19	156.38
7.0711	25.56	38.85	49.59	63.61	58.30	92.36	122.70	163.24
7.7459	27.25	41.44	52.58	69.22	59.33	94.12	125.33	168.86
8.9442	28.65	44.16	56.54	70.01	-	95.79	130.09	175.70
10.000	29.39	45.11	58.46	78.22	-	-	-	-
10.9544	-	46.41	60.07	79.02	-	-	-	-
11.8321	-	-	-	80.90	-	-	-	-
Slope (k_{id})	**1.977**	**3.262**	**4.429**	**6.301**	**10.644**	**15.695**	**22.312**	**29.563**
Intercept(C)	**9.261**	**12.326**	**13.675**	**13.187**	**16.641**	**29.325**	**33.641**	**46.663**
Correlation coefficient (r^2)	**0.8650**	**0.9022**	**0.9081**	**0.9243**	**0.9914**	**0.9851**	**0.9910**	**0.9932**

Table 28

Intraparticle Diffusion Rate Equation for the Adsorption of RB5 Dye from Aqueous Solution onto BR-SAC / BR-PAC

Conditions:
Adsorbent Dosage: 100mg BR-SAC / 50mg BR-PAC
pH : 6.8 ± 0.2
Temperature: 32 ± 2°C

$t^{1/2}$ (minutes)	Amount of dye adsorbed q (mg/g)							
	BR-SAC				BR-PAC			
	30mg/l	50mg/l	70mg/l	100 mg/l	30mg/l	50mg/l	70mg/l	100 mg/l
3.1623	13.17	19.57	25.56	32.25	40.27	62.22	79.94	102.22
4.4721	17.29	25.73	31.64	39.96	47.77	74.16	95.54	122.84
5.4772	20.46	30.86	38.28	47.65	54.00	84.12	108.24	139.06
6.3245	23.44	35.44	43.48	54.74	57.07	90.16	118.24	154.92
7.0711	25.07	38.31	47.15	59.00	58.28	93.42	124.07	167.62
7.7459	26.20	40.96	50.76	63.85	58.73	94.88	126.33	172.52
8.9442	27.34	43.16	54.12	68.22	-	95.66	127.62	174.96
10.000	28.03	44.61	55.22	71.69	-	-	-	175.76
10.9544	-	-	56.44	72.12	-	-	-	-
Slope (k_{id})	**1.923**	**3.318**	**4.135**	**5.409**	**10.9**	**17.37**	**25.01**	**35.34**
Intercept(C)	**9.514**	**12.261**	**15.262**	**18.052**	**15.655**	**23.470**	**22.947**	**21.478**
Correlation coefficient(r^2)	**0.8890**	**0.9192**	**0.9434**	**0.9553**	**0.9781**	**0.9660**	**0.9742**	**0.9580**

Table 29

Intraparticle Diffusion Rate Equation for the Adsorption of CR Dye from Aqueous Solution onto BR-SAC / BR-PAC

Conditions:
Adsorbent Dosage: 100mg BR-SAC / 50mg BR-PAC
pH : 6.8 ± 0.2
Temperature: 32 ± 2°C

$t^{1/2}$ (minutes)	Amount of dye adsorbed q(mg/g)							
	BR-SAC				BR-PAC			
	30mg/l	50mg/l	70mg/l	100 mg/l	30mg/l	50mg/l	70mg/l	100 mg/l
3.1623	11.95	15.83	18.79	22.48	41.48	65.52	85.74	112.44
4.4721	15.44	21.11	25.40	30.55	48.72	76.42	100.16	130.64
5.4772	18.37	25.34	30.93	39.54	53.16	84.22	111.46	146.90
6.3245	20.96	29.93	36.85	46.30	56.60	89.62	119.24	158.72
7.0711	23.30	33.66	42.36	53.22	59.04	93.42	125.04	169.04
7.7459	24.89	36.31	46.36	57.60	59.52	94.80	127.40	174.28
8.9442	26.33	39.87	50.88	65.50	-	96.32	129.42	177.00
10.000	27.27	42.38	53.61	70.25	-	-	-	178.00
10.9544	27.83	43.70	55.47	73.65	-	-	-	-
11.8321	-	44.21	57.84	76.14	-	-	-	-
Slope (k_{id})	**2.107**	**3.424**	**4.645**	**6.452**	**4.035**	**5.525**	**7.893**	**10.05**
Intercept(C)	**6.792**	**7.211**	**6.550**	**4.491**	**30.051**	**51.810**	**65.353**	**89.040**
Correlation coefficient(r^2)	**0.9427**	**0.9564**	**0.9621**	**0.9772**	**0.9680**	**0.9255**	**0.9337**	**0.9010**

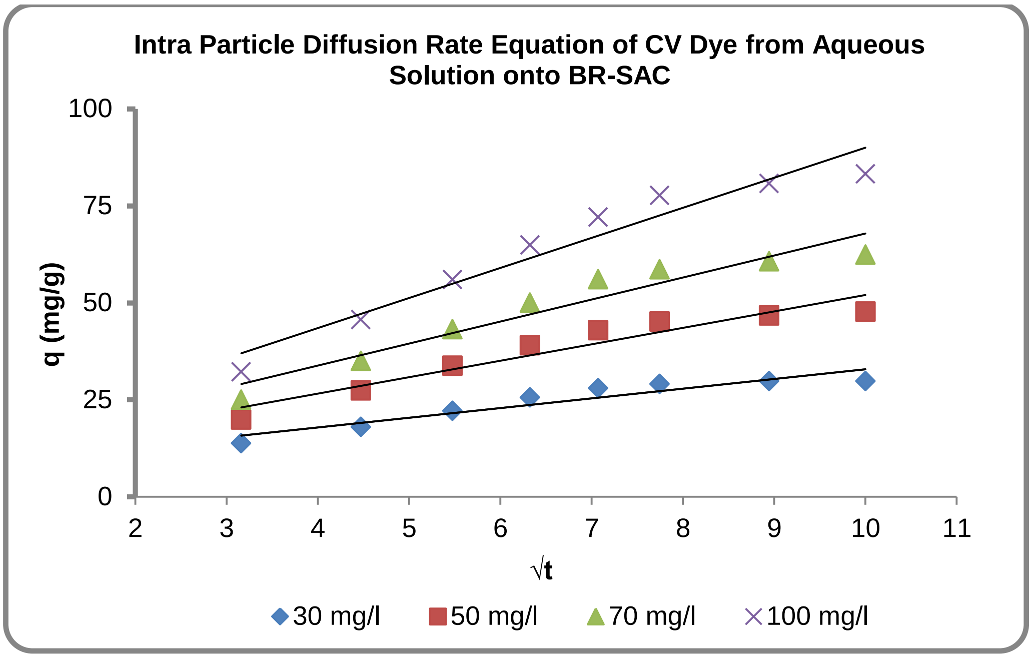
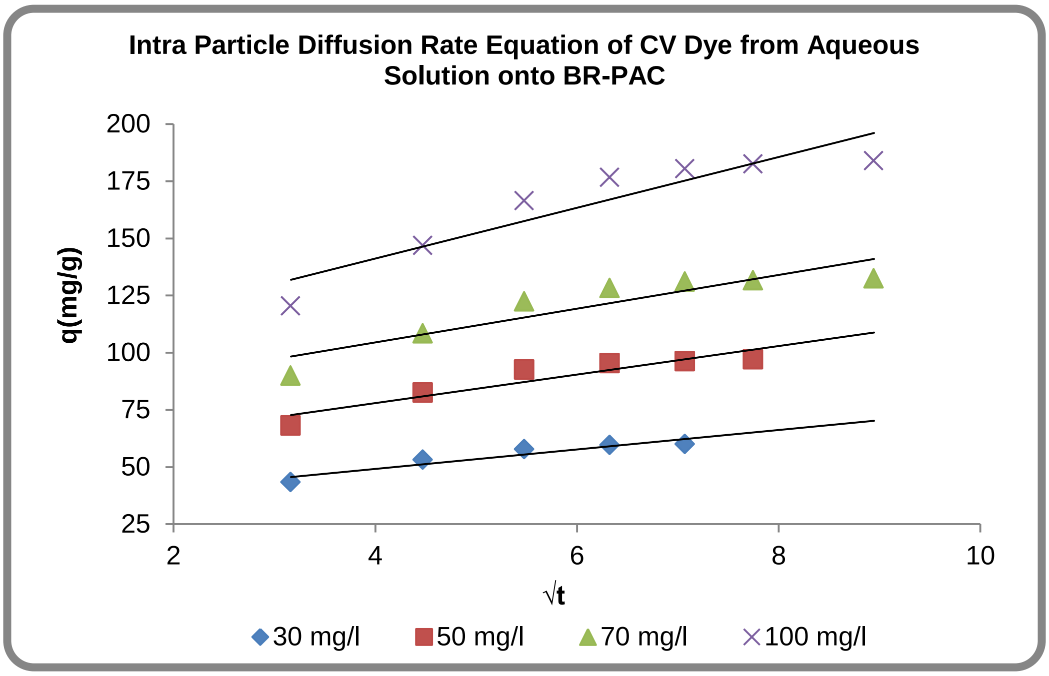


Figure 40



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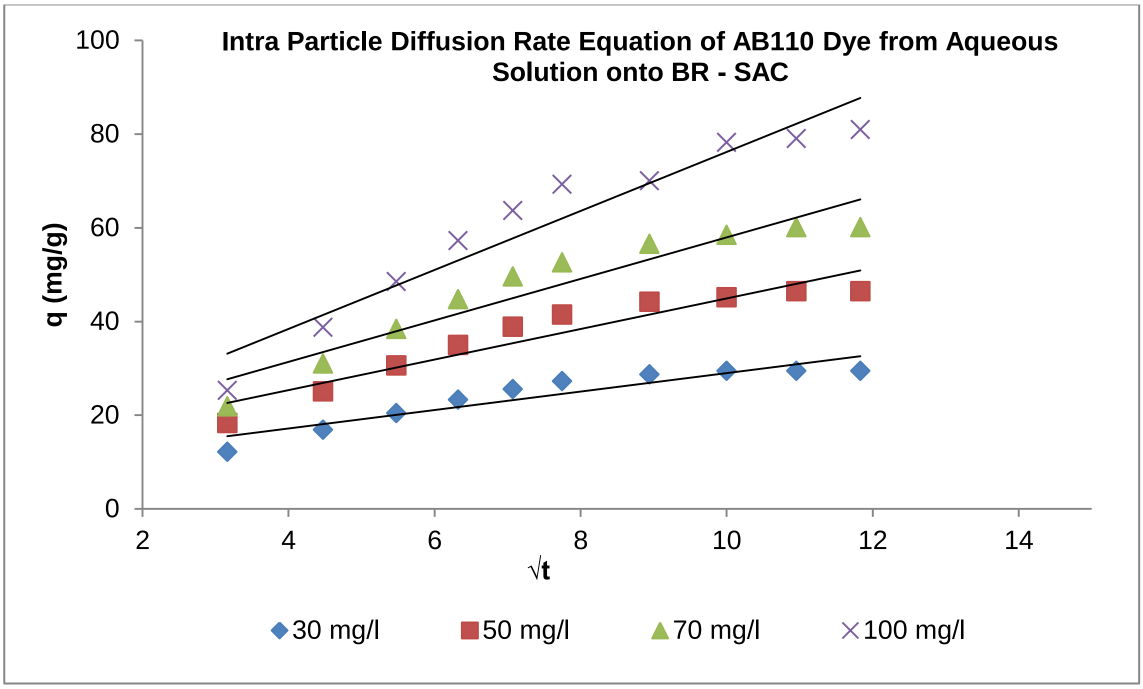

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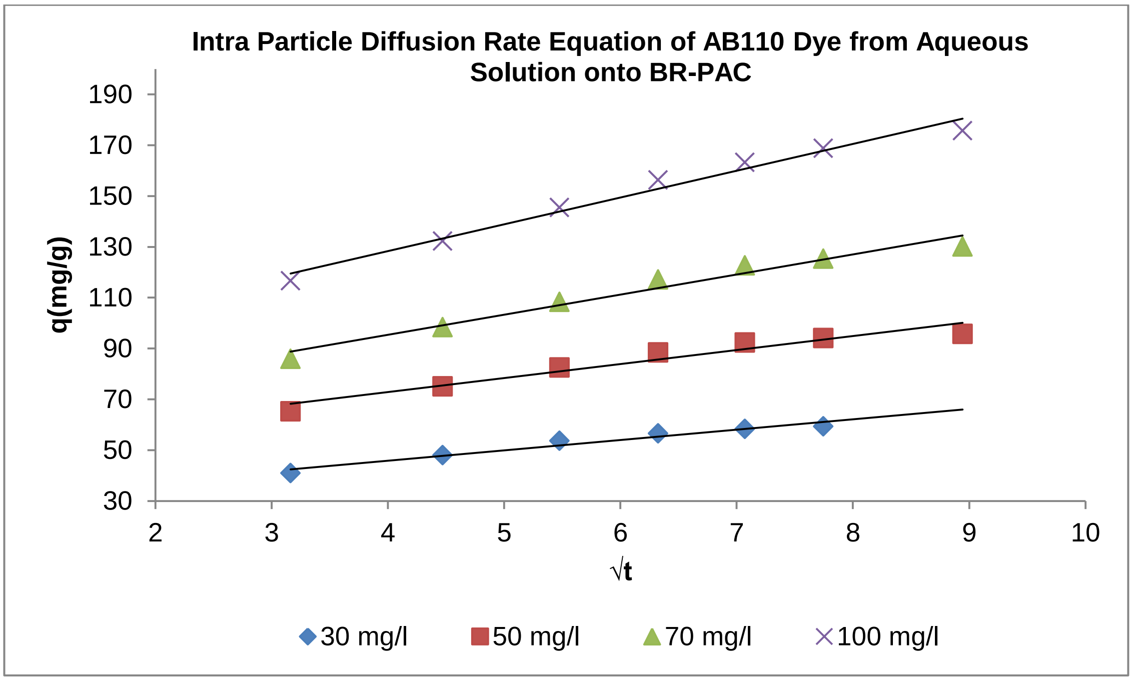

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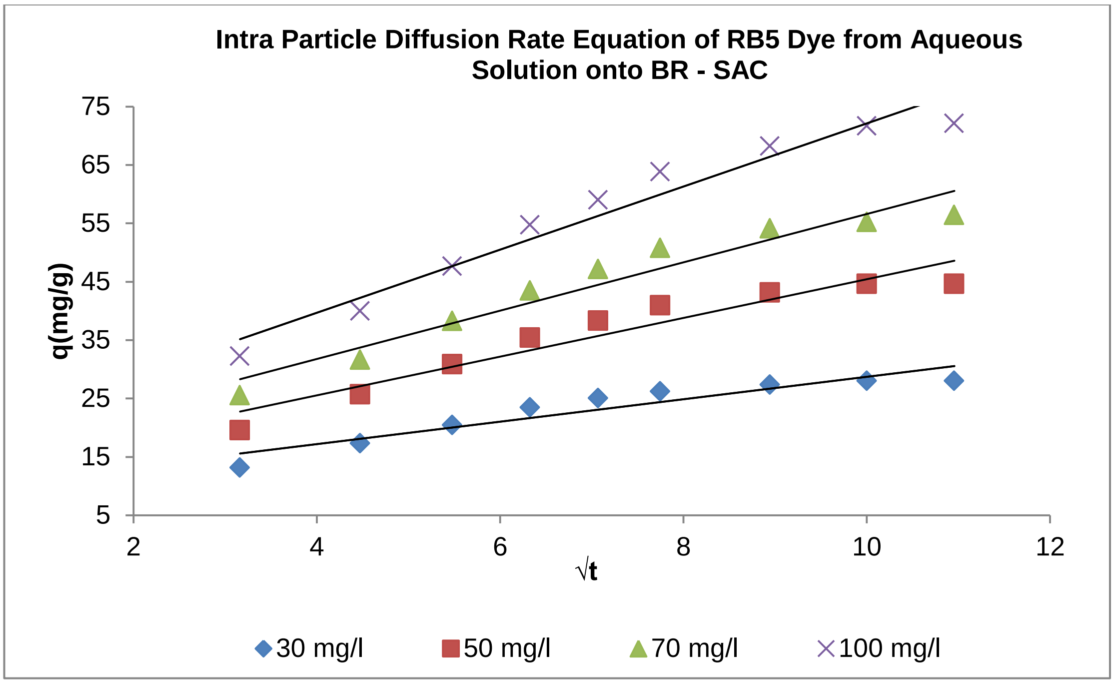

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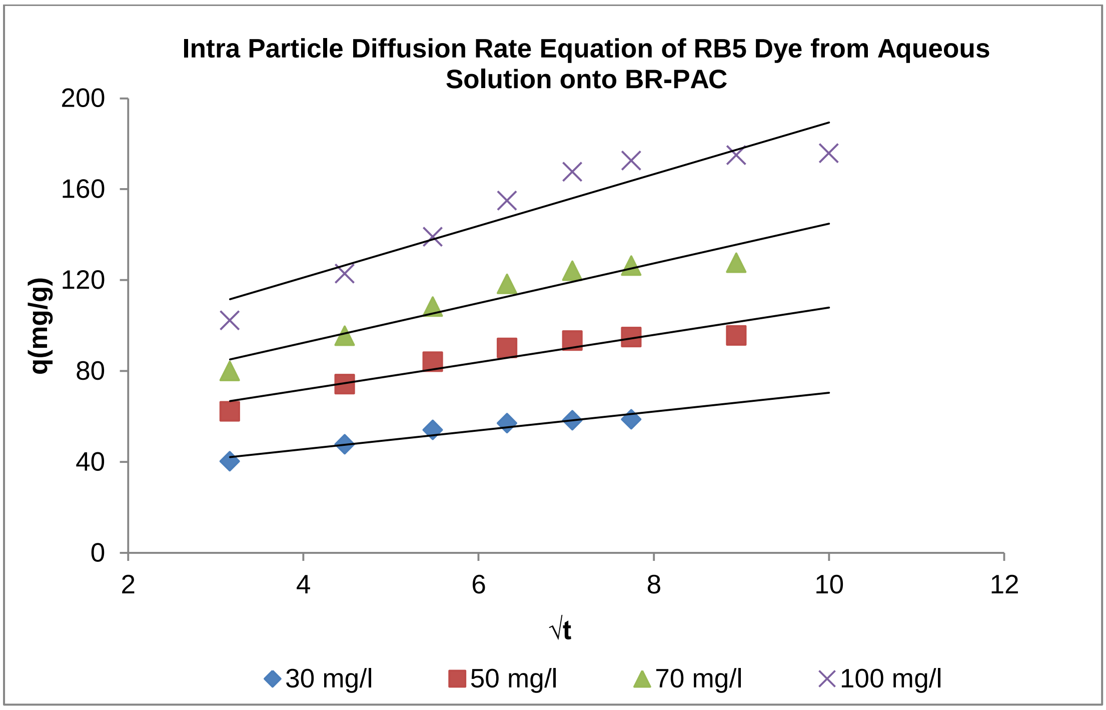

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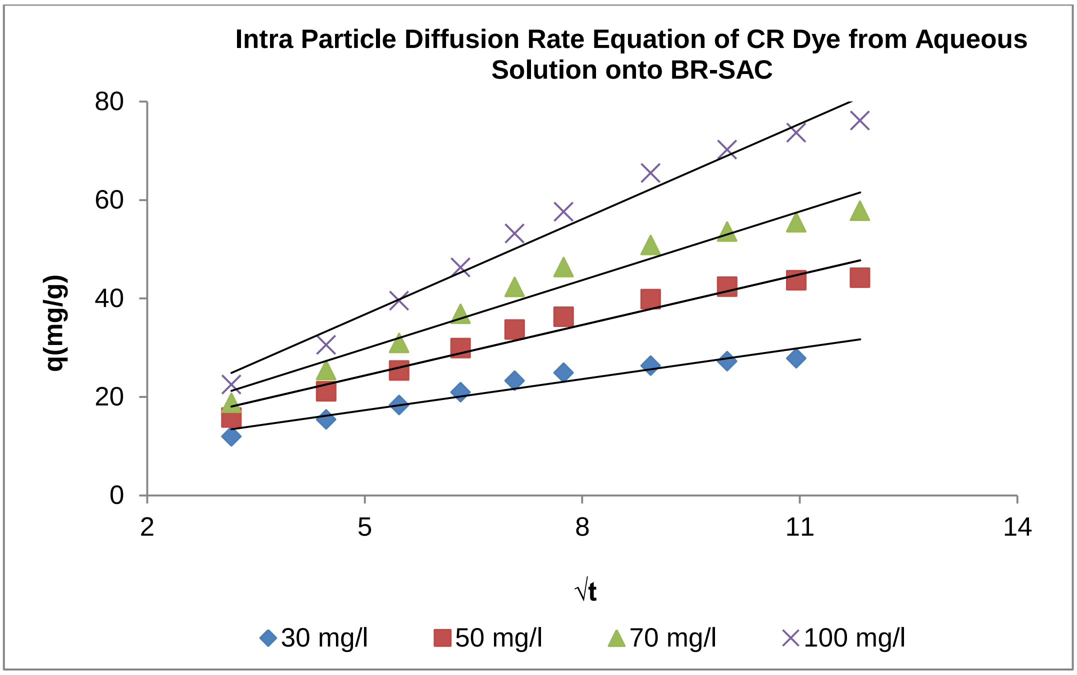

Figure 46

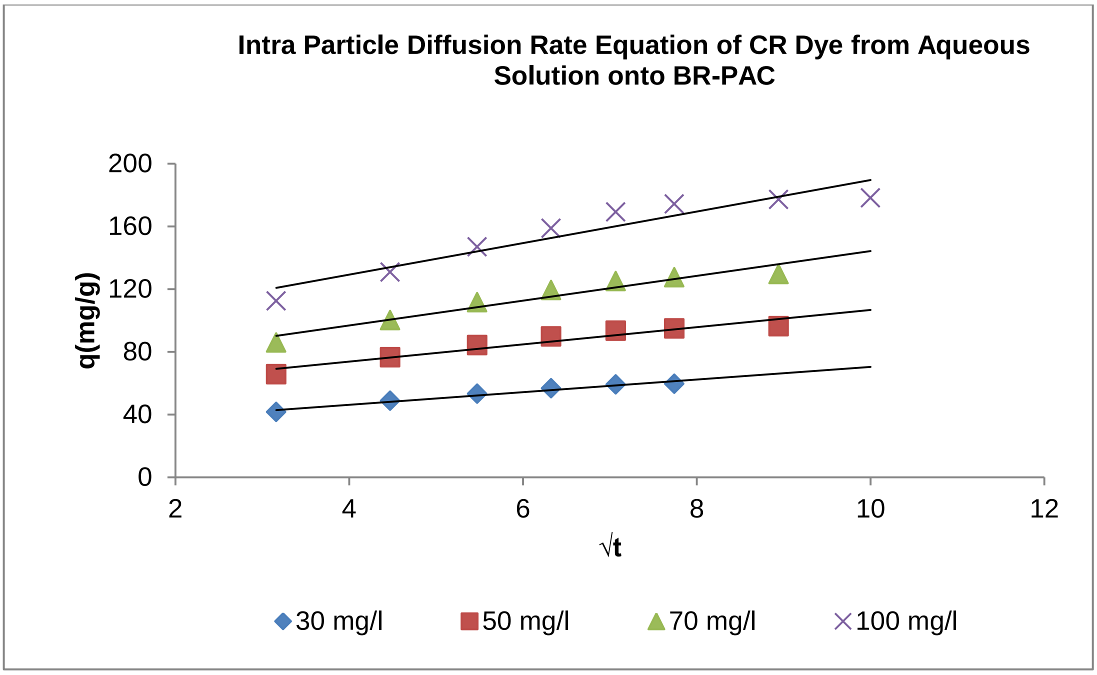

Figure 47

4.5.3 Elovich Kinetic Model

The kinetics of chemisorption of gases onto solids can be studied using the following Elovich equation **(Zeldowitsch, 1934).**

$$\frac{d_{q_t}}{dt} = \alpha\ e^{-\beta q_t}$$

where

'q_t' is the amount of dye adsorbed by the adsorbent at time 't'(mg/g)

'α' is the initial adsorption rate (mg g^{-1} min^{-1}) and

'β' is desorption constant (g mg^{-1}).

To study the Elovich rate equation, Chien and Clayton (1980) assumed αβ ≫ 1 and by pertaining the boundary conditions $q_t = 0$ at t=0 and $q_t = q_t$ and t = t, the above equation turn out to be

$$q = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t$$

The values α and β can be estimated by plotting a graph of q_t versus ln t. The value of α is calculated from the intercept and β from slope of the straight line plots. The α and β values obtained in this study for the adsorption of CV, AB110, RB5, and CR dyes from aqueous solution for both the adsorbents BR-SAC and BR-PAC were indicated in **Tables 30-33** and the graphical representation are shown in **Figures 48 -55.**

The value of initial adsorption rate α increases with increase in concentration of the dye solutions indicated the existence of more active sites on the surface of the BR-SAC and BR-PAC adsorbents for immediate adsorption of dyes from aqueous solution **(Satish patial *et al.,* 2011).** The values of β drops off with raise in initial concentration of the adsorbate solutions indicates the increase in adsorption of dye species with increase in dye concentration (**Ho and MC Kay, 2004, Sivakumar *et al*., 2014 and Theivarasu *et al*., 2010).**

Similar results were reported for adsorption of Direct Yellow 12 dye on Coconut Shell carbon **(Aseel Aljeboree *et al*., 2017),** adsorption of Light Green anionic dye on Surfactant modified Peanut Husk **(Zhao *et al*., 2014),** removal of Congo Red using seeds of Martynia Annua.L **(Sivakumar *et al*., 2014),** adsorption of Malachite Green dye onto Sea Shell **(Ali Shamei *et al*., 2016)** and adsorption of Rhodamine B using Cocoa Shell **(Theivarasu *et al*., 2010).**

Table 30

Elovich Rate Equation for the Adsorption of CV Dye from Aqueous Solution onto BR-SAC / BR-PAC

Conditions:
Adsorbent Dose: 100mg BR-SAC / 50mg BR-PAC
pH: 6.8 ± 0.2
Temperature: 32 ± 2°C

Time (minutes)	ln t	Amount dye adsorbed q_t (mg/g)							
		BR-SAC				BR-BAC			
		30mg/l	50mg/l	70mg/l	100 mg/l	30mg/l	50mg/l	70mg/l	100 mg/l
10	2.30	13.76	19.87	24.96	32.18	43.32	68.12	89.90	120.36
20	2.99	18.01	27.37	35.01	45.65	53.12	82.46	108.3	146.84
30	3.40	22.09	33.74	43.19	55.96	57.78	92.54	122.38	166.32
40	3.69	25.56	39.05	50.01	64.88	59.48	95.32	128.14	176.66
50	3.91	27.97	42.94	55.99	72.00	59.92	96.16	131.06	180.42
60	4.09	29.04	45.16	58.57	77.61	_	96.96	131.60	182.48
80	4.38	29.81	46.72	60.66	80.71	-	-	132.46	183.92
100	4.61	29.81	47.72	62.38	83.21	-	-	-	-
120	4.79	29.81	47.72	62.38	83.21	-	-	-	-
Slope(1/β)		**7.758**	**13.07**	**17.49**	**23.75**	**10.62**	**16.65**	**21.66**	**32.41**
Intercept (1/β)×ln(αβ)		**-3.977**	**-10.19**	**-15.39**	**-23.17**	**20.10**	**32.01**	**43.90**	**50.63**
Initial adsorption rate constant(α) (mg g^{-1} min^{-1})		**4.646**	**5.995**	**7.251**	**8.955**	**70.485**	**113.860**	**164.470**	**154.63**
Desorption Constant(β) (g mg^{-1})		**0.128**	**0.076**	**0.057**	**0.042**	**0.094**	**0.060**	**0.046**	**0.0309**
Correlation Coefficient (r^2)		**0.958**	**0.976**	**0.977**	**0.984**	**0.955**	**0.945**	**0.932**	**0.946**

Table 31

Elovich Rate Equation for the Adsorption of AB110 Dye from Aqueous Solution onto BR-SAC / BR-PAC

Conditions :
Adsorbent Dose: 100mg BR-SAC / 50mg BR-PAC
pH: 6.8 ± 0.2
Temperature: 32 ± 2°C

Time (minutes)	ln t	Amount dye adsorbed q_t (mg/g)							
		BR-SAC				BR-BAC			
		30mg/l	50mg/l	70mg/l	100 mg/l	30mg/l	50mg/l	70mg/l	100 mg/l
10	2.30	12.15	18.29	21.85	25.23	40.93	65.32	85.99	116.72
20	2.99	16.86	25.02	31.02	38.71	48.08	75.12	98.36	132.26
30	3.40	20.43	30.55	38.37	48.51	53.65	82.52	108.32	145.5
40	3.69	23.28	34.92	44.74	57.22	56.62	88.43	117.19	156.38
50	3.91	25.56	38.85	49.59	63.61	58.3	92.36	122.7	163.24
60	4.09	27.25	41.44	52.58	69.22	59.33	94.12	125.33	168.86
80	4.38	28.65	44.16	56.54	70.01	-	95.79	130.09	175.7
100	4.61	29.39	45.11	58.46	78.22	-	-	-	-
120	4.79	29.39	46.41	60.07	79.02	-	-	-	-
140	4.94	29.39	46.41	60.07	80.9	-	-	-	-
Slope(1/β)		**7.02**	**11.49**	**15.58**	**22.04**	**10.64**	**15.69**	**22.31**	**29.56**
Intercept (1/β)×ln(αβ)		**-3.24**	**-7.82**	**-13.59**	**-25.11**	**16.64**	**29.30**	**33.64**	**46.66**
Initial adsorption rate constant(α) (mg g^{-1} min^{-1})		**4.425**	**5.819**	**6.511**	**7.045**	**50.827**	**101.461**	**100.716**	**143.18**
Desorption Constant(β) (g mg^{-1})		**0.142**	**0.087**	**0.064**	**0.045**	**0.094**	**0.063**	**0.044**	**0.033**
Correlation Coefficient (r^2)		**0.959**	**0.975**	**0.979**	**0.985**	**0.991**	**0.985**	**0.991**	**0.993**

Table 32

Elovich Rate Equation for the Adsorption of RB5 from Aqueous Solution onto BR-SAC / BR-PAC

Conditions :

Adsorbent Dose: 100mg BR-SAC / 50mg BR-PAC
pH: 6.8 ± 0.2
Temperature: 32 ± 2°C

Time (minutes)	ln t	Amount dye adsorbed q_t (mg/g)							
		BR-SAC				BR-BAC			
		30 mg/l	50 mg/l	70 mg/l	100 mg/l	30 mg/l	50 mg/l	70 mg/l	100 mg/l
10	2.30	13.17	19.57	25.56	32.25	40.27	62.22	79.94	102.22
20	2.99	17.29	25.73	31.64	39.96	47.77	74.16	95.54	122.84
30	3.40	20.46	30.86	38.28	47.65	54	84.12	108.24	139.06
40	3.69	23.44	35.44	43.48	54.74	57.07	90.16	118.24	154.92
50	3.91	25.07	38.31	47.15	59.00	58.28	93.42	124.07	167.62
60	4.09	26.2	40.96	50.76	63.85	58.73	94.88	126.33	172.52
80	4.38	27.34	43.16	54.12	68.22	-	95.66	127.62	174.96
100	4.61	28.03	44.61	55.22	71.69	-	-	-	175.76
120	4.79	28.03	44.61	56.44	72.12	-	-	-	-
140	4.97	-	-	56.44	73.64	-	-	-	-
Slope(1/β)		**6.42**	**10.96**	**12.91**	**17.07**	**10.90**	**17.37**	**25.01**	**35.34**
Intercept (1/β)×ln(αβ)		**-1.16**	**-5.69**	**-4.578**	**-8.46**	**15.65**	**23.47**	**22.94**	**21.47**
Initial adsorption rate constant(α) (mg g^{-1} min^{-1})		**5.362**	**6.525**	**9.049**	**10.394**	**45.782**	**67.081**	**62.560**	**64.863**
Desorption Constant(β) (g mg^{-1})		**0.155**	**0.091**	**0.077**	**0.058**	**0.091**	**0.057**	**0.040**	**0.028**
Correlation Coefficient (r^2)		**0.968**	**0.979**	**0.974**	**0.983**	**0.978**	**0.966**	**0.974**	**0.958**

Table 33

Elovich Rate Equation for the Adsorption of CR Dye from Aqueous Solution onto BR-SAC / BR-PAC

Conditions :
Adsorbent Dose: 100mg BR-SAC / 50 mg BR-PAC
pH: 6.8 ± 0.2
Temperature: 32 ± 2°C

Time (minutes)	ln t	Amount dye adsorbed q_t (mg/g)							
		BR-SAC				BR-BAC			
		30mg/l	50mg/l	70mg/l	100 mg/l	30mg/l	50mg/l	70mg/l	100 mg/l
10	2.30	11.95	15.83	18.79	22.48	41.48	65.52	85.74	112.44
20	2.99	15.44	21.11	25.4	30.55	48.72	76.42	100.16	130.64
30	3.40	18.37	25.34	30.93	39.54	53.16	84.22	111.46	146.9
40	3.69	20.96	29.93	36.85	46.3	56.6	89.62	119.24	158.72
50	3.91	23.3	33.66	42.36	53.22	59.04	93.42	125.04	169.04
60	4.09	24.89	36.31	46.36	57.6	59.52	94.8	127.4	174.28
80	4.38	26.33	39.87	50.88	65.5	-	96.32	129.42	177
100	4.61	27.27	42.38	53.61	70.25	-	-	-	178
120	4.79	27.83	43.7	55.47	73.65	-	-	-	-
140	4.97	-	44.21	57.84	76.14	-	-	-	-
Slope(1/β)		**6.89**	**11.78**	**15.91**	**21.96**	**10.48**	**15.75**	**22.53**	**31.19**
Intercept (1/β)×ln(αβ)		**-4.34**	**-12.82**	**-20.37**	**-32.34**	**17.46**	**30.01**	**34.37**	**41.36**
Initial adsorption rate constant(α) (mg g^{-1} min^{-1})		**3.666**	**3.967**	**4.415**	**5.047**	**55.437**	**105.852**	**103.561**	**117.78**
Desorption Constant(β) (g mg^{-1})		**0.145**	**0.084**	**0.062**	**0.045**	**0.095**	**0.063**	**0.044**	**0.032**
Correlation Coefficient (r^2)		**0.984**	**0.985**	**0.984**	**0.985**	**0.994**	**0.981**	**0.983**	**0.966**

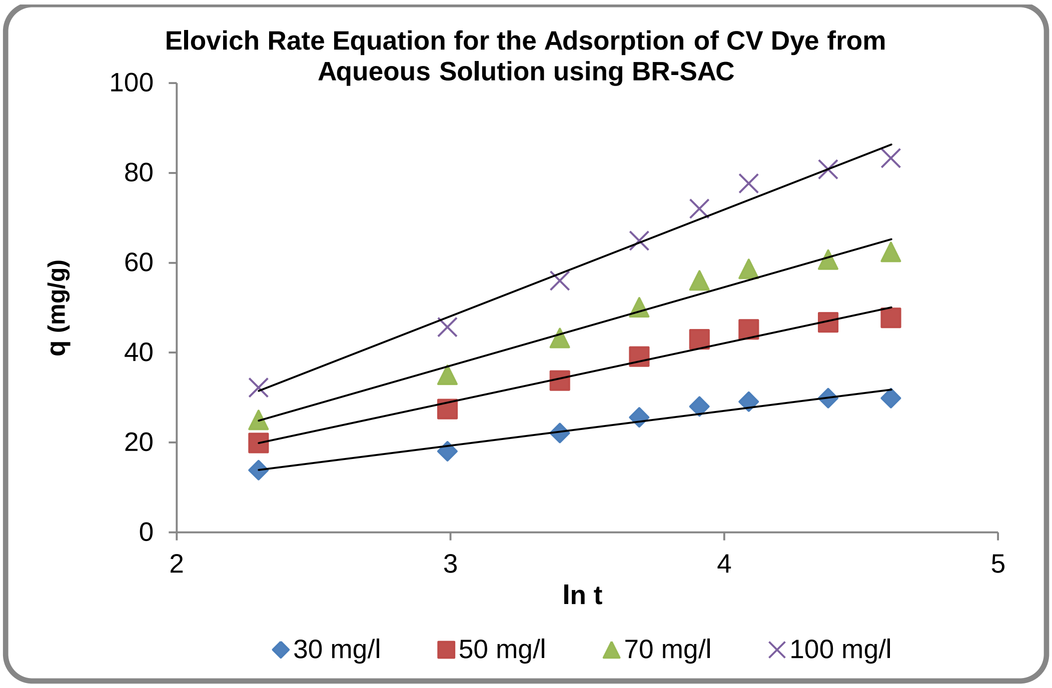

Figure 48

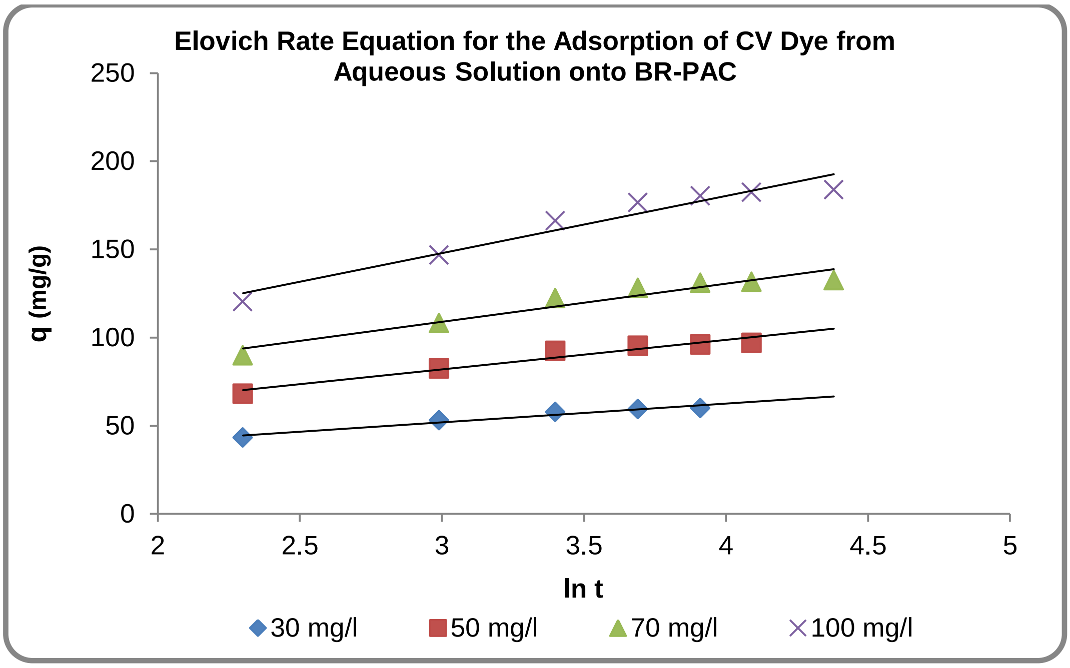

Figure 49

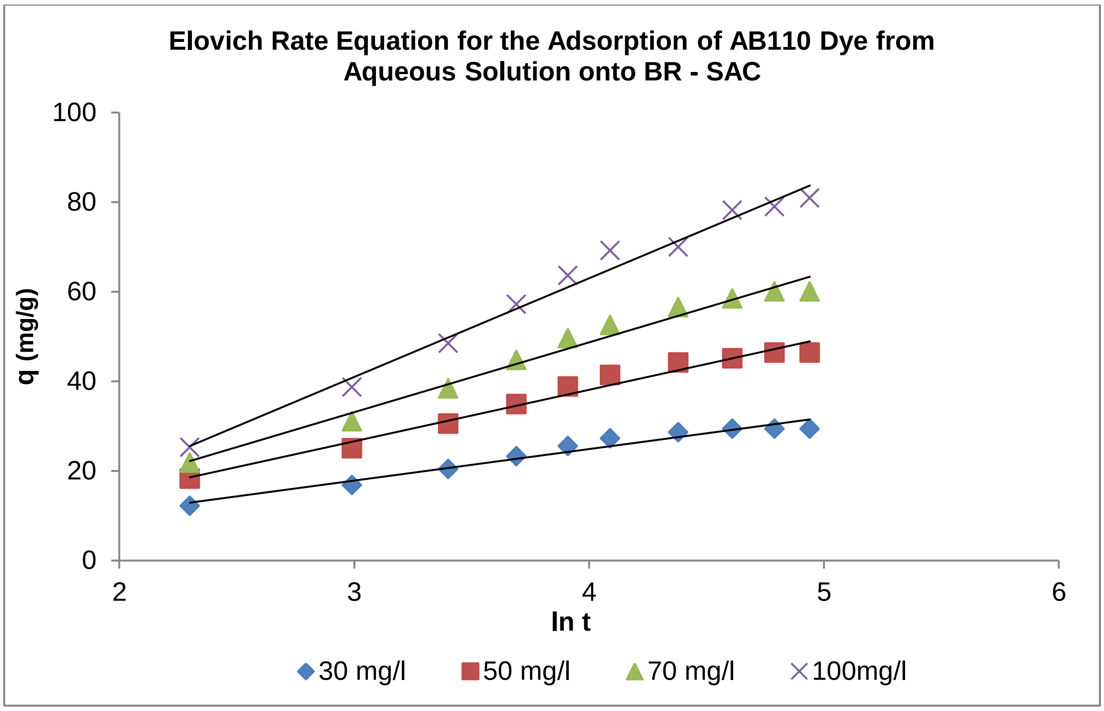

Figure 50

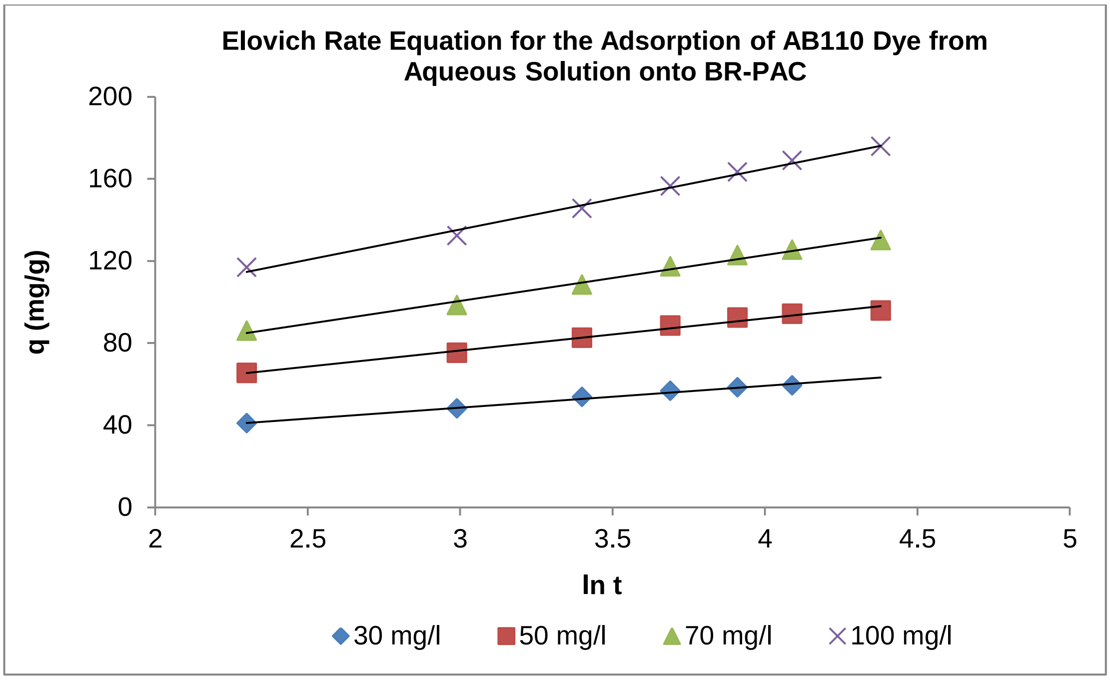

Figure 51

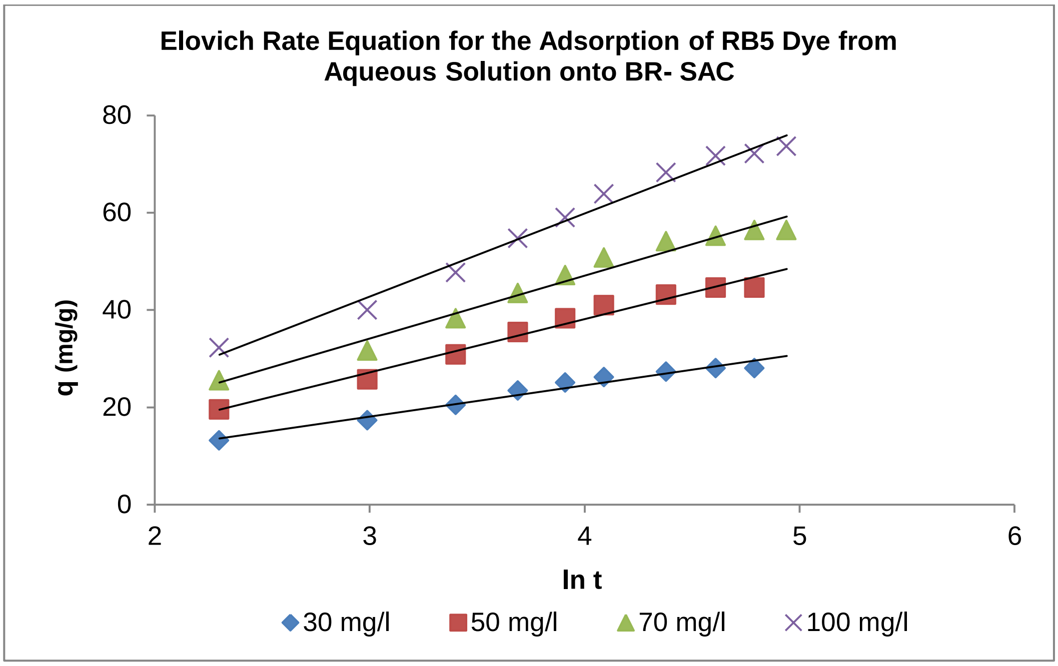

Figure 52

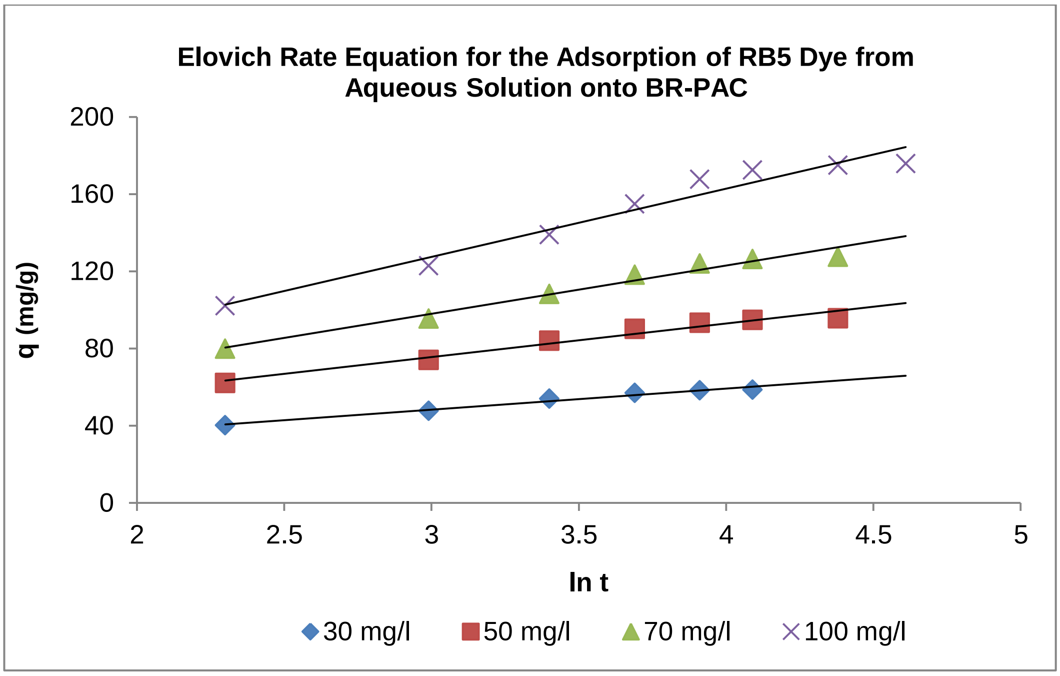

Figure 53

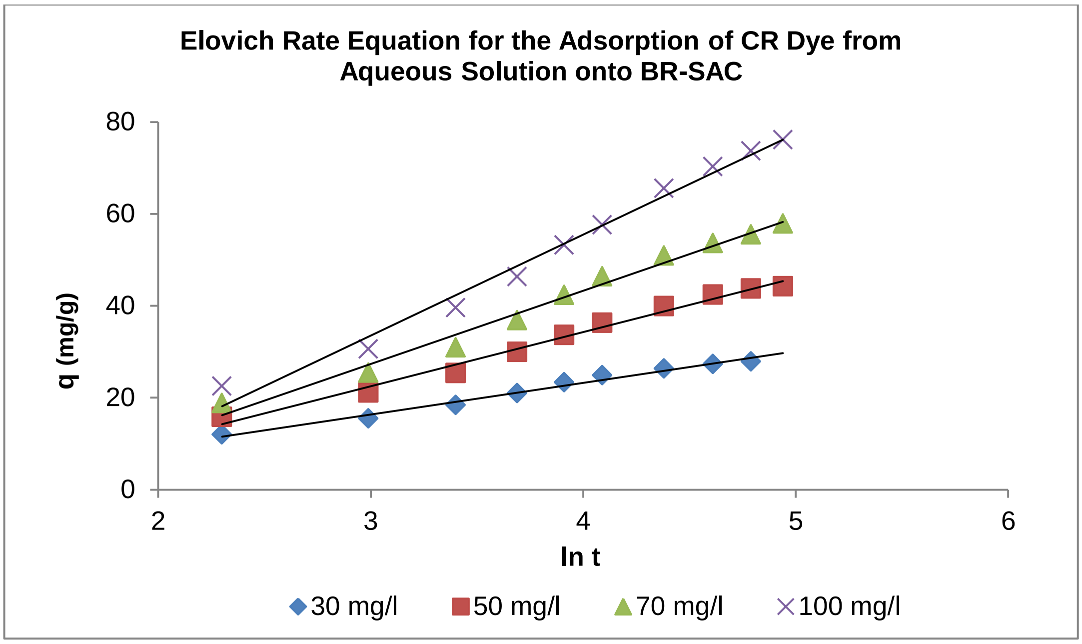

Figure 54

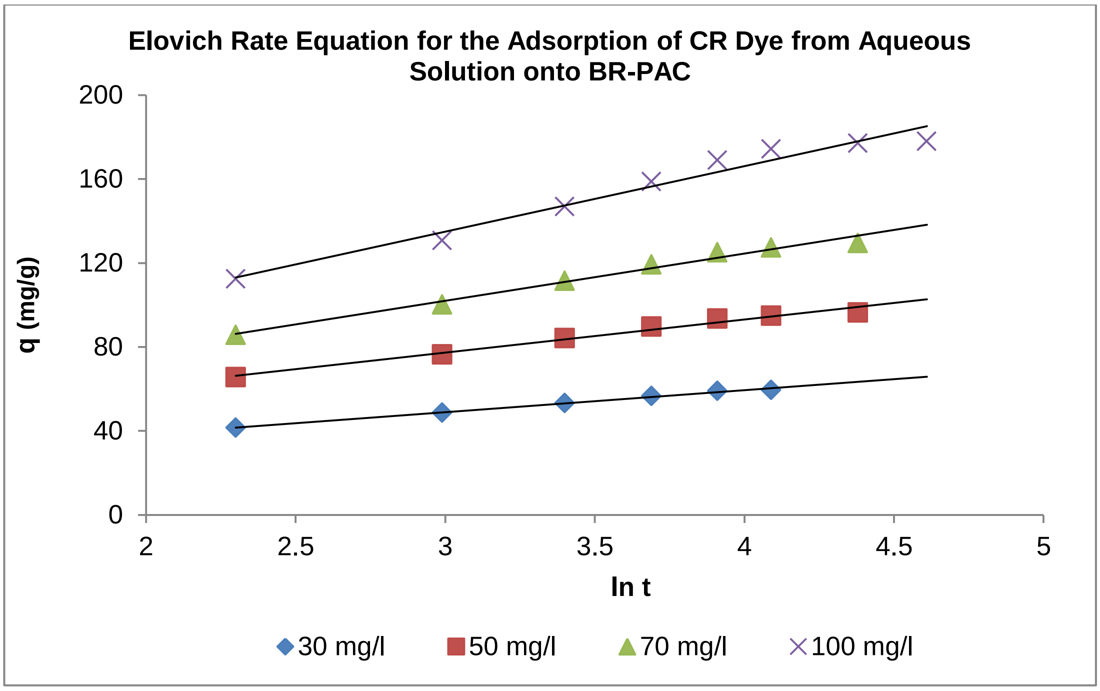

Figure 55

4.6 Adsorption Isotherms

The adsorption isotherm can be used to interpret the interaction between the adsorbate and adsorbent of any system and the estimation of adsorption capacity of the adsorbent **(Bharathi Ramesh., 2013)**.

The correlation between the mass of the adsorbate that is retained per unit mass of the adsorbent and the concentration of the adsorbate at equilibrium can be explained by adsorption isotherms **(Ayesha Wasti *et al*., 2016).**

In the current study the adsorption capacities of the adsorbents for the removal of dyes from aqueous solution was obtained by demonstrating the experimental data with the Langmuir and Frendlich adsorption isotherm models.

Adsorption isotherms were studied by varying the initial concentration of the CV, AB110, RB5 and CR dye solutions using the adsorbents BR-SAC and BR-PAC.

4.6.1 Langmuir Adsorption Isotherm:

Irvin Langmuir developed Langmuir adsorption isotherm to illustrate the surface coverage of the adsorbate on a solid adsorbent surface. Langmuir adsorption isotherm model describes monolayer coverage of the adsorbate over a homogeneous adsorbent surface with energetically equivalent adsorption sites **(Aparna Roy *et al*., 2013).** Moreover it is considered that the existence of adsorbed molecules at one site will not affect the adsorption of molecules at neighboring site (**Valliammai *et al*., 2013; Renugadevi *et al*., 2009a).** The linear form Langmuir adsorption equation is generally expressed as **(Langmuir, 1916)**

$$\frac{C_e}{q_e} = \frac{1}{Q_m k_L} + \frac{1}{Q_m} C_e$$

where

C_e is the concentration of dye solution at equilibrium (mg/l)

q_e is the amount of dye adsorbed per unit mass of adsorbent (mg/g)

Q_m is theoretical monolayer adsorption capacity (mg/g) and

k_L is Langmuir equilibrium constant (l/mg) related to the affinity of the binding sites

The plots of C_e/q_e versus C_e at different temperatures were found to be linear indicating the applicability of Langmuir isotherm model **(Figures 56 - 63).** The correlation coefficient values (r^2) close to unity suggest the monolayer coverage of the dye molecules on the surface of the adsorbents (BR-SAC and BR-PAC). The parameters Q_m and k_L have been calculated from the slope and intercept of the plots (C_e/q_e versus C_e) and the results are presented in **Tables 34-41.**

The necessary characteristics of the Langmuir isotherm can be articulated by a dimensionless constant called equilibrium parameter (or separation factor R_L) which can be explained using the equation

$$\mathbf{R_L = 1/1 + k_L C_0}$$

where

C_0 is the initial concentration (mg/l)

k_L is the Langmuir constant

The R_L values signifies whether the studied adsorption process is favorable or unfavorable **(Sumanjit Kaur *et al*., 2013; Qingwen Lin *et al*., 2016; Parimalam *et al*., 2012).**

R_L Value	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$R_L < 1$	Favourable
$R_L = 0$	Irreversible

From **Tables 34 - 41** it was found that R_L values for the removal of dyes (CV, AB 110, RB 5 and CR) lies in the range 0.0228 to 0.3650 indicates the favorable uptake of dyes onto BR-SAC and BR-PAC adsorbents.

Similar results have been reported on adsorption of Cibacron Reactive Yellow dye on modified Alumina **(Ayesha wasti and Ali Awan, 2016)**, removal of Reactive Red 2 and Reactive Yellow145A using Wild Almond shell and Coir pith **(Thitame and Shukla, 2016),** removal of Direct Red 23 using powdered Tourmaline (**Na Liu *et al*., 2016),** removal of Acid Blue 93 using Cellulose based Bioadsorbent **(Lin Liu *et al*., 2015)** , removal of Congo Red on Rice husk (**Kumaraswamy *et al.,* 2014),** on modified Jute fiber **(Aparna Roy *et al*., 2013)** and Ground nut shell charcoal **(Sumanjit Kaur *et al*., 2013),** removal of Crystal Violet dye using Chitosan **(Mona Shouman *et al*., 2012)** adsorption of

Reactive Black 5 onto Mangrove Bark **(Tan Lean Seey *et al*., 2012)** and adsorption of Malachite Green dye on paper industry waste sludge **(Anita Thakur *et al*., 2016).**

Table 34

Langmuir Adsorption Isotherm for the Adsorption of CV Dye from Aqueous Solution onto BR-SAC

Temperature (°C)	C_o (mg/l)	C_e	C_e / q_e	Slope	Intercept	Q_m	k_L	R_L	Correlation Coefficient (r^2)
30°C	30	0.57	0.02	0.009	0.049	111.11	0.183	0.1536	0.9781
	50	3.30	0.07					0.0982	
	70	10.23	0.17					0.0779	
	90	17.15	0.23					0.0570	
	110	25.22	0.30					0.0472	
	130	34.36	0.36					0.0402	
	150	47.84	0.47					0.0350	
40°C	30	0.30	0.01	0.008	0.035	125.05	0.228	0.1273	0.9820
	50	2.28	0.05					0.0805	
	70	7.62	0.12					0.0588	
	90	15.11	0.20					0.0463	
	110	20.22	0.22					0.0382	
	130	31.02	0.31					0.0326	
	150	44.43	0.42					0.0283	
50°C	30	0.05	0.002	0.007	0.028	128.20	0.278	0.1045	0.9780
	50	1.41	0.03					0.0654	
	70	6.16	0.10					0.0476	
	90	12.95	0.17					0.0374	
	110	17.90	0.19					0.0308	
	130	28.16	0.27					0.0262	
	150	40.9	0.37					0.0228	

Langmuir Adsorption Isotherm for the Adsorption of CV Dye from Aqueous Solution onto BR-SAC

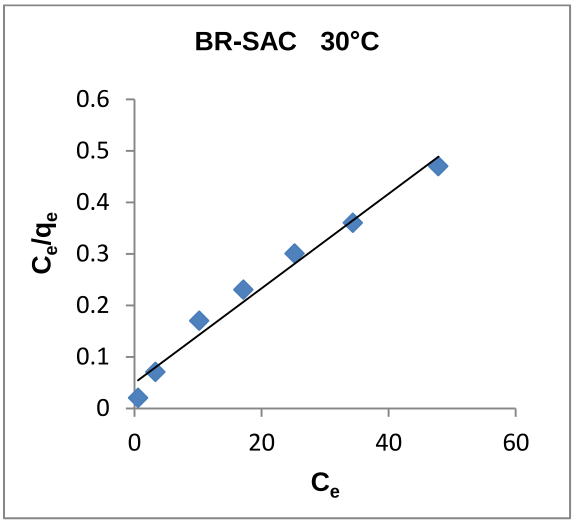

Figure 56a

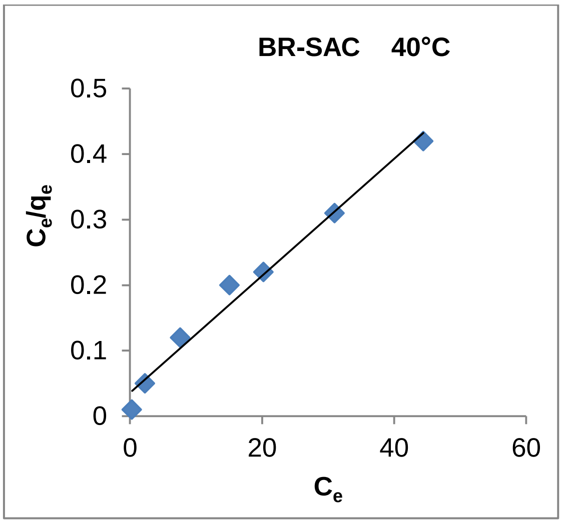

Figure 56 b

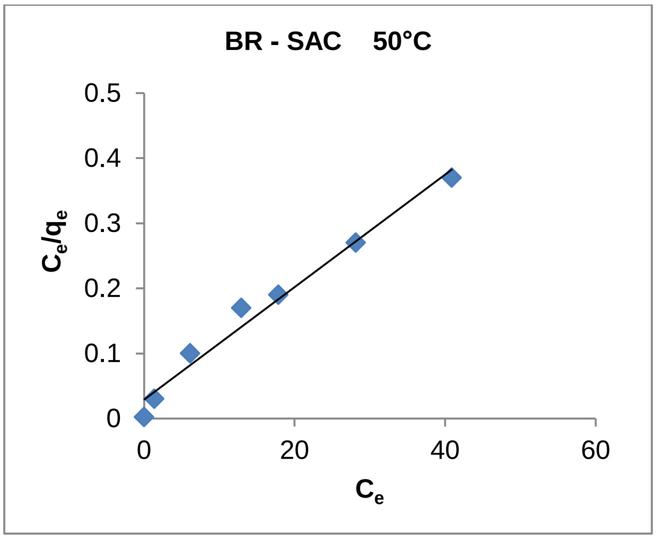

Figure 56 c

Table 35

Langmuir Adsorption Isotherm for the Adsorption of CV Dye from Aqueous Solution onto BR-PAC

Temperature (°C)	C_o (mg/l)	C_e	C_e/q_e	Slope	Intercept	Q_m	k_L	R_L	Correlation Coefficient (r^2)
30°C	30	0.64	0.01	0.004	0.031	250.00	0.1333	0.2000	0.9521
	50	4.56	0.05					0.1305	
	70	10.18	0.08					0.0968	
	90	19.69	0.14					0.0769	
	110	28.94	0.18					0.0638	
	130	37.61	0.2					0.0546	
	150	47.03	0.22					0.0476	
40°C	30	0.31	0.005	0.0038	0.021	263.16	0.1905	0.1489	0.9745
	50	3.46	0.04					0.1051	
	70	8.05	0.06					0.0698	
	90	11.93	0.08					0.0551	
	110	19.65	0.11					0.0455	
	130	30.01	0.15					0.0388	
	150	40.28	0.18					0.0338	
50°C	30	0.12	0.002	0.0037	0.014	270.27	0.2857	0.1045	0.9782
	50	1.96	0.02					0.0654	
	70	5.92	0.046					0.0476	
	90	9.79	0.06					0.0374	
	110	16.03	0.085					0.0308	
	130	25.27	0.12					0.0262	
	150	35.37	0.15					0.0233	

Langmuir Adsorption Isotherm for the Adsorption of CV Dye from Aqueous Solution onto BR-PAC

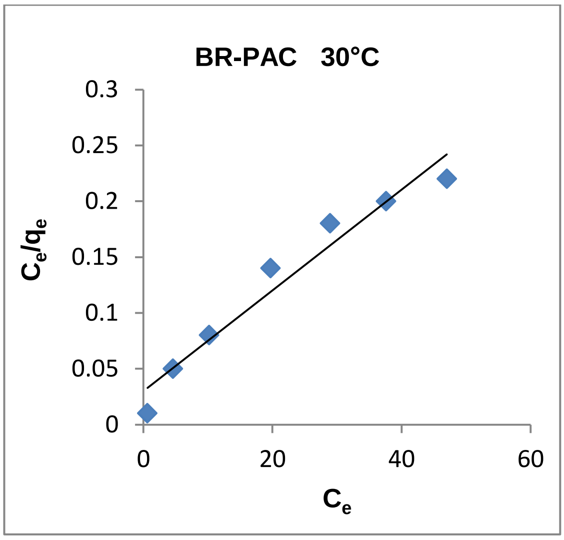

Figure 57 a

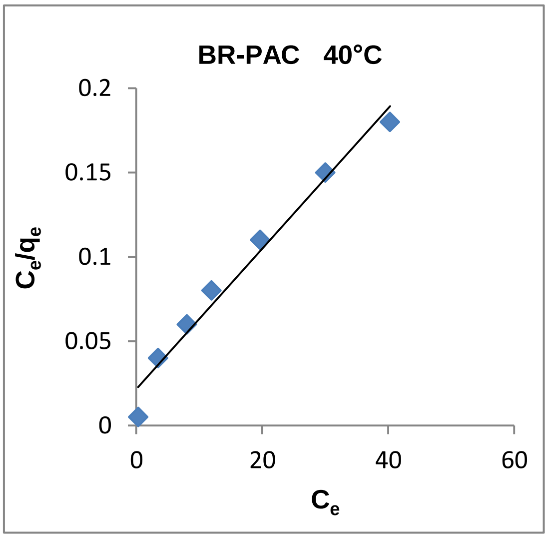

Figure 57 b

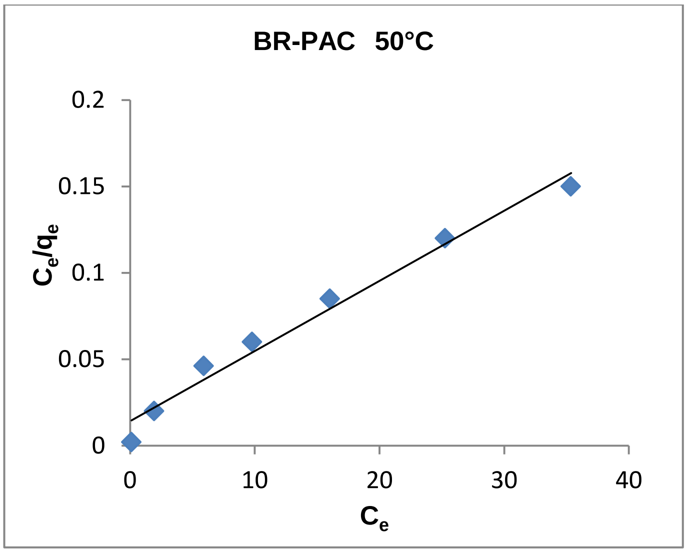

Figure 57 c

Table 36

Langmuir Adsorption Isotherm for the Adsorption of AB110 Dye from Aqueous Solution onto BR-SAC

Temperature (°C)	C_o (mg/l)	C_e	C_e/q_e	Slope	Intercept	Q_m	k_L	R_L	Correlation Coefficient (r^2)
30°C	30	1.44	0.05	0.0070	0.057	142.85	0.1228	0.2135	0.9902
	50	4.19	0.09					0.1401	
	70	8.63	0.14					0.1042	
	90	13.29	0.17					0.0832	
	110	20.31	0.22					0.0689	
	130	28.35	0.28					0.0589	
	150	40.61	0.37					0.0515	
40°C	30	0.61	0.02	0.0067	0.043	149.25	0.1628	0.1699	0.9716
	50	3.28	0.07					0.1094	
	70	7.44	0.12					0.0807	
	90	11.43	0.14					0.0639	
	110	18.43	0.2					0.0529	
	130	24.9	0.24					0.0451	
	150	35.07	0.3					0.0393	
50°C	30	0.38	0.01	0.0066	0.031	151.51	0.2258	0.1286	0.9784
	50	2.36	0.05					0.0814	
	70	5.15	0.08					0.0595	
	90	9.5	0.12					0.0469	
	110	16.46	0.17					0.0387	
	130	23.02	0.21					0.0329	
	150	32.04	0.27					0.0287	

Langmuir Adsorption Isotherm for the Adsorption of AB110 Dye from Aqueous Solution onto BR-SAC

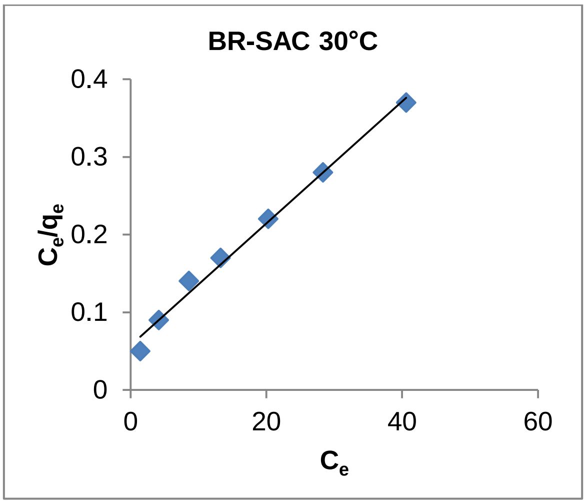

Figure 58 a

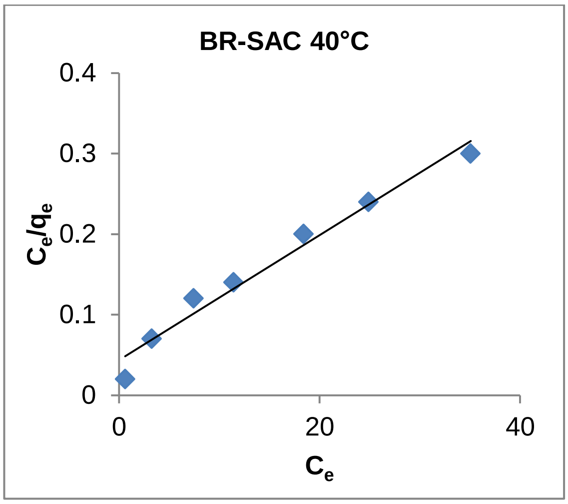

Figure 58 b

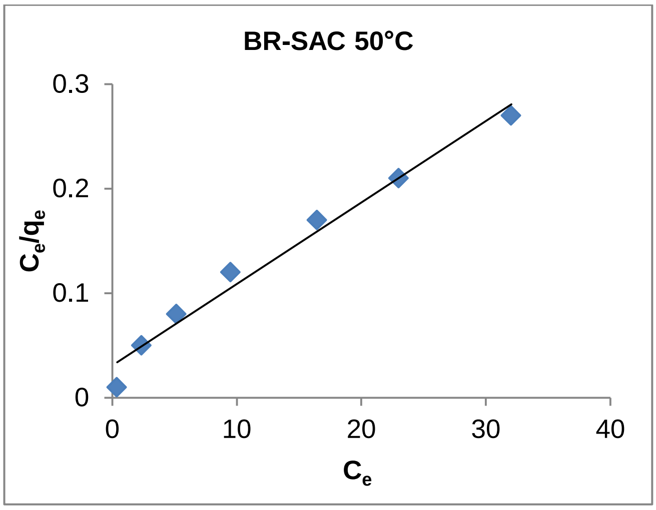

Figure 58 c

Table 37

Langmuir Adsorption Isotherm for the Adsorption of AB110 Dye from Aqueous Solution onto BR-PAC

Temperature (°C)	C_o (mg/l)	C_e	C_e/q_e	Slope	Intercept	Q_m	k_L	R_L	Correlation Coefficient (r^2)
30°C	30	2.82	0.05	0.004	0.045	250.00	0.0889	0.2727	0.993
	50	6.05	0.07					0.1837	
	70	12	0.1					0.1384	
	90	21.29	0.15					0.1111	
	110	28.9	0.18					0.1023	
	130	41.22	0.23					0.0796	
	150	52.5	0.27					0.0698	
40°C	30	1.89	0.03	0.0035	0.031	285.71	0.129	0.2584	0.988
	50	4.89	0.05					0.1342	
	70	11.01	0.09					0.0997	
	90	16.55	0.11					0.0793	
	110	23.97	0.14					0.0658	
	130	38.12	0.21					0.0563	
	150	46.77	0.23					0.0491	
50°C	30	0.94	0.016	0.003	0.027	333.33	0.111	0.2308	0.971
	50	3.64	0.04					0.1526	
	70	8.64	0.07					0.1139	
	90	14.29	0.09					0.0909	
	110	19.29	0.11					0.0756	
	130	27.03	0.13					0.0648	
	150	38.52	0.17					0.0566	

Langmuir Adsorption Isotherm for the Adsorption of AB110 Dye from Aqueous Solution onto BR-PAC

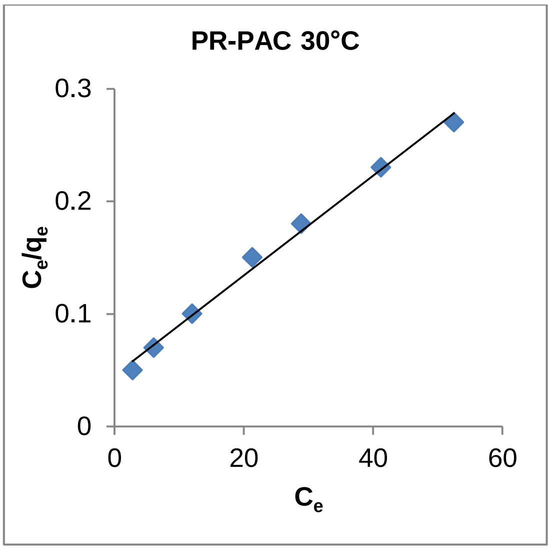

Figure 59 a

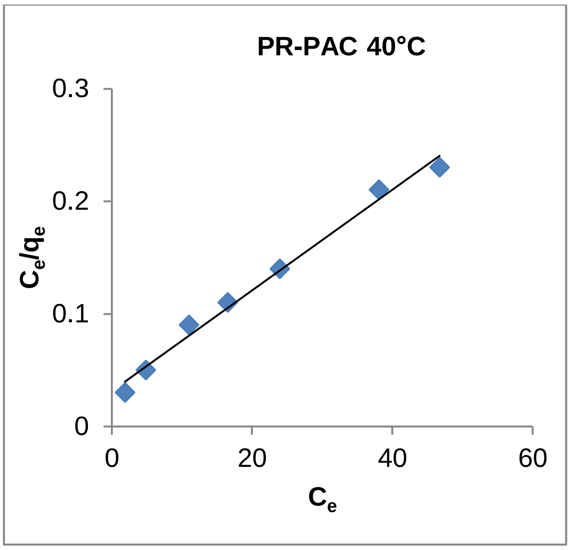

Figure 59 b

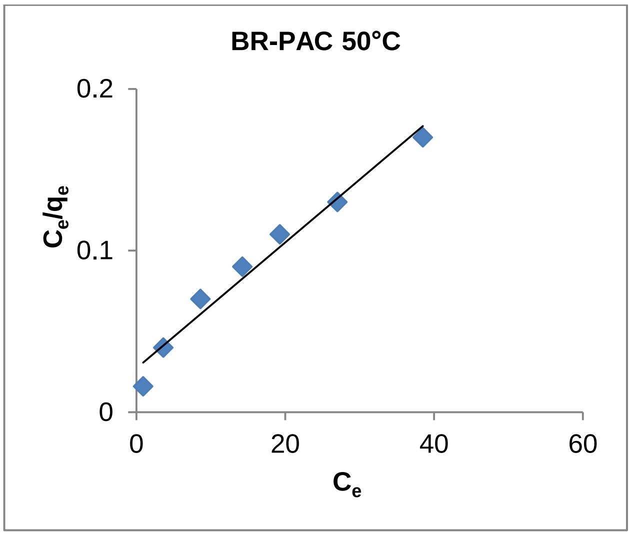

Figure 59 c

Table 38

Langmuir Adsorption Isotherm for the Adsorption of RB5 Dye from Aqueous Solution onto BR-SAC

Temperature (°C)	C_o (mg/l)	C_e	C_e/q_e	Slope	Intercept	Q_m	k_L	R_L	Correlation Coefficient (r^2)
30°C	30	2.5	0.09	0.0080	0.085	125.00	0.0941	0.2616	0.9950
	50	5.63	0.13					0.1753	
	70	11.61	0.2					0.1318	
	90	18.84	0.26					0.1056	
	110	26.87	0.32					0.0881	
	130	38.86	0.42					0.0756	
	150	52.22	0.53					0.0662	
40°C	30	1.97	0.07	0.0075	0.072	133.33	0.1111	0.2308	0.9912
	50	5.39	0.12					0.1526	
	70	9.8	0.16					0.1139	
	90	14.73	0.19					0.0909	
	110	22.06	0.25					0.0756	
	130	33.5	0.35					0.0648	
	150	42.89	0.4					0.0566	
50°C	30	0.79	0.03	0.0070	0.044	142.86	0.1591	0.1732	0.9845
	50	3.14	0.07					0.1117	
	70	7.11	0.11					0.0824	
	90	12.05	0.15					0.0653	
	110	19.52	0.21					0.0541	
	130	28.47	0.28					0.0461	
	150	36.81	0.32					0.0402	

Langmuir Adsorption Isotherm for the Adsorption of RB5 Dye from Aqueous Solution onto BR-SAC

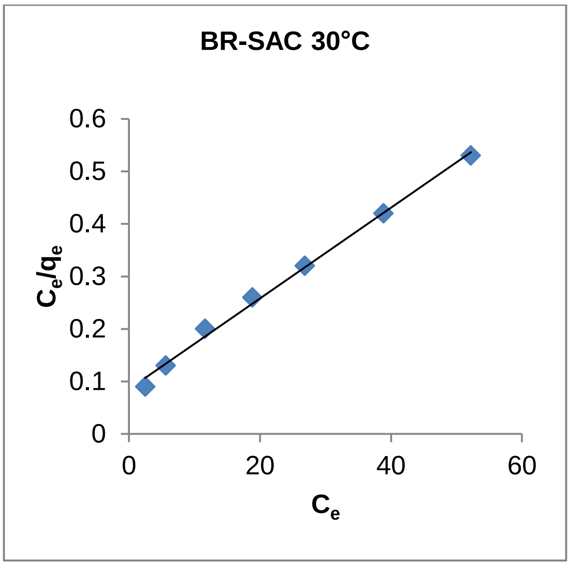

Figure 60 a

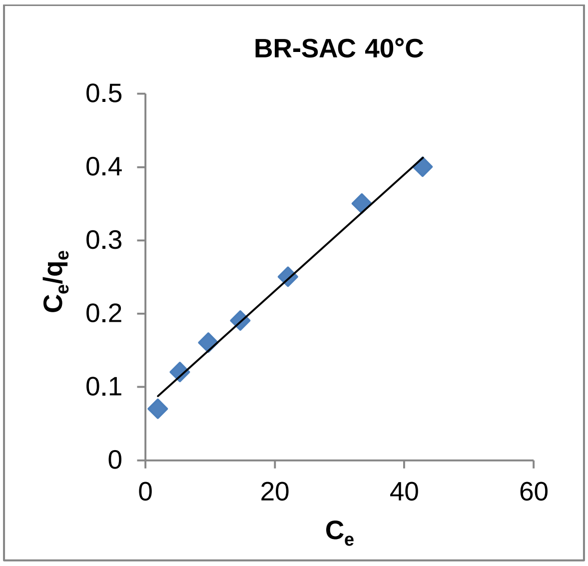

Figure 60 b

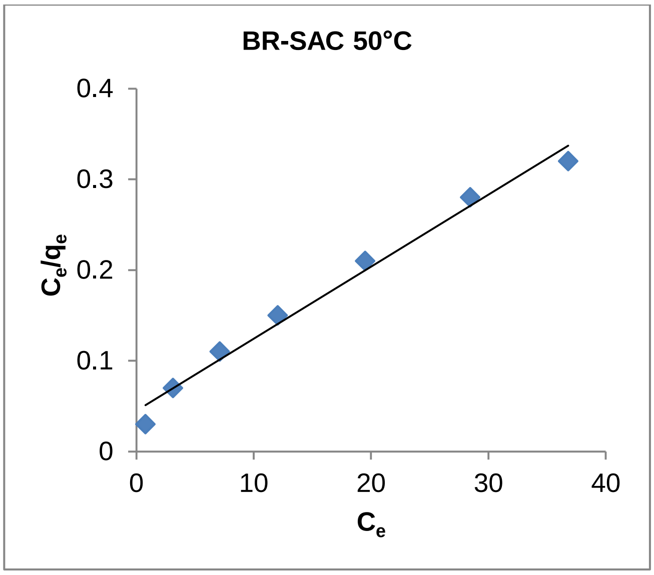

Figure 60 c

Table: 39

Langmuir Adsorption Isotherm for the Adsorption of RB5 Dye from Aqueous Solution onto BR-PAC

Temperature (°C)	C_o (mg/l)	C_e	C_e/q_e	Slope	Intercept	Q_m	k_L	R_L	Correlation Coefficient (r^2)
30°C	30	4.01	0.08	0.004	0.069	250.00	0.058	0.3650	0.9950
	50	9.15	0.11					0.2564	
	70	16.93	0.16					0.1976	
	90	26.88	0.21					0.1608	
	110	36.72	0.25					0.1355	
	130	49.48	0.31					0.1171	
	150	65.15	0.38					0.1031	
40°C	30	2.44	0.04	0.0038	0.041	263.16	0.0976	0.2545	0.9884
	50	6.17	0.07					0.1701	
	70	13.19	0.12					0.1277	
	90	19.91	0.14					0.1022	
	110	29.48	0.18					0.0852	
	130	45.49	0.27					0.0731	
	150	56.18	0.3					0.0639	
50°C	30	1.36	0.02	0.0035	0.027	285.71	0.1481	0.1837	0.9895
	50	4.81	0.05					0.1190	
	70	10.06	0.08					0.0880	
	90	16.85	0.11					0.0698	
	110	24.09	0.14					0.0578	
	130	37.51	0.2					0.0494	
	150	49.14	0.24					0.0431	

Langmuir Adsorption Isotherm for the Adsorption of RB5 Dye from Aqueous Solution onto BR-PAC

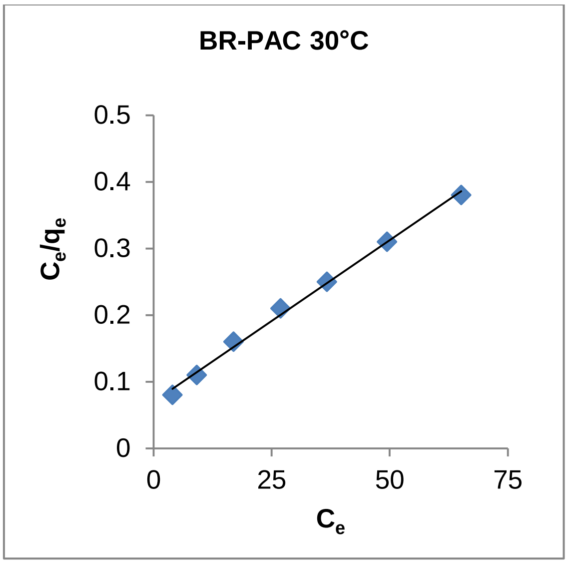

Figure 61 a

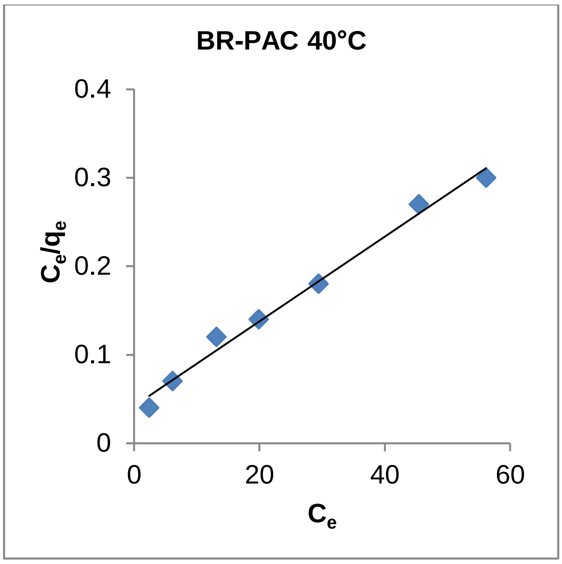

Figure 61 b

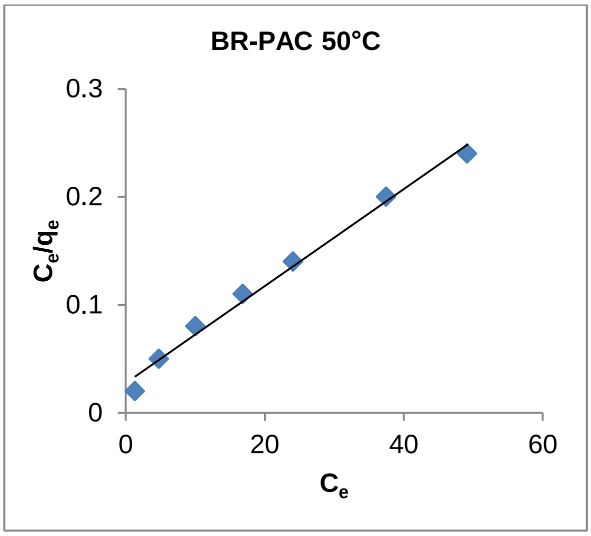

Figure 61 c

Table 40

Langmuir Adsorption Isotherm for the Adsorption of CR Dye from Aqueous Solution onto BR-SAC

Temperature (°C)	C_o (mg/l)	C_e	C_e/q_e	Slope	Intercept	Q_m	k_L	R_L	Correlation Coefficient (r^2)
30°C	30	3.37	0.12	0.009	0.107	111.11	0.0841	0.2838	0.9852
	50	7.02	0.16					0.1921	
	70	12.81	0.22					0.1452	
	90	23.17	0.35					0.1167	
	110	31.79	0.41					0.0976	
	130	44.06	0.51					0.0838	
	150	54.24	0.57					0.0734	
40°C	30	2.17	0.08	0.0084	0.084	119.05	0.0952	0.2593	0.9895
	50	6.2	0.14					0.1736	
	70	11.33	0.19					0.0305	
	90	19.78	0.28					0.1045	
	110	26.45	0.31					0.0872	
	130	40.61	0.45					0.0747	
	150	50.93	0.51					0.0654	
50°C	30	1.31	0.04	0.008	0.066	125.00	0.1212	0.2157	0.9783
	50	5.42	0.12					0.1416	
	70	10.3	0.17					0.1054	
	90	18	0.25					0.0839	
	110	25.66	0.3					0.0698	
	130	37.85	0.41					0.0597	
	150	47.45	0.46					0.0521	

Langmuir Adsorption Isotherm for the Adsorption of CR Dye from Aqueous Solution onto BR-SAC

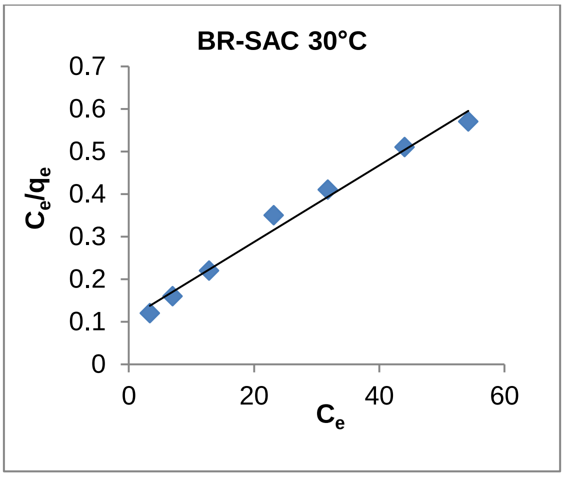

Figure 62 a

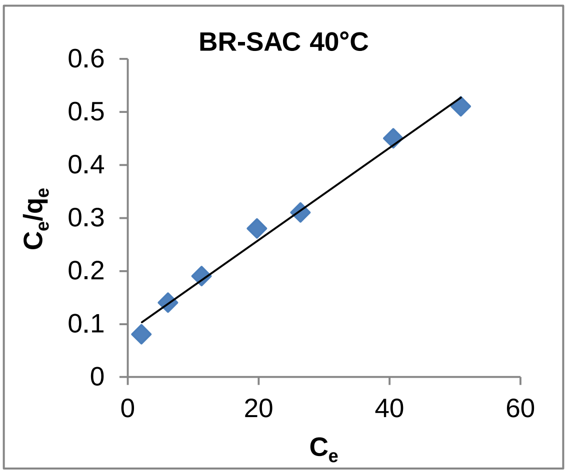

Figure 62 b

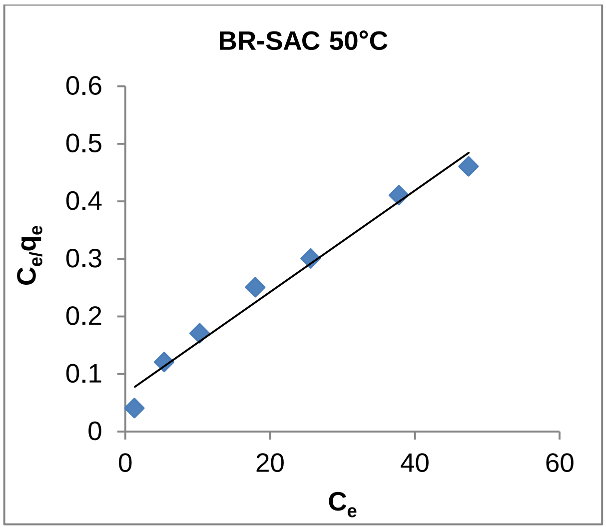

Figure 62 c

Table 41

Langmuir Adsorption Isotherm for the Adsorption of CR Dye from Aqueous Solution onto BR-PAC

Temperature (°C)	C_o (mg/l)	C_e	C_e/q_e	Slope	Intercept	Q_m	k_L	R_L	Correlation Coefficient (r^2)
30°C	30	2.45	0.04	0.005	0.055	200.00	0.0909	0.2683	0.976
	50	8.36	0.1					0.1803	
	70	17.41	0.16					0.1358	
	90	25.2	0.19					0.1089	
	110	36.56	0.25					0.0909	
	130	48.72	0.31					0.078	
	150	60.54	0.34					0.0683	
40°C	30	1.63	0.03	0.0044	0.046	227.27	0.087	0.277	0.974
	50	7.27	0.08					0.1869	
	70	14.43	0.13					0.141	
	90	22.26	0.16					0.1133	
	110	30.85	0.19					0.0946	
	130	41.56	0.23					0.0812	
	150	55.85	0.29					0.0712	
50°C	30	0.85	0.01	0.004	0.027	250.00	0.1481	0.1837	0.979
	50	5.32	0.06					0.119	
	70	10.08	0.08					0.088	
	90	16.37	0.11					0.0698	
	110	25.38	0.15					0.0578	
	130	36.23	0.19					0.0494	
	150	48.66	0.24					0.0431	

Langmuir Adsorption Isotherm for the Adsorption of CR Dye from Aqueous Solution onto BR-PAC

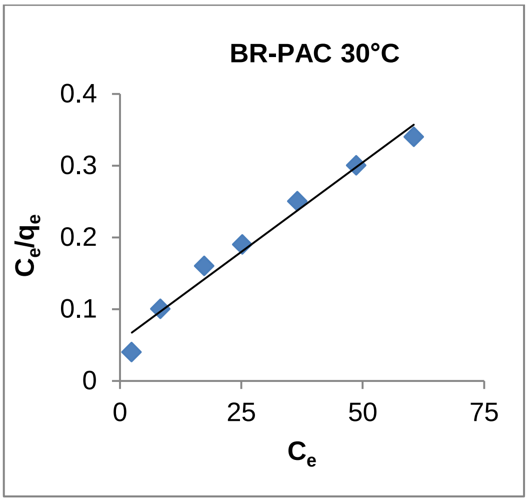

Figure 63 a

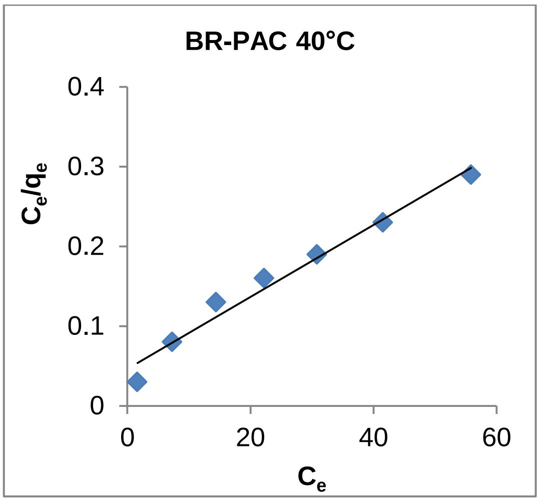

Figure 63 b

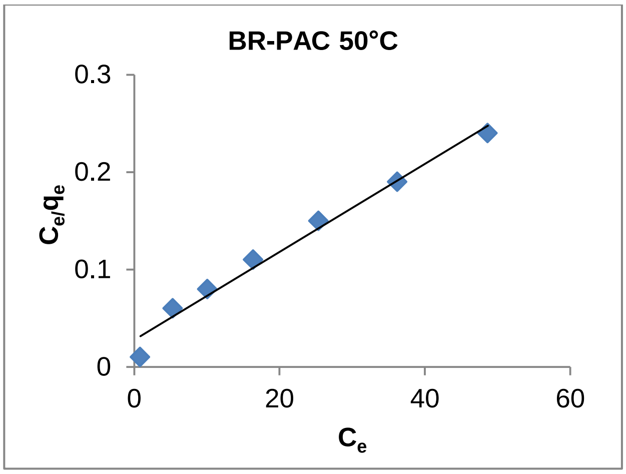

Figure 63 c

4.6.2 Freundlich Adsorption Isotherm

The Freundlich adsorption isotherm model assumes adsorption of dye molecules on a heterogeneous adsorbent surface **(Aparna Roy *et al*., 2013; Mona Shouman, 2012, Das *et al.,* 2006 and Lin Liu *et al*., 2015).** This model is commonly used to describe all physical adsorption process. The linear form of Freundlich equation is given by **(Freundlich, 1906 and Qingwen Lin *et al*., 2016)**

$$\log q_e = \log (K_f) + 1/n \log C_e$$

where

C_e is the concentration of dye solution at equilibrium (mg/l)

q_e is the amount of dye adsorbed per unit mass of adsorbent (mg/g)

K_f is Freunlich constant (Adsorption capacity mg/g)

n is the heterogeneity factor (Adsorption intensity)

The Freundlich adsorption isotherm plots obtained ((log q_e versus log C_e) were linear which confirms the successfulness of Freundlich adsorption isotherm for the removal of dyes (CV, AB110, RB5 and CR) from aqueous solution using the adsorbents BR-SAC and BR-PAC. The value of n is calculated from the slope and K_f value from the intercept of the linear plots and revealed in **Figures 64 - 71 and Tables 42 - 49.**

The greater K_f values obtained showed the higher adsorption capacity of the adsorbents used in this study. The values of 'n' greater than unity showed stronger adsorption intensity and the adsorption process was favourable **(Lin Liu *et al.,* 2015, Ayesha Wasti and Ali Awan, 2016).** From **Tables 42 - 49** it was found that 'n' values were greater than unity (2.03 to 5.10) representing the effective adsorption of the dyes onto the adsorbents BR-SAC and BR-PAC. The high correlation coefficient (r^2) confirms the validity of Freundlich adsorption isotherm with the experimental data.

Similar results were obtained for the adsorption of Acid Blue 93 using a Cellulose based bioadsorbent**(Lin Liu *et al*., 2015)**, adsorption of Reactive Black 5 onto Biomass Fly ash **(Pengthamkeerati *et al*., 2008)**, removal of Malachite Green dye using paper industry waste sludge **(Anita Thakur *et al*., 2016)** and Adsorption of Cibacron Reactive Yellow dye on modified Alumina **(Ayesha wasti and Ali Awan, 2016).**

Table : 42

Freundlich Adsorption Isotherm of CV Dye from Aqueous Solution onto BR-SAC

Temperature (°C)	C_o (mg/l)	log C_e	log q_e	Slope	Intercept	K_f	n	Correlation coefficient (r^2)
30°C	30	-0.24	1.47	0.281	1.524	33.4195	3.55	0.9892
	50	0.52	1.67					
	70	1.00	1.77					
	90	1.23	1.86					
	110	1.4	1.93					
	130	1.54	1.98					
	150	1.68	2.00					
40°C	30	-0.52	1.47	0.257	1.591	38.9942	3.89	0.9891
	50	0.36	1.68					
	70	0.88	1.79					
	90	1.18	1.87					
	110	1.3	1.95					
	130	1.49	1.99					
	150	1.65	2.02					
50°C	30	-1.3	1.47	0.196	1.692	49.2039	5.10	0.9690
	50	0.15	1.68					
	70	0.79	1.8					
	90	1.11	1.89					
	110	1.25	1.96					
	130	1.45	2.00					
	150	1.61	2.04					

Freundlich Adsorption Isotherm of CV Dye from Aqueous Solution onto BR-SAC

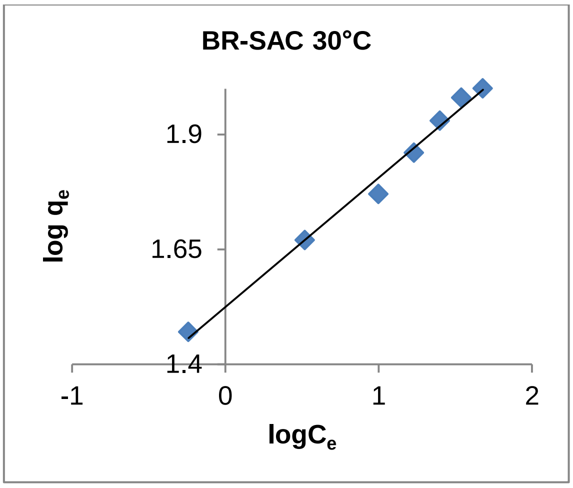

Figure 64 a

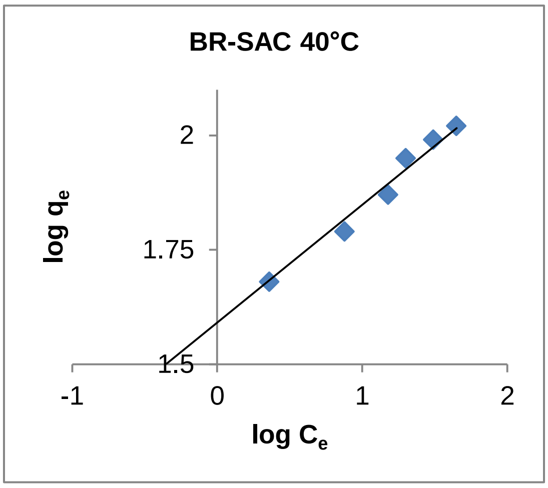

Figure 64 b

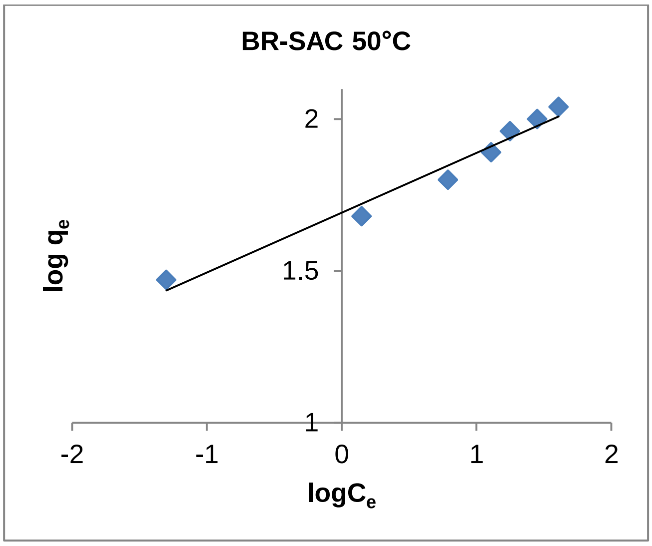

Figure 64c

Table 43

Freundlich Adsorption Isotherm of CV Dye from Aqueous Solution onto BR-PAC

Temperature (°C)	C_o (mg/l)	log C_e	log q_e	Slope	Intercept	K_f	n	Correlation coefficient (r^2)
30°C	30	-0.19	1.77	0.285	1.8	63.0957	3.5087	0.9851
	50	0.66	1.96					
	70	1.01	2.08					
	90	1.29	2.15					
	110	1.46	2.21					
	130	1.57	2.26					
	150	1.67	2.31					
40°C	30	-0.51	1.77	0.278	1.877	75.3355	3.5971	0.9702
	50	0.54	1.97					
	70	0.91	2.09					
	90	1.08	2.19					
	110	1.29	2.26					
	130	1.48	2.30					
	150	1.60	2.34					
50°C	30	-0.92	1.77	0.244	1.959	90.9902	4.0983	0.9760
	50	0.29	1.98					
	70	0.77	2.11					
	90	0.99	2.20					
	110	1.20	2.27					
	130	1.40	2.32					
	150	1.55	2.36					

Freundlich Adsorption Isotherm of CV Dye from Aqueous Solution onto BR-PAC

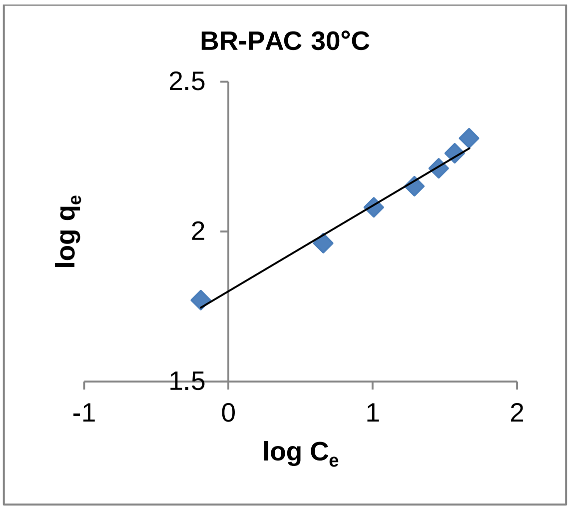

Figure 65 a

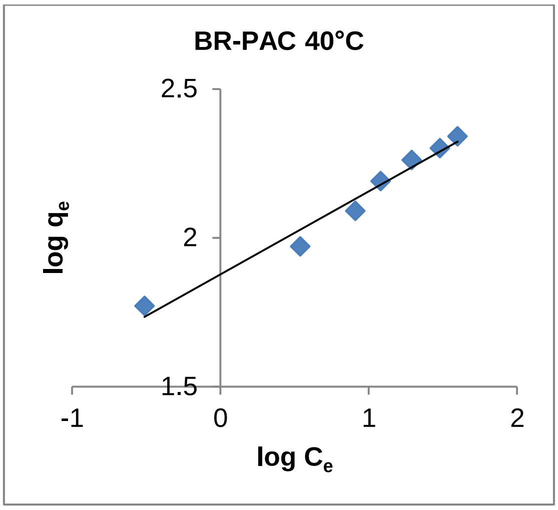

Figure 65 b

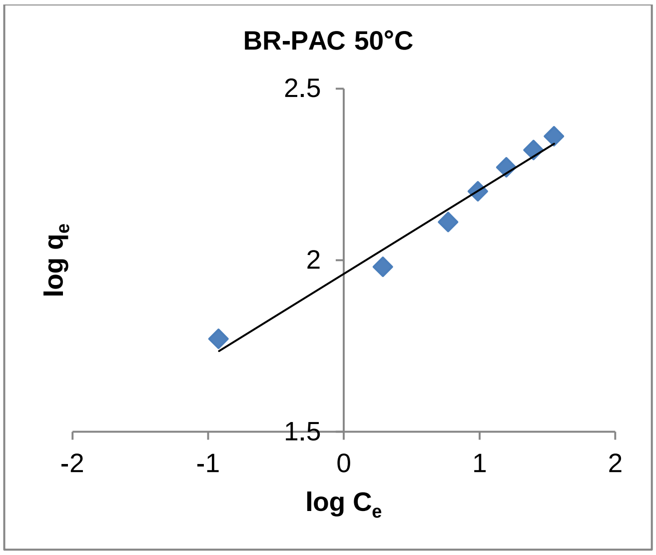

Figure 65 c

Table 44

Freundlich Adsorption Isotherm of AB110 Dye from Aqueous Solution onto BR-SAC

Temperature (°C)	C_o (mg/l)	log C_e	log q_e	Slope	Intercept	K_f	n	Correlation coefficient (r^2)
30°C	30	0.16	1.45	0.414	1.397	24.9459	2.4154	0.9951
	50	0.62	1.66					
	70	0.94	1.79					
	90	1.12	1.88					
	110	1.31	1.95					
	130	1.45	2.00					
	150	1.61	2.04					
40°C	30	-0.21	1.47	0.346	1.52	33.1131	2.8901	0.9921
	50	0.51	1.67					
	70	0.87	1.80					
	90	1.06	1.89					
	110	1.26	1.96					
	130	1.39	2.02					
	150	1.54	2.06					
50°C	30	-0.42	1.47	0.316	1.587	38.6366	3.1645	0.9968
	50	0.37	1.68					
	70	0.71	1.81					
	90	0.98	1.90					
	110	1.22	1.97					
	130	1.36	2.03					
	150	1.51	2.07					

Freundlich Adsorption Isotherm of AB110 Dye from Aqueous Solution onto BR-SAC

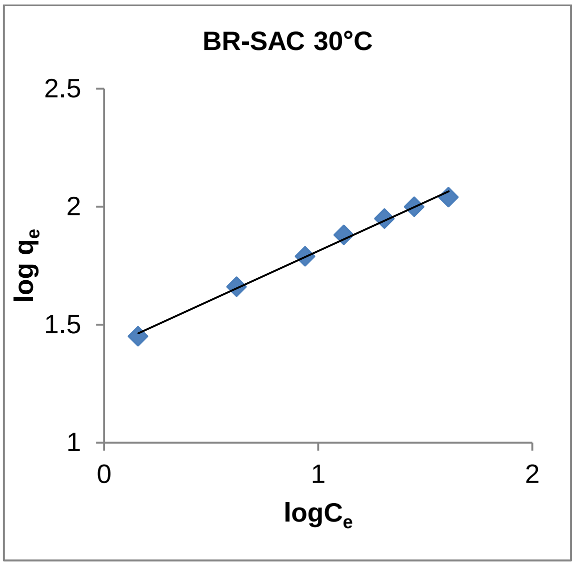

Figure 66 a

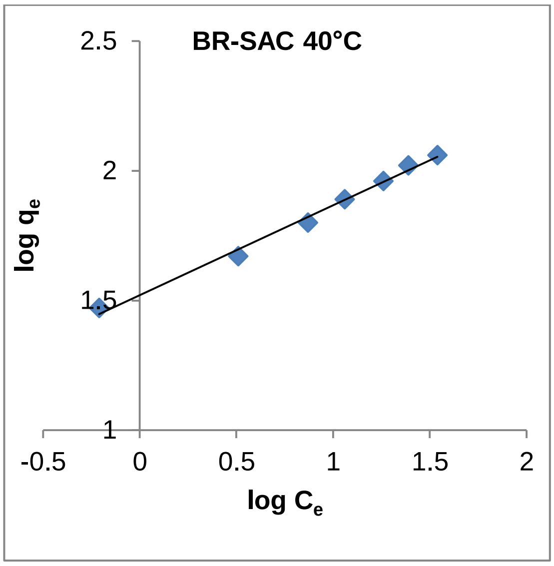

Figure 66 b

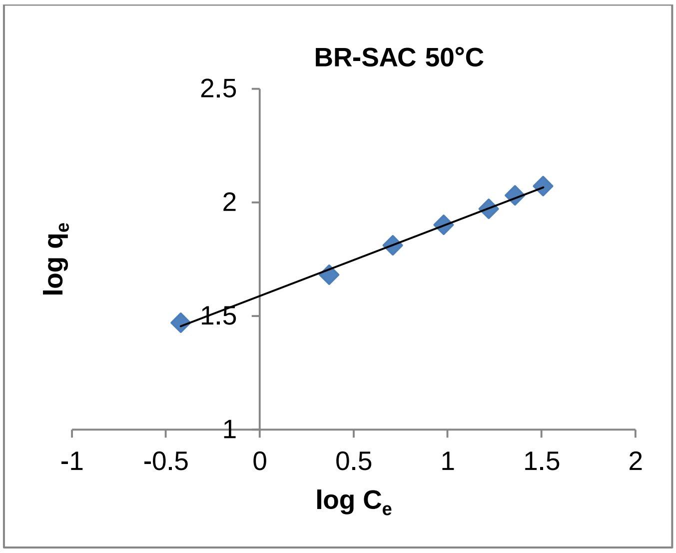

Figure 66 c

Table 45

Freundlich Adsorption Isotherm of AB110 Dye from Aqueous Solution onto BR-PAC

Temperature (°C)	C_o (mg/l)	log C_e	log q_e	Slope	Intercept	K_f	n	Correlation coefficient (r^2)
30°C	30	0.45	1.73	0.426	1.575	37.5837	2.3474	0.9841
	50	0.78	1.94					
	70	1.08	2.06					
	90	1.33	2.14					
	110	1.46	2.21					
	130	1.61	2.25					
	150	1.72	2.29					
40°C	30	0.27	1.75	0.394	1.663	46.0256	2.5381	0.9896
	50	0.69	1.95					
	70	1.04	2.07					
	90	1.22	2.17					
	110	1.38	2.23					
	130	1.58	2.26					
	150	1.67	2.31					
50°C	30	-0.03	1.76	0.376	1.759	57.4116	2.6595	0.9950
	50	0.56	1.96					
	70	0.93	2.09					
	90	1.15	2.18					
	110	1.28	2.26					
	130	1.43	2.31					
	150	1.58	2.35					

Freundlich Adsorption Isotherm of AB110 Dye from Aqueous Solution onto BR-PAC

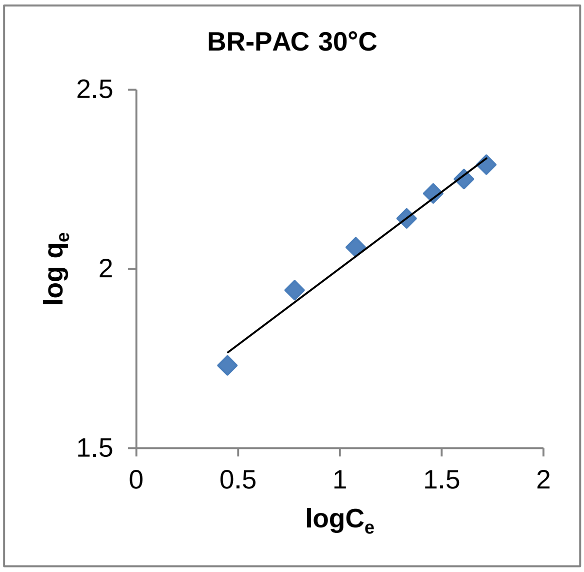

Figure 67 a

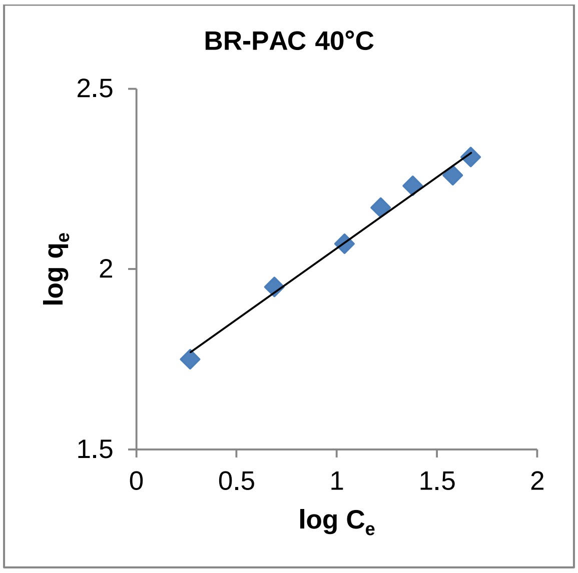

Figure 67 b

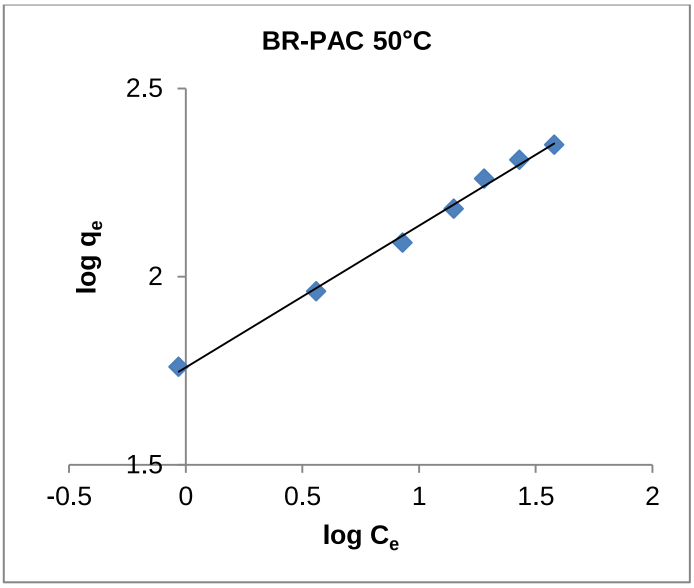

Figure 67 c

Table 46

Freundlich Adsorption Isotherm of RB5 Dye from Aqueous Solution onto BR-SAC

Temperature (°C)	C_o (mg/l)	log C_e	log q_e	Slope	Intercept	K_f	n	Correlation coefficient (r^2)
30°C	30	0.40	1.44	0.413	1.31	20.4174	2.4213	0.9830
	50	0.75	1.65					
	70	1.06	1.76					
	90	1.27	1.85					
	110	1.43	1.92					
	130	1.59	1.96					
	150	1.72	1.99					
40°C	30	0.29	1.36	0.491	1.264	18.3654	2.0366	0.9905
	50	0.73	1.65					
	70	0.99	1.78					
	90	1.17	1.88					
	110	1.34	1.94					
	130	1.52	1.98					
	150	1.63	2.03					
50°C	30	-0.10	1.46	0.357	1.495	31.261	2.8011	0.9992
	50	0.50	1.67					
	70	0.85	1.80					
	90	1.08	1.89					
	110	1.29	1.96					
	130	1.45	2.01					
	150	1.56	2.05					

Freundlich Adsorption Isotherm of RB5 Dye from Aqueous Solution onto BR-SAC

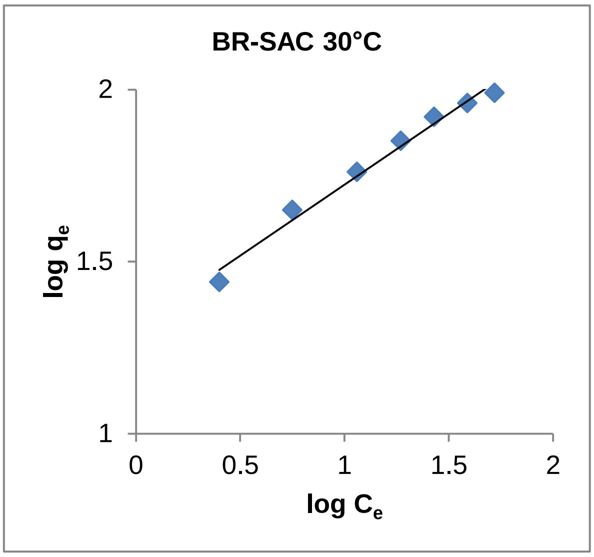

Figure 68 a

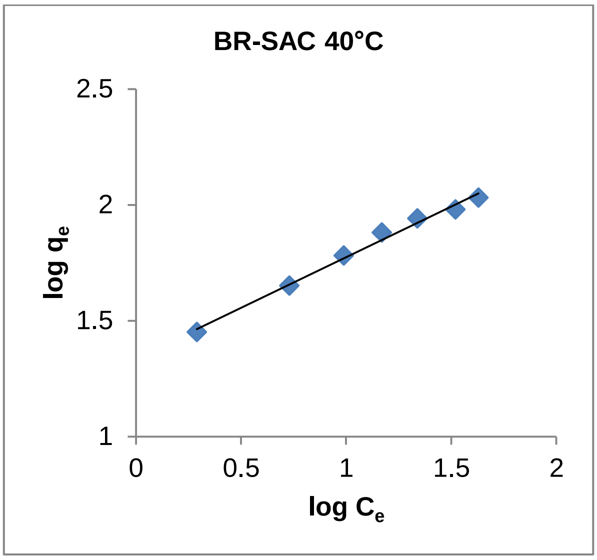

Figure 68 b

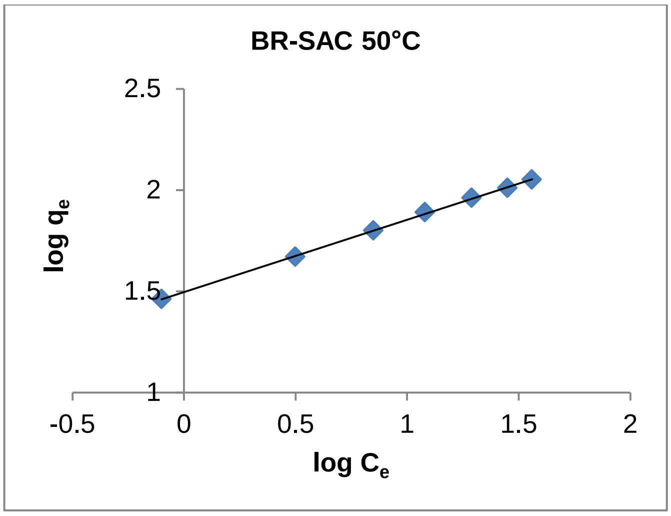

Figure 68 c

Table 47

Freundlich Adsorption Isotherm of RB5 Dye from Aqueous Solution onto BR-PAC

Temperature (°C)	C_o (mg/l)	log C_e	log q_e	Slope	Intercept	K_f	n	Correlation coefficient (r^2)
30°C	30	0.60	1.71	0.425	1.482	30.3389	2.3529	0.9860
	50	0.96	1.91					
	70	1.23	2.02					
	90	1.43	2.10					
	110	1.56	2.16					
	130	1.69	2.20					
	150	1.81	2.22					
40°C	30	0.39	1.74	0.385	1.616	41.3047	2.5974	0.9814
	50	0.79	1.94					
	70	1.12	2.05					
	90	1.30	2.15					
	110	1.47	2.21					
	130	1.66	2.23					
	150	1.75	2.27					
50°C	30	0.13	1.76	0.355	1.717	52.1195	2.8169	0.9956
	50	0.68	1.95					
	70	1.00	2.08					
	90	1.22	2.16					
	110	1.38	2.23					
	130	1.57	2.27					
	150	1.69	2.30					

Freundlich Adsorption Isotherm of RB5 Dye from Aqueous Solution onto BR-PAC

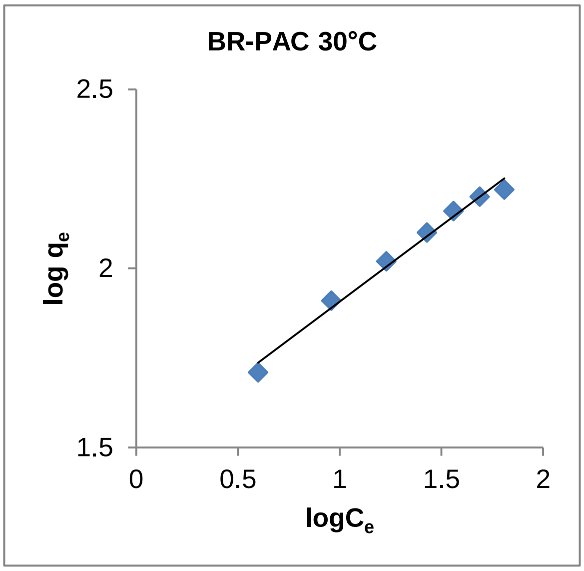

Figure 69 a

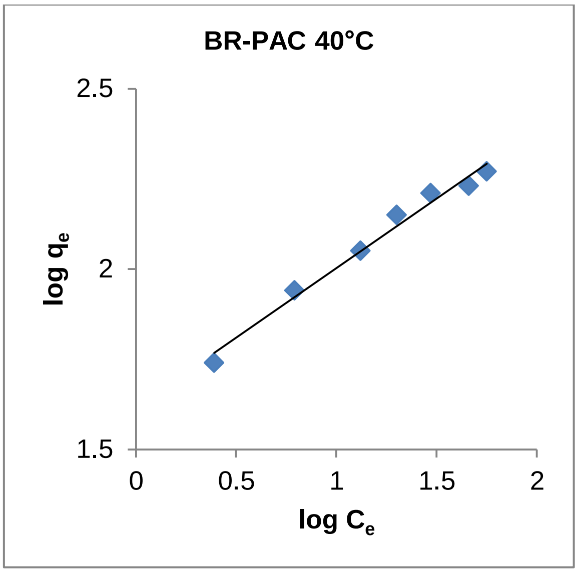

Figure 69 b

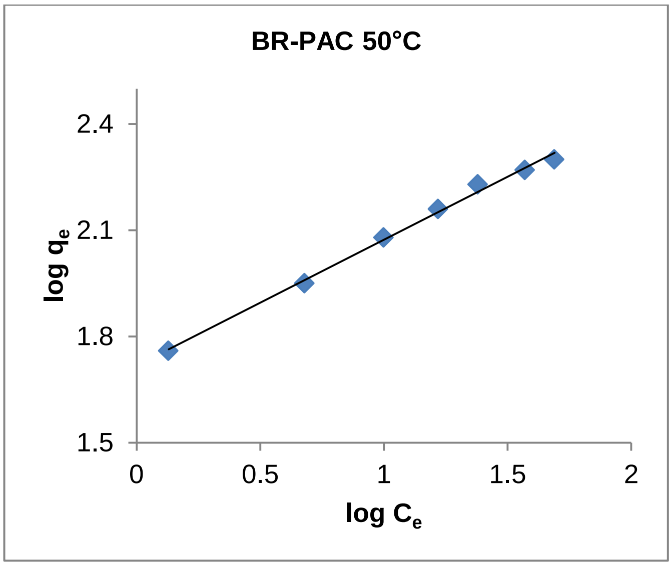

Figure 69 c

Table 48

Freundlich Adsorption Isotherm of CR Dye from Aqueous Solution onto BR-SAC

Temperature (°C)	C_o (mg/l)	log C_e	log q_e	Slope	Intercept	K_f	n	Correlation coefficient (r^2)
30°C	30	0.53	1.42	0.44	1.227	16.8655	2.2727	0.9785
	50	0.85	1.63					
	70	1.11	1.76					
	90	1.36	1.82					
	110	1.50	1.89					
	130	1.64	1.93					
	150	1.73	1.98					
40°C	30	0.33	1.44	0.402	1.323	21.0378	2.4875	0.9901
	50	0.79	1.64					
	70	1.05	1.77					
	90	1.29	1.85					
	110	1.42	1.92					
	130	1.61	1.95					
	150	1.70	1.99					
50°C	30	0.12	1.46	0.358	1.408	25.5858	2.7933	0.9958
	50	0.73	1.65					
	70	1.01	1.77					
	90	1.25	1.86					
	110	1.41	1.93					
	130	1.58	1.96					
	150	1.67	2.01					

Freundlich Adsorption Isotherm of CR Dye from Aqueous Solution onto BR-SAC

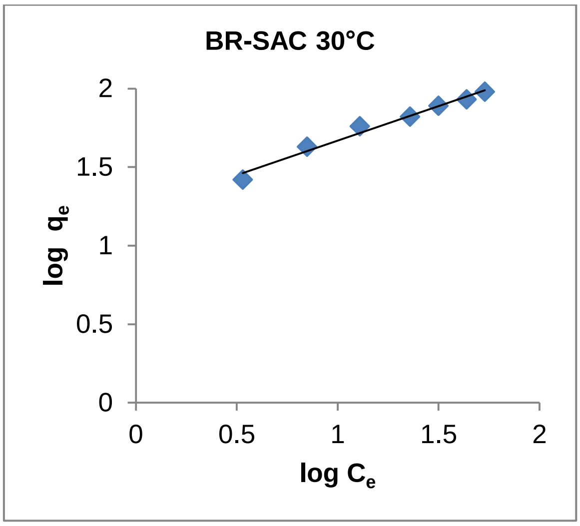

Figure 70 a

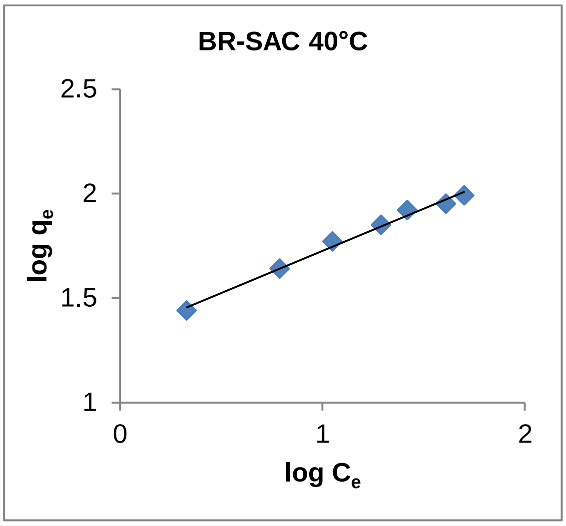

Figure 70 b

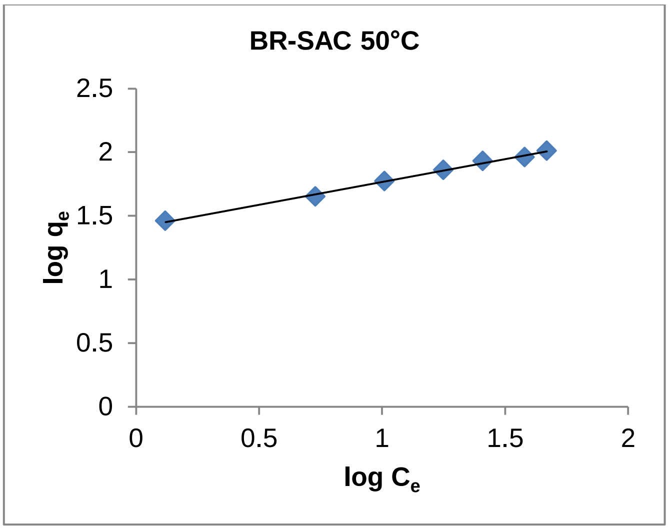

Figure 70 c

Table 49

Freundlich Adsorption Isotherm of CR Dye from Aqueous Solution onto BR-PAC

Temperature (°C)	C_o (mg/l)	log C_e	log q_e	Slope	Intercept	K_f	n	Correlation coefficient (r^2)
30°C	30	0.38	1.74	0.367	1.589	38.815	2.7247	0.9954
	50	0.92	1.92					
	70	1.24	2.02					
	90	1.40	2.11					
	110	1.56	2.17					
	130	1.69	2.21					
	150	1.78	2.25					
40°C	30	0.21	1.75	0.353	1.654	45.0816	2.8328	0.9880
	50	0.86	1.93					
	70	1.16	2.04					
	90	1.35	2.13					
	110	1.49	2.20					
	130	1.62	2.24					
	150	1.74	2.27					
50°C	30	-0.07	1.76	0.324	1.761	57.6766	3.0864	0.9871
	50	0.72	1.95					
	70	1.00	2.08					
	90	1.21	2.17					
	110	1.40	2.23					
	130	1.56	2.27					
	150	1.69	2.31					

Freundlich Adsorption Isotherm of CR Dye from Aqueous Solution onto BR-PAC

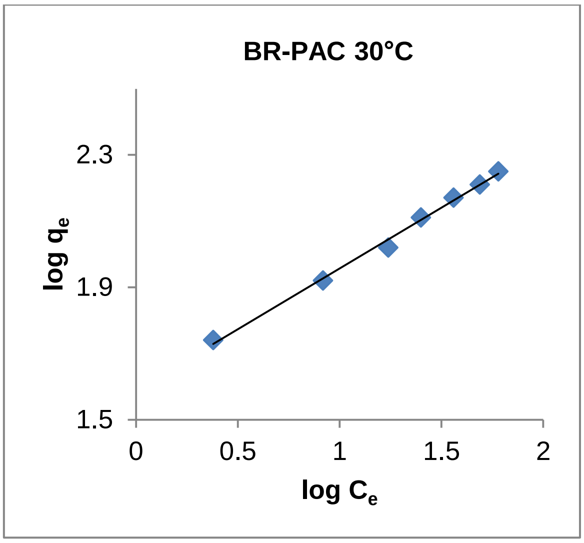

Figure 71 a

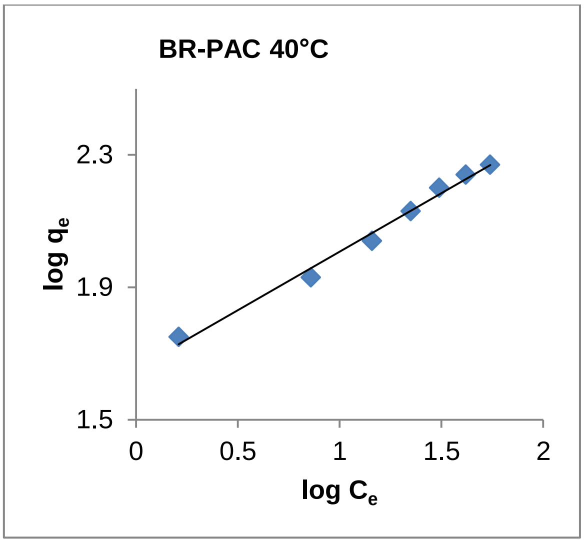

Figure 71 b

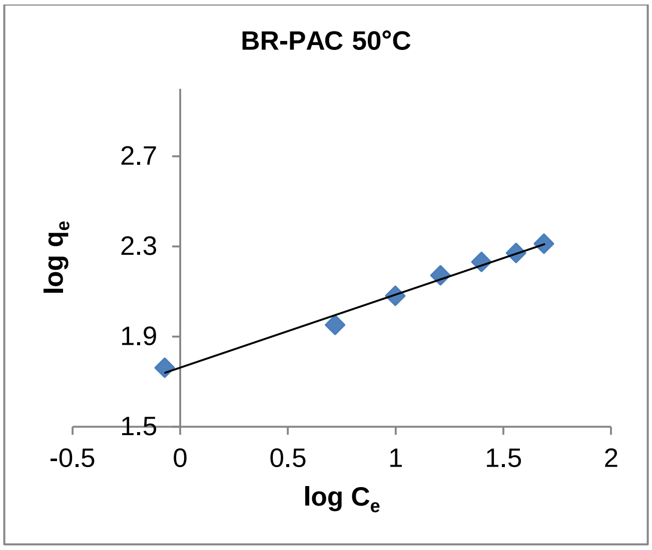

Figure 71 c

4.7 Thermodynamic Studies

The thermodynamic factors help to deliberate the inherent energetic changes that are associated with the adsorption process **(Lan Chen and Bo Bai, 2013).** The thermodynamic parameters like **enthalpy change (ΔH), entropy change (ΔS) and Gibb's free energy change (ΔG)** for the adsorption of CV, AB110, RB5 and CR dyes from aqueous solution onto the adsorbents BR-SAC and BR-PAC were calculated using the following relations **(Sartape *et al.,* 2017).**

$$K_c = q_e / C_e$$

where

K_c is equilibrium constant
q_e is amount of dye adsorbed at equilibrium and
C_e is equilibrium concentration of dye adsorbed

The above equation is used to calculate equilibrium constant (K_c) and substituted in the following equation to calculate the Gibb's free energy change (ΔG) of adsorption process **(Sartape *et al.,* 2017).**

$$\Delta G = - RT \ln K_c$$

where

R is gas constant (8.314 J/K/mole) and

T is temperature in Kelvin

The change in enthalpy (ΔH) and change in entropy (ΔS) were designed using the subsequent Van't Hoff equation

$$\ln K_c = (\Delta S / R) - (\Delta H / RT)$$

The thermodynamic parameters were studied by conducting batch mode adsorption experiments using 100ml dye solution of initial concentration 100mg/l with 100mg BR - SAC adsorbent **/** 50 mg BR – PAC adsorbent at three different temperatures (303, 313, 323 K) and at pH 6.8 ± 0.2.

The values of ΔH and ΔS were calculated from the slope and intercept of Van't Hoff plots obtained by plotting ln K_c Vs 1/T **(Figures 72 and 73)** and the results are listed in **Tables 50 and 51.**

The negative values of ΔG obtained for the adsorption of dyes revealed that the adsorption process is feasible and spontaneous and the positive values of ΔH confirms that the adsorption process is endothermic and physical forces like Van der Waal's and hydrogen bonding interactions may be involved in the adsorption **(Chakraborty *et al.,* 2011).** The ΔH values for the adsorption of CV, AB 110, RB 5 and CR dyes were in the range 5.0424 to 16.8774 kJ/mol **(Tables 50 and 51),** revealed that adsorption of dyes would be due to physical adsorption. Generally the heat evolved during physical adsorption is in the range 2.1 to 20.9 kJ/mol and heat evolved during chemical adsorption is in the range of 80 – 200 kJ/mol **(Chakraborty *et al.,* 2011).**

The positive values of ΔS revealed good affinity of all the dyes (CV, AB 110, RB 5 and CR) towards both the adsorbents BR-SAC and BR-PAC and increased disorderliness at solid solution interface which may possibly remove some of the adsorbed water molecules from the adsorbent surface leading to higher dye removal **(Rehman *et al.,* 2012).**

Similar results were reported for the removal of Reactive Brilliant Red K-2BP and Acid Red 18 using Magnetic amine/Fe_3O_4 functionalized Bio polymer resin **(Wen Song *et al.,* 2016),** Removal of Malachite Green using Wood Apple shell **(Sartape *et al.,* 2017),** removal of Direct Yellow using Coconut shell activated carbon **(Aseel Aljeboree *et al.,* 2017),** removal of Methylene Blue by the Raspberry like TiO2@ Yeast micropores **(Lan Chen and Bo Bai, 2013)** & Bael tree bark **(Valliammai *et al.,* 2013)** and removal of Crystal Violet dye using Chitosan **(Mona shouman *et al.,* 2012).**

Table 50

Thermodynamic Parameters for the Removal of Dyes from Aqueous Solution Using BR-SAC

Name of the dye	T (K)	1/T	q_e	C_e	K_c	lnKc	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/K/mol)
CV	303	0.0033	82.21	17.79	4.6211	1.5306	-3.8558	10.234	46.5251
	313	0.0032	84.10	15.90	5.2893	1.6657	-4.3346		
	323	0.0031	85.53	14.47	5.9108	1.7768	-4.7715		
AB110	303	0.0033	78.88	21.12	3.7348	1.3177	-3.3195	11.49	48.9700
	313	0.0032	81.66	18.34	4.4525	1.4935	-3.8855		
	323	0.0031	83.12	16.88	4.9242	1.5941	-4.2788		
RB5	303	0.0033	72.48	27.52	2.6337	0.9684	-2.3906	12.072	48.0500
	313	0.0032	76.41	23.59	3.2391	1.1753	-3.0585		
	323	0.0031	77.88	22.12	3.5208	1.2588	-3.3804		
CR	303	0.0033	71.62	28.38	2.5236	0.9257	-2.3320	5.0424	24.2935
	313	0.0032	72.54	27.46	2.6416	0.9714	-2.5279		
	323	0.0031	74.02	25.98	2.8491	1.0470	-2.8116		

Thermodynamic Parameters for the Removal of Dyes from Aqueous Solution Using BR-SAC

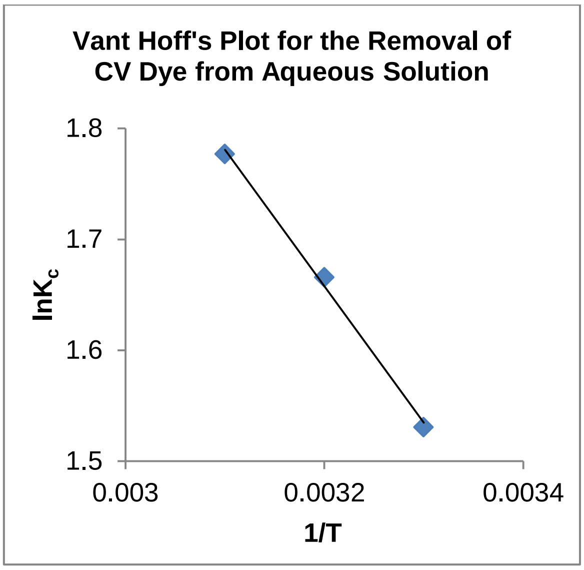

Figure 72 a

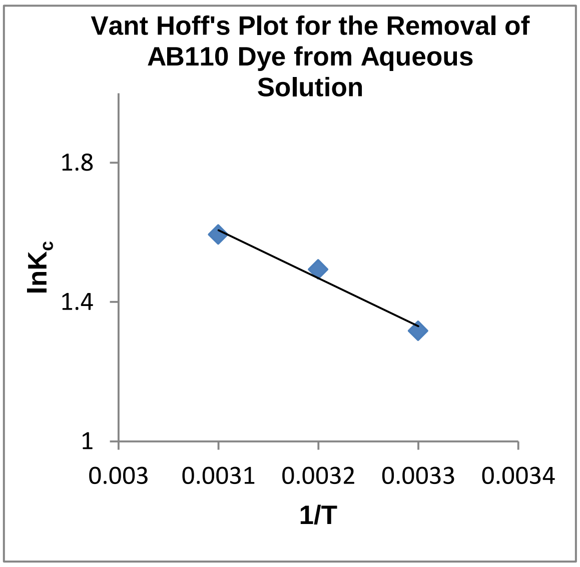

Figure 72 b

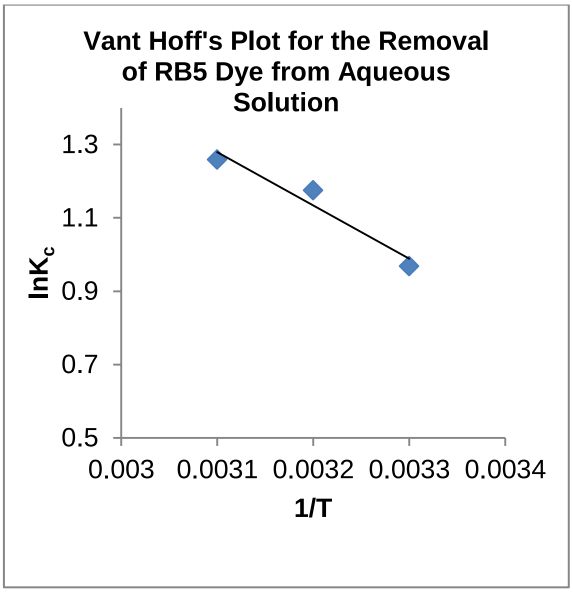

Figure 72 c

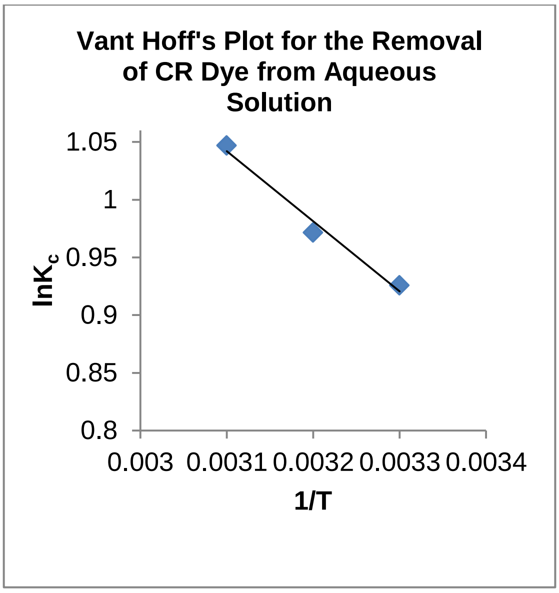

Figure 72 d

Table 51

Thermodynamic Parameters for the Removal of Dyes from Aqueous Solution Using BR-PAC

Name of the dye	T (K)	1/T	q_e	C_e	K_c	lnKc	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/K/mol)
CV	303	0.0033	185.36	7.32	25.32	3.2316	-8.1409		
	313	0.0032	187.76	6.12	30.68	3.4236	-8.9092	16.8774	82.5248
	323	0.0031	190.40	5.00	38.08	3.6376	-9.4661		
AB110	303	0.0033	173.32	13.34	12.99	2.5644	-6.4601		
	313	0.0032	175.54	12.23	14.35	2.6639	-6.9322	9.1205	51.397
	323	0.0031	178.00	11.02	16.18	2.7839	-7.4760		
RB5	303	0.0033	172.24	13.88	12.41	2.5184	-6.3442		
	313	0.0032	179.68	11.5	15.51	2.7418	-7.1349	16.9107	76.80
	323	0.0031	180.62	9.69	18.64	2.9253	-7.8557		
CR	303	0.0033	173.84	13.08	13.29	2.5870	-6.5170		
	313	0.0032	175.32	11.8	14.85	2.6980	-7.0210	11.0576	57.949
	323	0.0031	179.32	10.34	17.34	2.8531	-7.6618		

Thermodynamic Parameters for the Removal of Dyes from Aqueous Solution Using BR-PAC

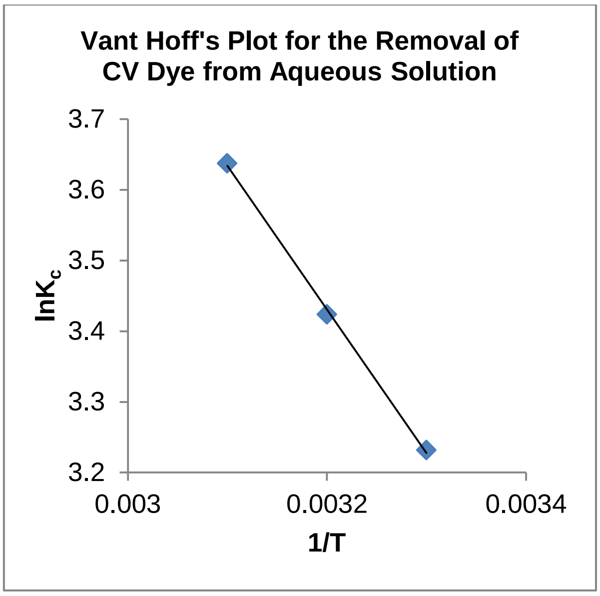

Figure73 a

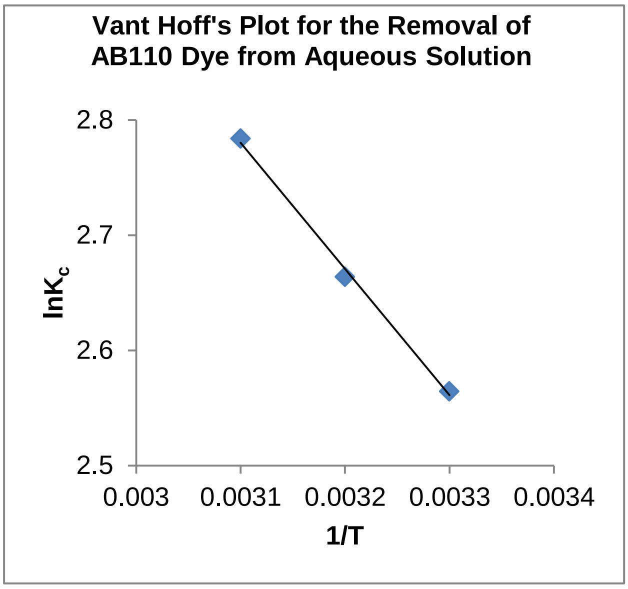

Figure73 b

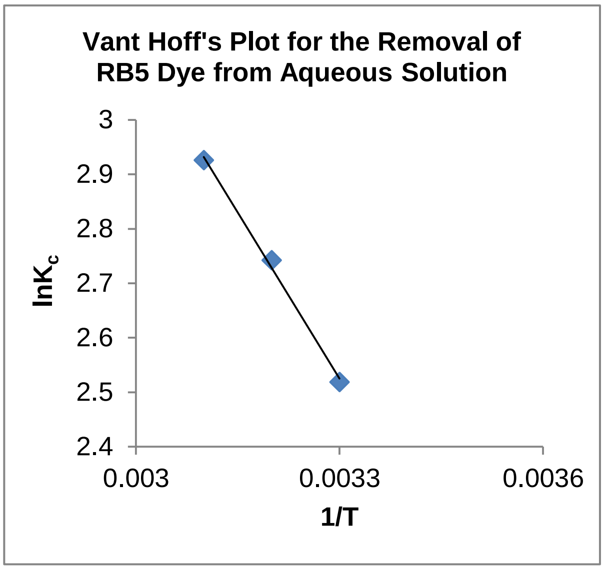

Figure73 c

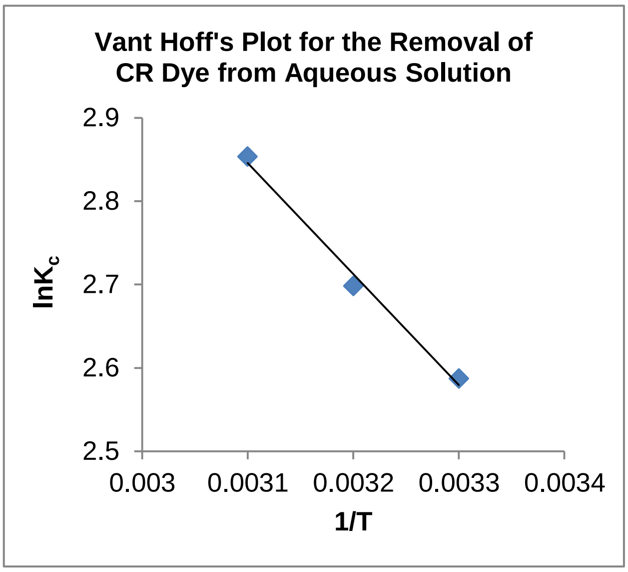

Figure73 d

4.8 Field Emission Scanning Electron Microscope Studies

The surface area, attached functional groups and morphology of adsorbents are considered as necessary for an effective adsorption process. The surface morphology of BR-SAC and BR-PAC adsorbents before and after adsorption of the dyes has been visualized using **Field Emission Scanning Electron Microscope (FESEM).** The FESEM images of the adsorbents BR-SAC and BR-PAC (Plate A and Plate B) and CV, AB110, RB5 and CR dye loaded BR-SAC **/** BR-PAC adsorbents (Plate C to Plate J) clearly designate the existence of large number of pores on the exterior surface of the adsorbents BR-SAC and BR-PAC, afford suitable binding sites for the adsorption of the dye molecules. The FESEM images of BR-PAC adsorbent also revealed that nano porous (diameter in the range of 19 to 25 nm) carbon surface responsible for its superior adsorption capacity **(Figures 74 - 83).**

FESEM Image of the Adsorbent BR-SAC (Plate A)

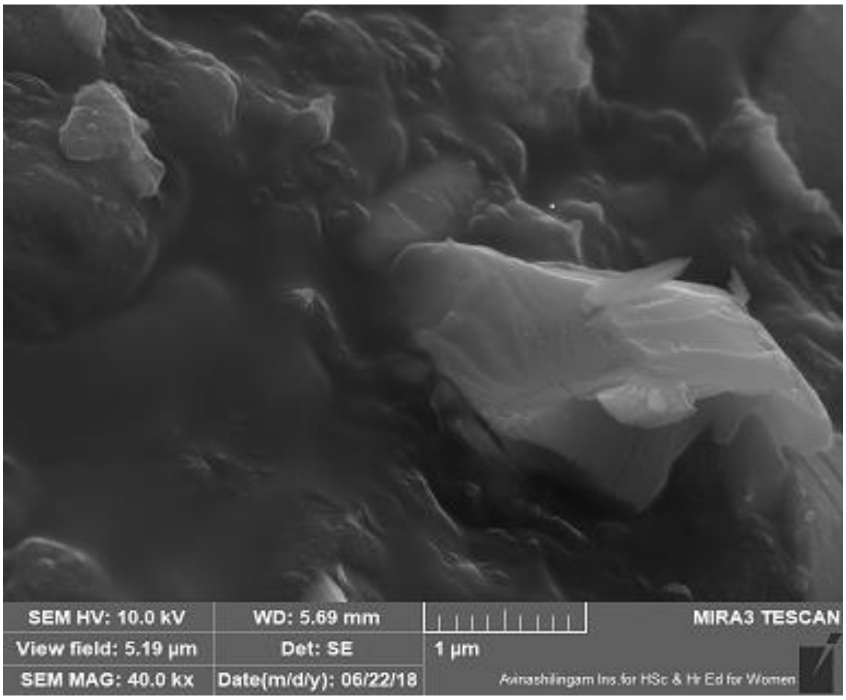

Figure 74

FESEM Image of the Adsorbent BR-PAC (Plate B)

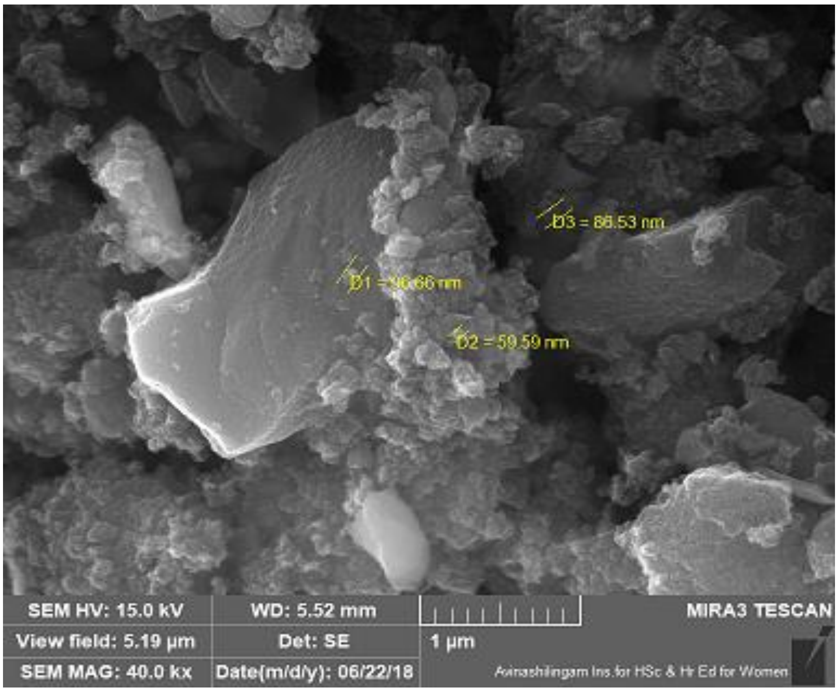

Figure 75

FESEM Image of the CV Dye Loaded BR-SAC Adsorbent (Plate C)

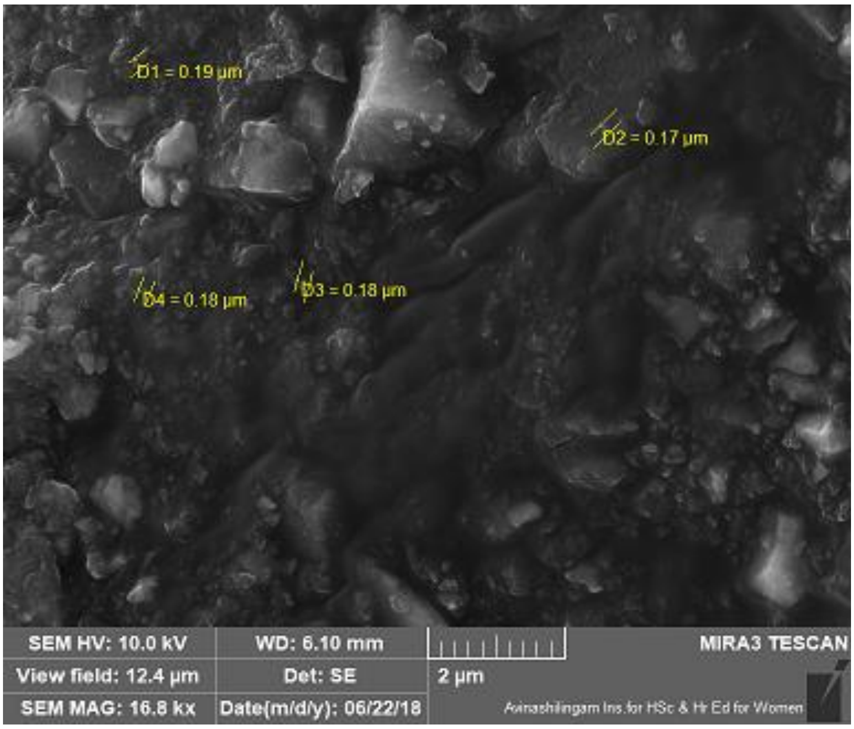

Figure 76

FESEM Image of the CV Dye Loaded BR-PAC Adsorbent (Plate D)

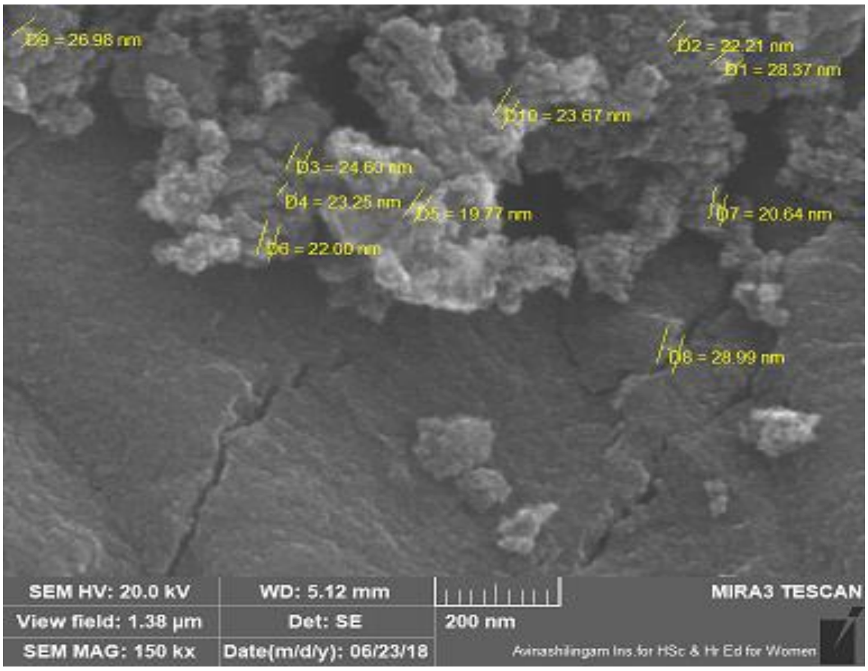

Figure 77

FESEM Image of the AB110 Dye Loaded BR-SAC Adsorbent (Plate E)

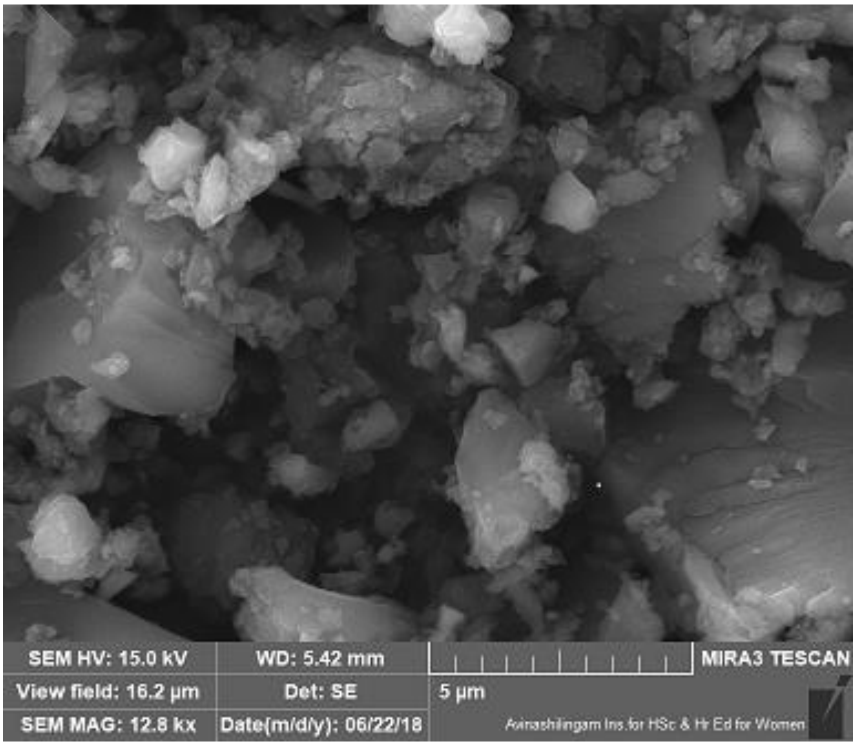

Figure 78

FESEM Image of the AB110 Dye Loaded BR-PAC Adsorbent (Plate F)

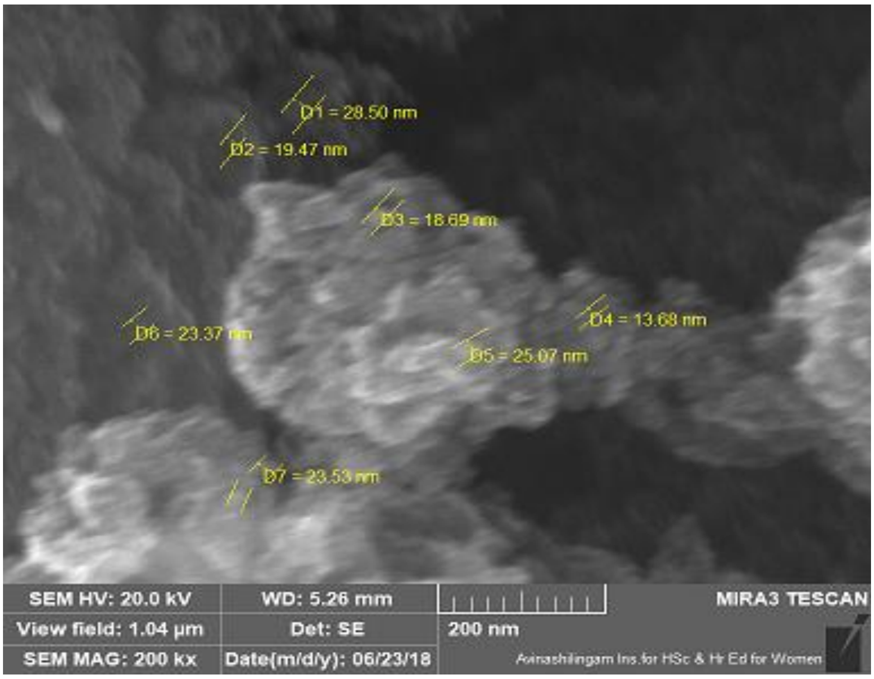

Figure 79

FESEM Image of the RB5 Dye Loaded BR-SAC Adsorbent (Plate G)

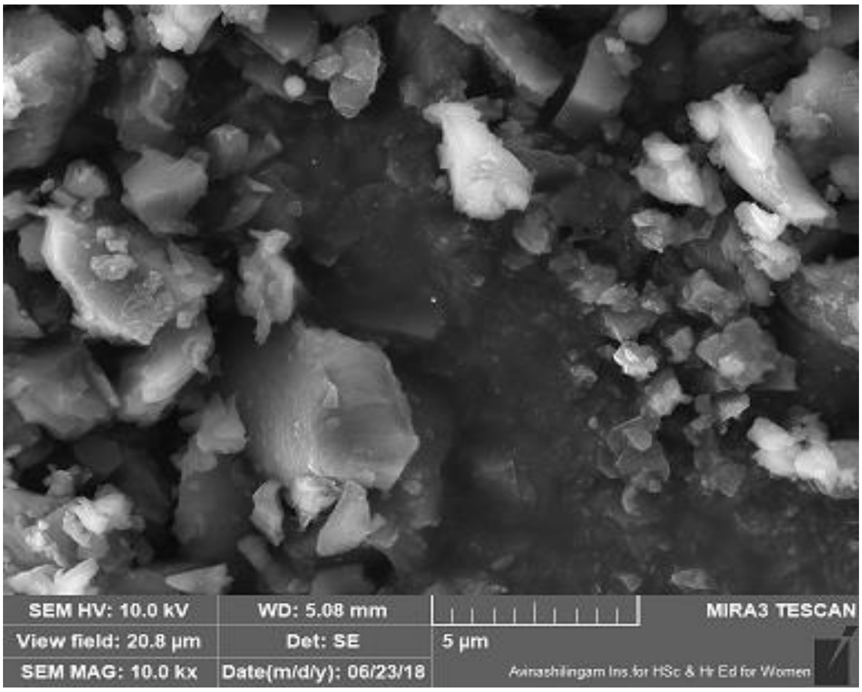

Figure 80

FESEM Image of the RB5 Dye Loaded BR-PAC Adsorbent (Plate H)

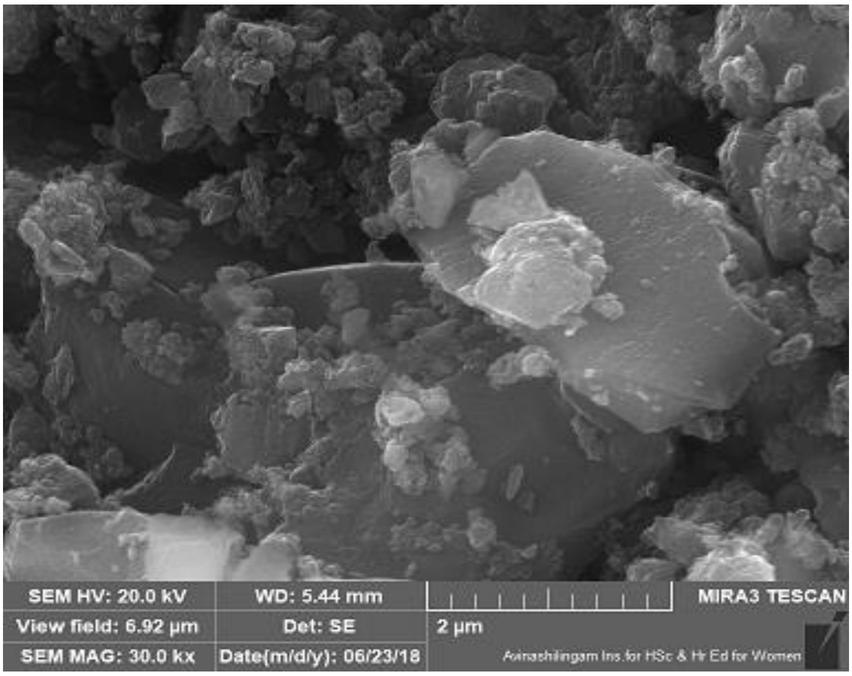

Figure 81

FESEM Image of the CR Dye Loaded BR-SAC Adsorbent (Plate I)

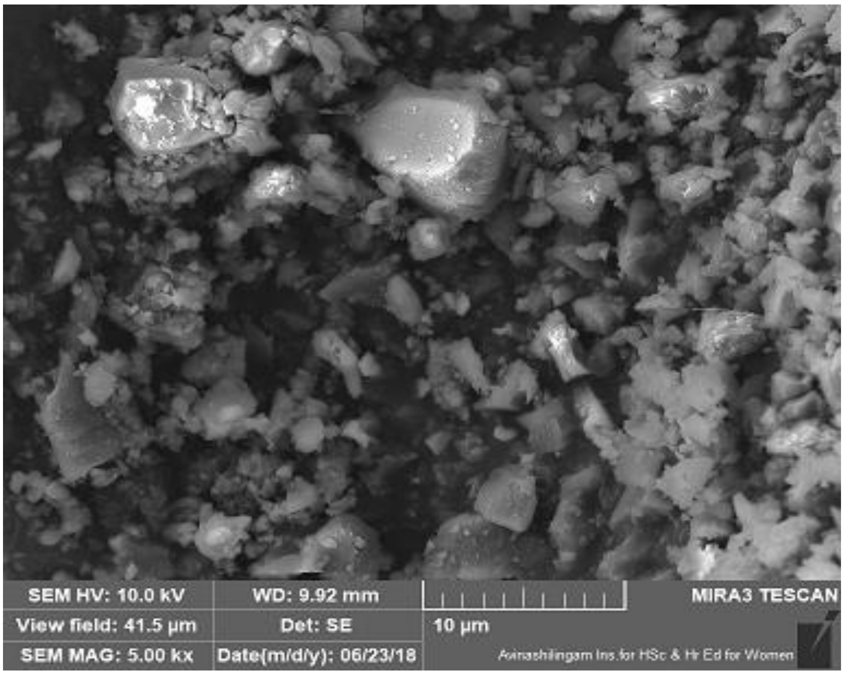

Figure 82

FESEM Image of the CR Dye Loaded BR-PAC Adsorbent (Plate J)

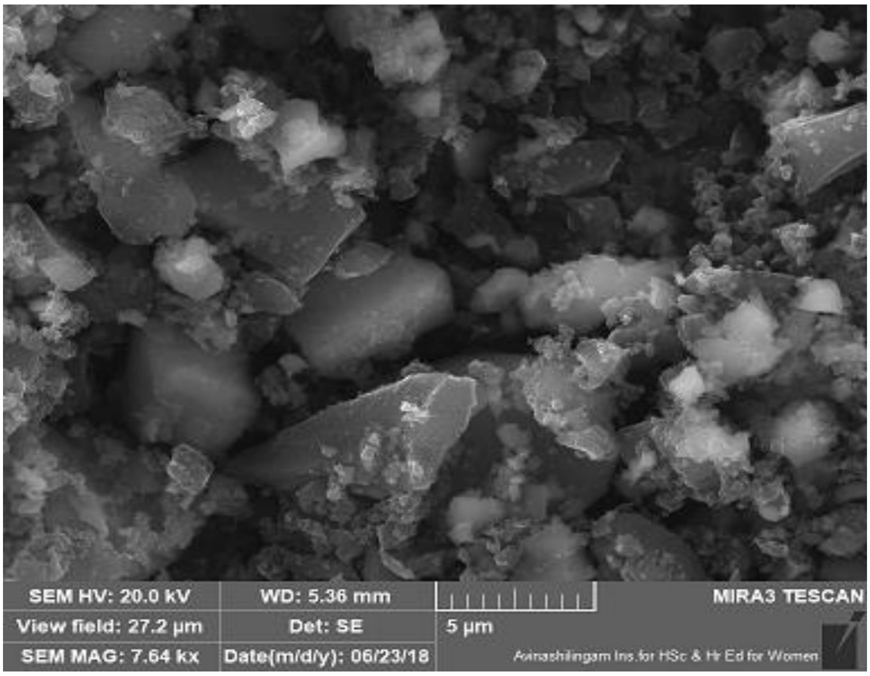

Figure 83

4.9 FT-IR Spectral Analysis

The FT-IR spectrum of the adsorbents BR-SAC and BR-PAC were shown in **Figures 84 and 85.** The peaks exist in infrared spectrum gives significant information about the various surface functional groups present on the surface of the adsorbents.

The regions of the spectrum for various functional groups present are shown below **(Sharma, 2012)**

The peak obtained at 3724.54 and 3657.04 cm^{-1} corresponds to free O-H group.

Peak detected at 2978.09 cm^{-1} was due to O-H stretching of carboxylic acid.

The peak at 2891.30 cm^{-1} corresponds to N-H stretching of $–NH_2$ group.

Peak at 2303.01 cm^{-1} corresponds to the presence of –C=O group.

The peak at 1577.77 cm^{-1} corresponds to N-H bending of $–NH_2$ group

The peak obtained at 1379.10 cm^{-1} corresponds to O-H bending of –COOH group

Peaks at 1238.30 cm^{-1}, 1153.43 cm^{-1} and 1076.28 cm^{-1} are attributed to the C-H vibration modes of alcohol, ether and ester groups **(Valliammai *et al.,* 2013).**

The existence of various functional groups -COOH, -C=O and –OH on the adsorbents BR-SAC and BR-PAC was confirmed by FTIR spectrum. The possibility of the formation of hydrogen bonds between the surface functional groups of both the adsorbents with the adsorbate dye molecules may be responsible for the adsorption of CV, AB 110, RB5 and CR dyes onto BR-SAC and BR-PAC adsorbents **(Aparna Roy *et al.,* 2013).**

The development of hydrogen bond between the adsorbate molecules and the functional groups that exist on the surface of the adsorbents may be responsible for the adsorption of CV, AB 110, RB5 and CR dyes onto BR-SAC and BR-PAC adsorbents **(Aparna Roy *et al.,* 2013).**

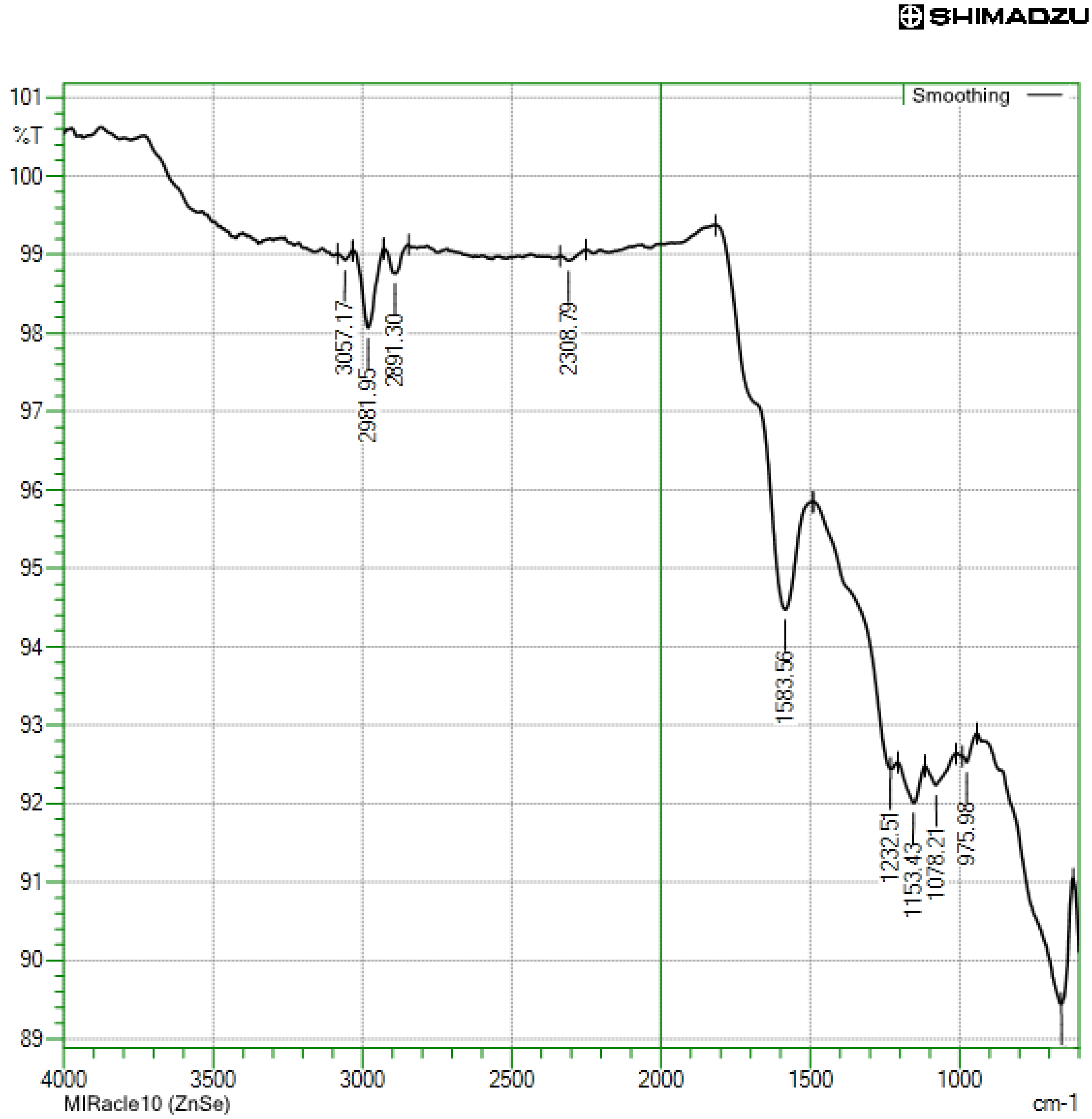

Figure 84 IR Spectrum of BR-SAC

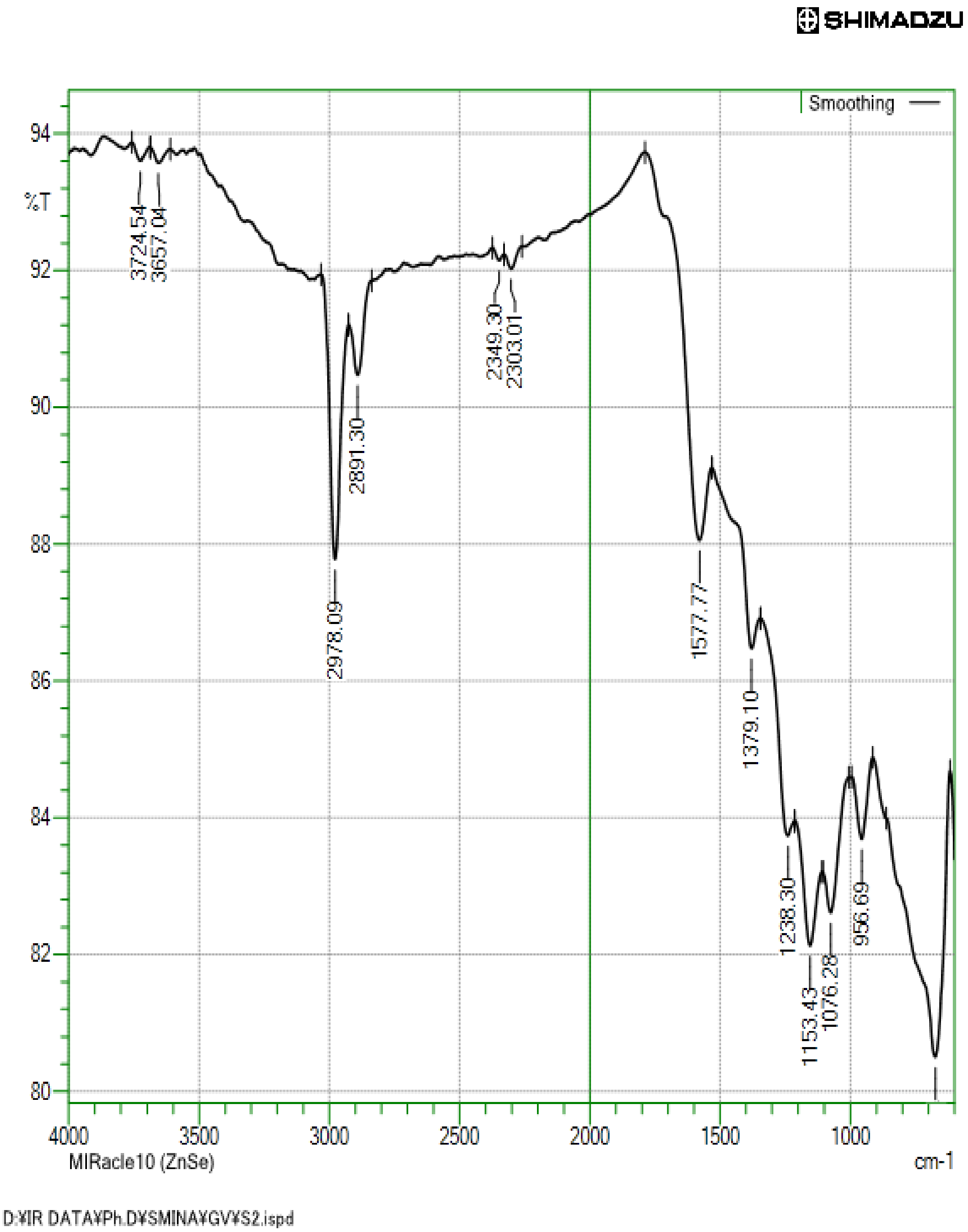

Figure 85 IR Spectrum of BR-PAC

4.10 Efficiency of BR-SAC and BR-PAC in the Removal of Dyes from Textile Dyeing Industry Effluent by Adsorption

The textile dyeing industry effluent containing CV dye (Sample 1), AB110 dye (Sample 2), RB5 dye (Sample 3) and CR dye (Sample 4) were collected from Balamurugan bleaching and dyeing unit Tirupur, the **"Banian City"** of the South India, Tamil Nadu and Sri Ganga bleaching and dyeing unit, Udumalpet, Tirupur district, Tamil Nadu. To compare the dye removal efficiency of the adsorbents BR-SAC and BR-PAC with commercial activated carbon (CAC) batch mode adsorption experiments were conducted using 100 ml of diluted dyeing industry effluent of the dye concentration 100 mg/l with 100 mg of adsorbents (BR-SAC/ BR-PAC and CAC) at 32 ± 2°C and at pH 6.8 ± 0.2. The results of the study were given in **tables 52 & 53 and figures 86 - 89.**

From the results it was evident that among the two adsorbents the dye removal efficiency of the adsorbent BR-PAC was higher and very much closer to the removal efficiency of commercial activated carbon which could be attributed to the greater surface area of both the adsorbents (BET Surface area of BR-PAC 1083.440 m^2/g and CAC 1137.962 m^2/g). The dye removal efficiency of BR-SAC was relatively poor due to low surface area of the adsorbent (BET Surface area of BR-SAC 288.700 m^2/g) **(Monal Dutta *et al.,* 2011 and Mui *et al.,* 2010).** The removal of dyes by adsorption using commercial activated carbon is quite expensive, it is highly advantageous to use BR-PAC as a substitute since *Bauhenia racemosa* is available in large quantities as natural bio waste and the process is cost effective.

The percentage removal of dyes from the dyeing industrial effluents using BR-SAC, BR-PAC and CAC adsorbents **(Tables 52 & 53 and Figures 86 - 89)** were found to be lesser compared to that of aqueous solutions **(Tables 54 & 55 and Figures 90 to 93) .** This perhaps due to the adsorption of other pollutants (detergents, cellulose fibres, oils, greases, suspended solids, water hardening metal ions like Ca^{2+} and Mg^{2+}, sulphates, carbonates and chlorides) commonly exist in the effluent, compete for the adsorption sites on the surface of the adsorbent and consequently the removal efficiency of the dyes by the adsorbents decreases **(Lin Liu *et al.,* 2015).**

Table 52

Adsorption of CV Dye and AB110 Dye from Dyeing Industry Effluent onto BR- SAC/BR- PAC and CAC

Conditions:
Adsorbent Dosage: 100mg
pH: 6.8±0.2
Temperature: 32 ± 2°C

Time in Minutes	Removal of CV dye (%) (Sample 1)			Removal of AB110 dye (%) (Sample 2)		
	Adsorbents used			Adsorbents used		
	BR-SAC	BR-PAC	CAC	BR-SAC	BR-PAC	CAC
10	20.1	40.8	42.0	18.7	39.2	40.4
20	21.4	45.6	46.8	19.9	43.3	44.5
30	21.9	49.8	50.4	21.6	47.0	47.8
40	22.8	54.3	54.2	22.4	50.6	51.6
50	24.6	56.6	58.1	23.3	53.9	55.9
60	25.5	59.2	61.6	24.1	56.2	58.0
90	27.4	63.6	65.2	25.4	60.6	61.2
120	28.6	65.8	67.4	26.7	62.4	64.4
150	29.7	68.7	69.3	27.2	65.1	66.8
180	30.2	69.3	71.5	28.4	66.5	68.4

Table 53

Adsorption of RB5 Dye and CR Dye from Dyeing Industry Effluent onto BR- SAC/BR- PAC and CAC

Conditions:
Adsorbent Dosage: 100mg
pH: 6.8±0.2
Temperature: 32 ± 2°C

Time in Minutes	Removal of RB5 dye (%) (Sample 3)			Removal of CR dye (%) (Sample 4)		
	Adsorbents used			Adsorbents used		
	BR-SAC	BR-PAC	CAC	BR-SAC	BR-PAC	CAC
10	17.6	40.1	42.3	16.5	38.47	40.2
20	19.0	44.6	47.5	18.4	43.6	45.4
30	21.2	48.4	51.4	20.1	47.3	50.6
40	22.0	51.3	55.1	21.6	51.8	54.8
50	23.8	54.7	58.0	22.8	54.4	57.3
60	24.6	57.6	61.6	24.4	57.2	60.2
90	25.4	60.4	64.2	24.2	60.1	63.0
120	26.0	63.2	66.1	25.0	62.4	65.6
150	26.6	66.8	68.2	25.6	64.7	67.8
180	27.1	67.3	69.7	26.4	65.4	69.0

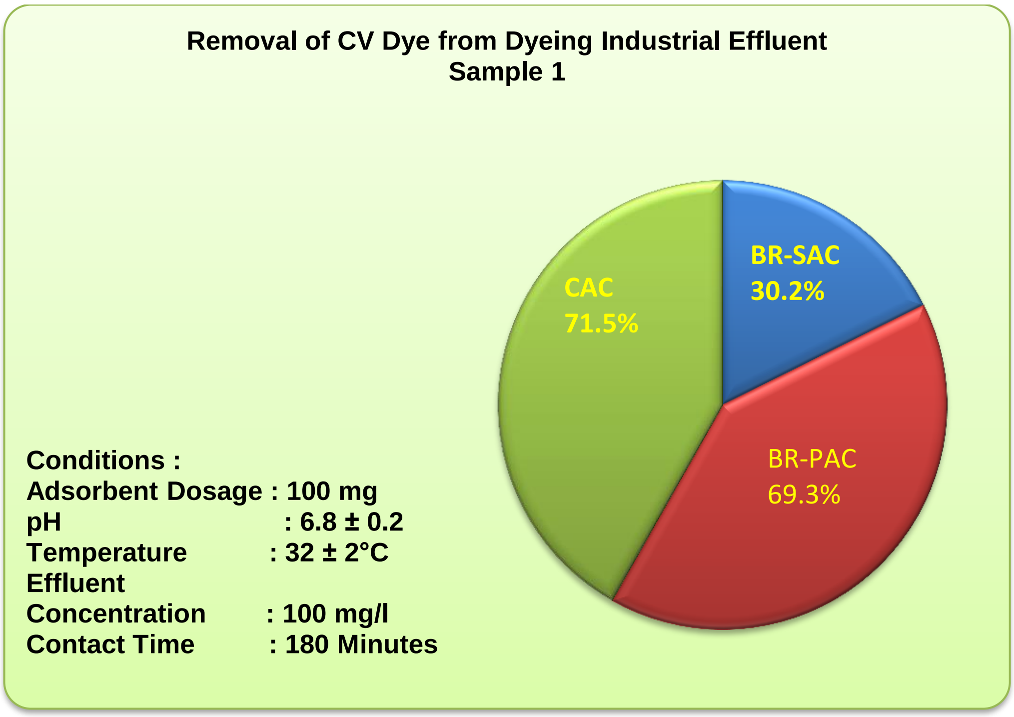

Figure 86

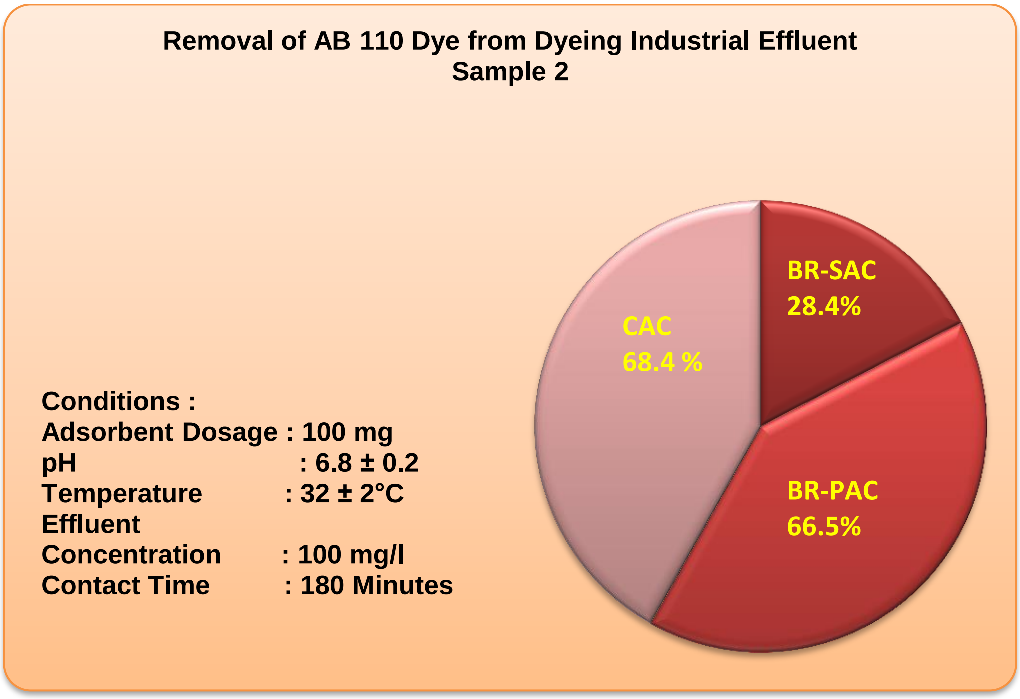

Figure 87

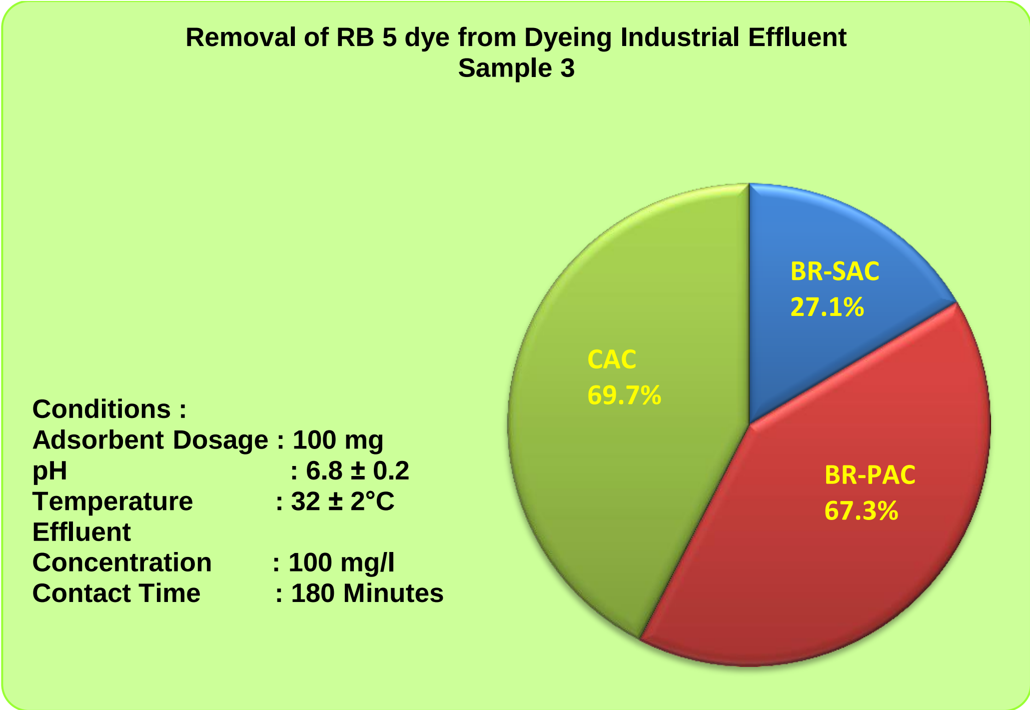

Figure 88

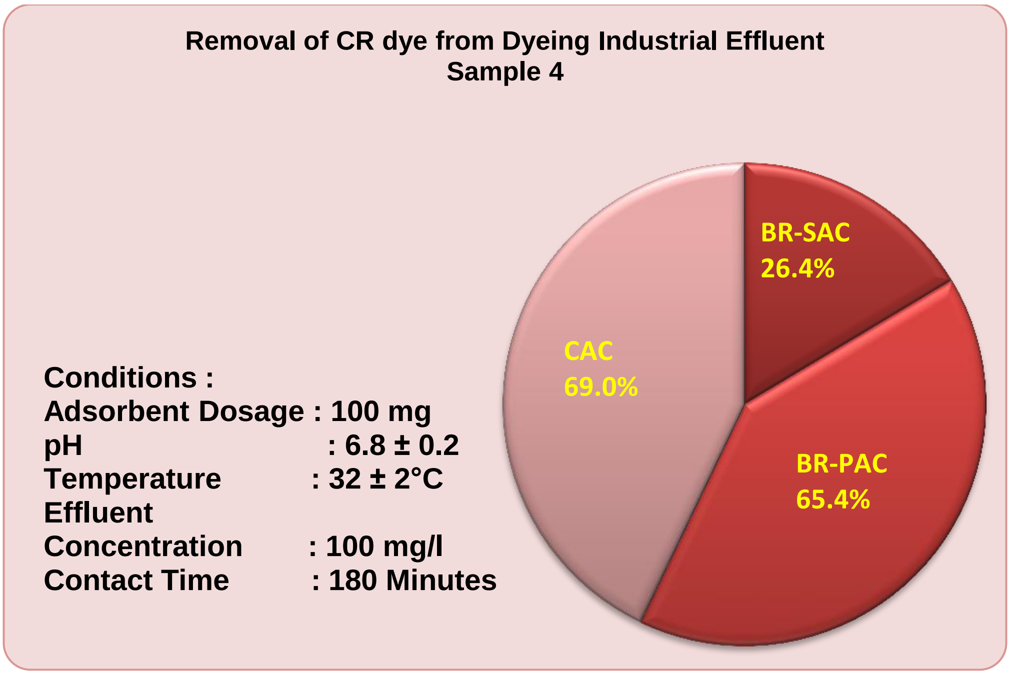

Figure 89

Table 54

Efficiency of Adsorbents BR-SAC, BR-PAC and CAC in the Adsorption of CV and AB110 Dyes from Aqueous Solution

Conditions:
Dye Concentration 100mg/l
Adsorbent Dose: 50mg pH: 6.8 ± 0.2
Temperature: 32 ± 2°C

Time in Minutes	Removal of CV dye (%)			Removal of AB110 dye (%)		
	Adsorbents Used			Adsorbents Used		
	BR-SAC	BR-PAC	CAC	BR-SAC	BR-PAC	CAC
10	21.18	60.18	61.82	19.21	58.36	60.36
20	32.42	73.42	74.64	29.64	66.13	97.42
30	40.16	83.16	85.23	36.71	72.75	74.15
40	48.77	88.33	89.45	42.83	78.19	80.82
50	54.53	90.21	91.72	47.92	81.62	82.67
60	56.21	91.24	93.68	51.10	84.43	86.41
80	58.02	91.96	93.68	54.02	87.85	89.80
100	59.41	91.96	93.68	57.18	87.85	90.12
120	60.01	91.96	93.68	57.85	87.85	90.18

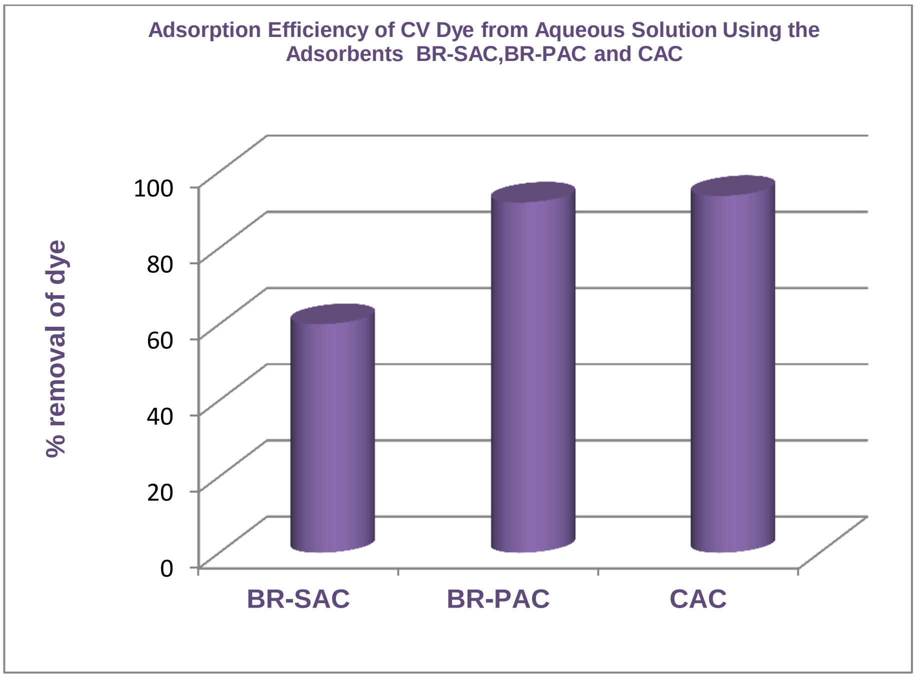

Figure 90

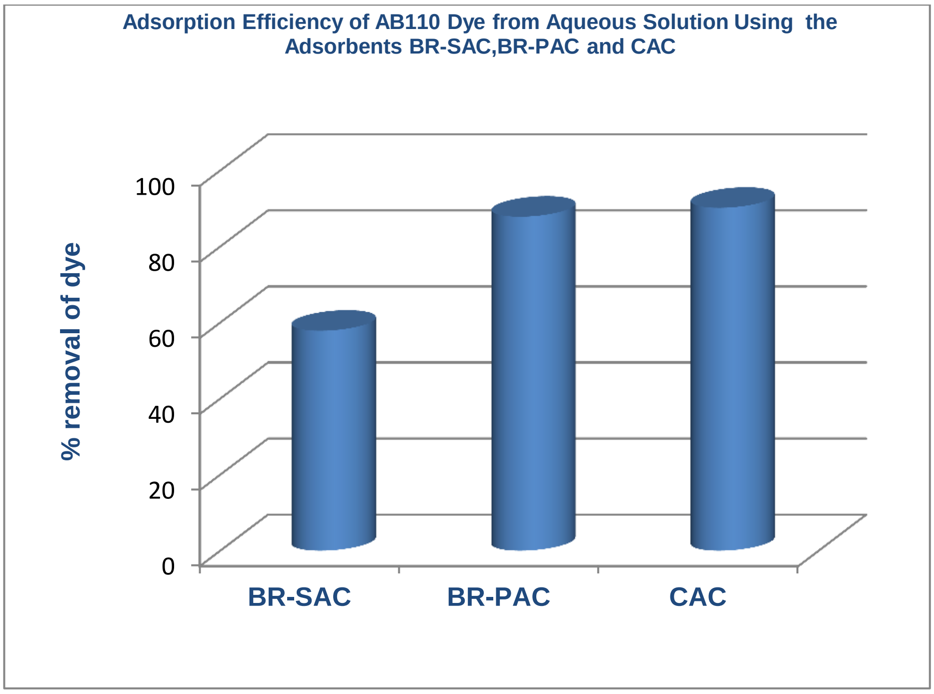

Figure 91

Table 55

Efficiency of Adsorbents BR-SAC, BR-PAC and CAC in the Adsorption of RB5 and CR Dyes from Aqueous Solution

Dye Concentration 100mg/l
Adsorbent Dose : 50m
pH: 6.8 ± 0.2
Temperature: 32 ± 2°C

Time in Minutes	Removal of RB5 dye (%)			Removal of CR dye (%)		
	Adsorbents Used			Adsorbents Used		
	BR-SAC	BR-PAC	CAC	BR-SAC	BR-PAC	CAC
10	21.02	51.11	53.44	18.16	56.22	58.88
20	31.43	61.22	64.21	27.42	65.32	69.41
30	39.12	69.53	72.30	35.50	73.45	75.11
40	46.64	77.40	78.86	41.41	79.36	81.36
50	50.22	83.81	85.43	45.12	84.52	86.21
60	53.41	86.26	89.52	49.06	87.14	89.04
80	56.36	87.48	91.10	53.62	88.50	90.62
100	58.22	87.88	91.01	56.14	89.00	90.54
120	58.98	88.02	91.56	56.48	89.24	91.02

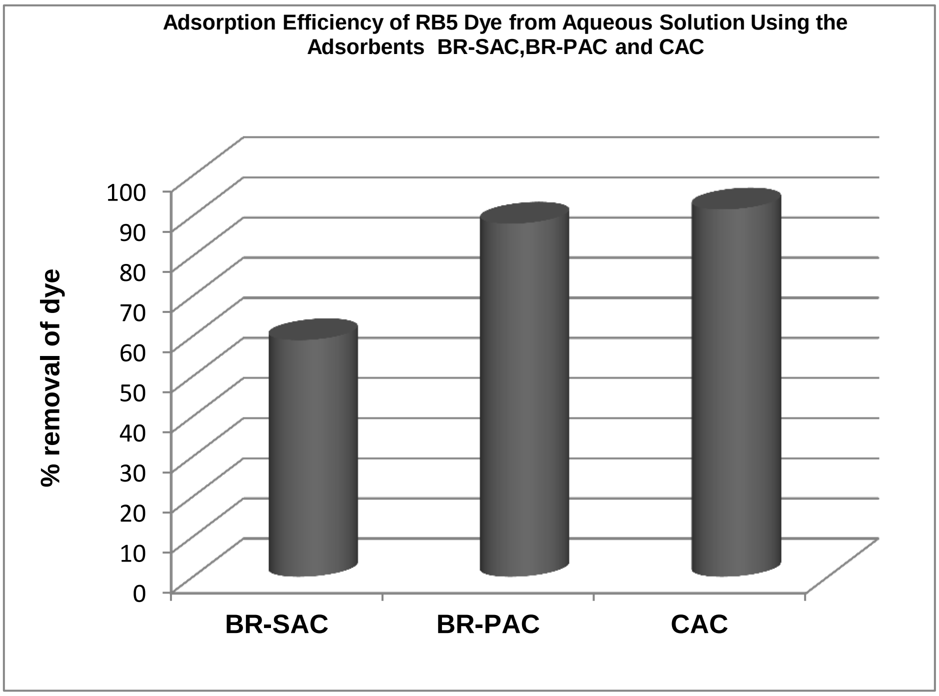

Figure 92

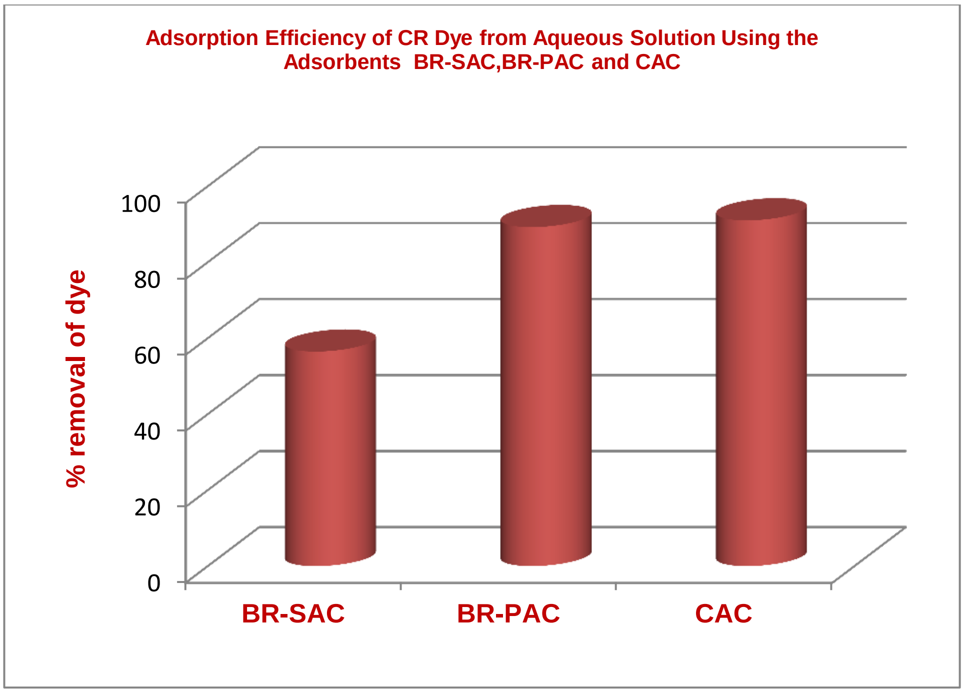

Figure 93

4.10.1 Characterisation of Raw and Treated Dyeing Industrial Effluents

The characteristics such as Colour, Odour, Turbidity, pH, BOD, COD, Total suspended solids, Total dissolved solids and Chloride content of effluent samples were determined before and after adsorption studies. The results revealed that most of the water pollution parameters determined for the effluent samples 1, 2, 3 and 4 (before adsorption) were not within the permissible limit of Bureau of Indian standards (BIS) **(Gomathi *et al*., 2017, Jayaseelan *et al.,* 2015).** Whereas BR-PAC treated effluents were closely in accordance with BIS permissible limits **(Tables 56 & 57)**. Thus the prepared low-cost, eco - friendly adsorbent BR-PAC can be used for the removal of CV, AB110, RB5 and CR dye pollutants from dyeing industry waste water.

Table 56

Physico – Chemical Parameters of Textile Industry Effluent (Samples 1 & 2)

S.No	Water pollution Parameters	Effluent before treatment (Sample 1)	Effluent after treatment (Adsorbent BR-PAC) (Sample 1)	Effluent before treatment (Sample 2)	Effluent after treatment (Adsorbent BR-PAC) (Sample 2)	BIS Permissible limits
1.	Colour	Blue	Colourless	Brown	Colourless	-
2.	Odour	Unpleasant	Agreeable	Unpleasant	Agreeable	-
3.	Turbidity (NTU)	80.5	10.5	89.5	11.2	10
4.	pH	8.7	6.5	8.9	6.8	6.5-8.5
5.	BOD (mg/l)	340	BDL	470	20	50
6.	COD (mg/l)	806	BDL	1790	60	250
7.	Total Suspended Solids (mg/l)	5980	120	6850	185	100
8.	Chloride (mg/l)	1450	490	1890	510	600
9.	Total Dissolved solids(mg/l)	3656	900	4895	1080	2100

BDL – Below detectable limit

Table 57

Physico – Chemical Parameters of Textile Industry Effluent (Samples 3 &4)

S.No	Water pollution Parameters	Effluent before treatment (Sample 3)	Effluent after treatment (Adsorbent BR-PAC) (Sample 3a)	Effluent before treatment (Sample 4)	Effluent after treatment (Adsorbent BR-PAC) (Sample 4a)	BIS Permissible limits
1.	**Colour**	Gray	Colourless	Red	Colourless	-
2.	**Odour**	Unpleasant	Agreeable	Unpleasant	Agreeable	-
3.	**Turbidity (NTU)**	85.5	12.5	90.5	15.2	10
4.	**pH**	8.5	6.3	8.0	6.1	6.5-8.5
5.	**BOD (mg/l)**	392	56	270	10	50
6.	**COD (mg/l)**	886	BDL	1926	40	250
7.	**Total Suspended Solids (mg/l)**	4290	100	5250	163	100
8.	**Chloride (mg/l)**	1220	320	1658	320	600
9.	**Total Dissolved solids(mg/l)**	4556	680	3805	1658	2100

BDL – Below detectable limit

4.11 Mechanism of Adsorption

The presence of carbonyl, carboxylic acid, hydroxyl and amine groups on the surface of the adsorbents favours the adsorption of dye molecules (CV, AB110, RB5 and CR) containing amine, sulphonate and azo functional groups in their structure. Thus multiple possibilities for Van der Waals forces of attraction and as well as hydrogen bonding between adsorbent surface and adsorbate species during the adsorption process. The hydrogen bonding may occurs between nitrogen, sulphur and oxygen atoms of the adsorbate and hydroxyl, carbonyl, and carboxyl groups of the adsorbent **(Figures 94 - 97).**

A similar mechanism was observed on adsorption of Congo Red dye using chemically modified Ligno Cellulosic Jute Fiber **(Aparna Roy *et al*., 2013)** and adsorption of Acid Blue 93 dye using a cellulose – based bioadsorbent **(Lin Liu *et al.,* 2015).**

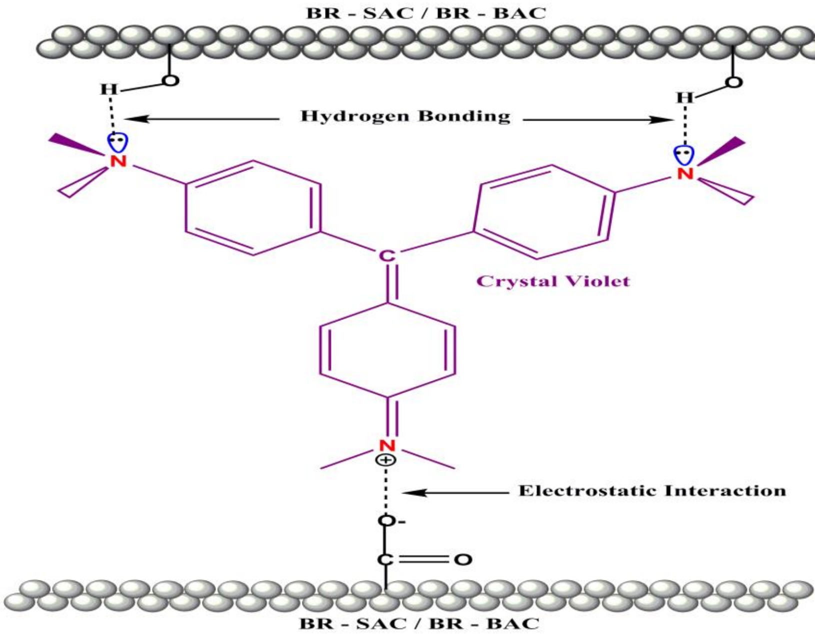

Figure 94 Mechanism of Adsorption of CV Dye onto BR-SAC/BR-PAC

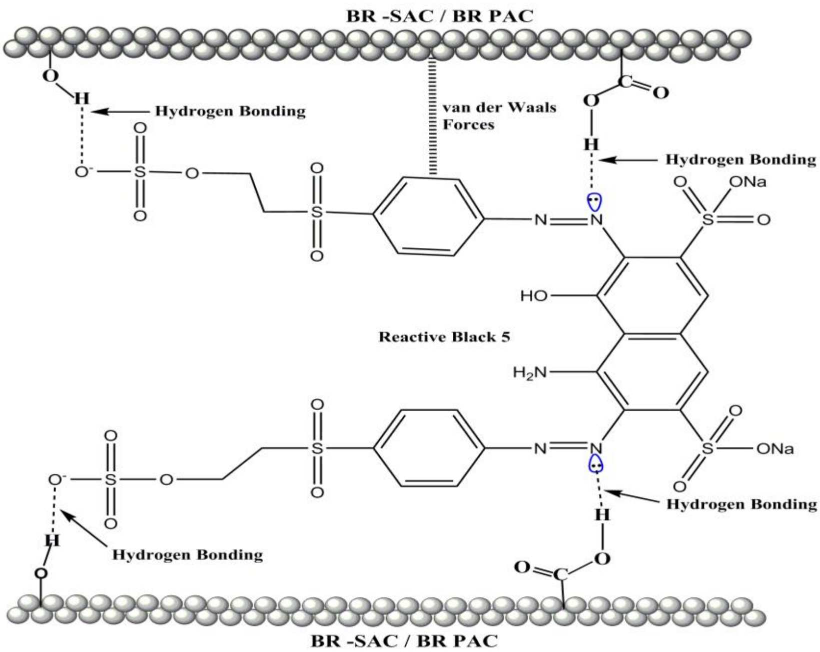

Figure 95 Mechanism of Adsorption of AB110 Dye onto BR-SAC/BR-PAC

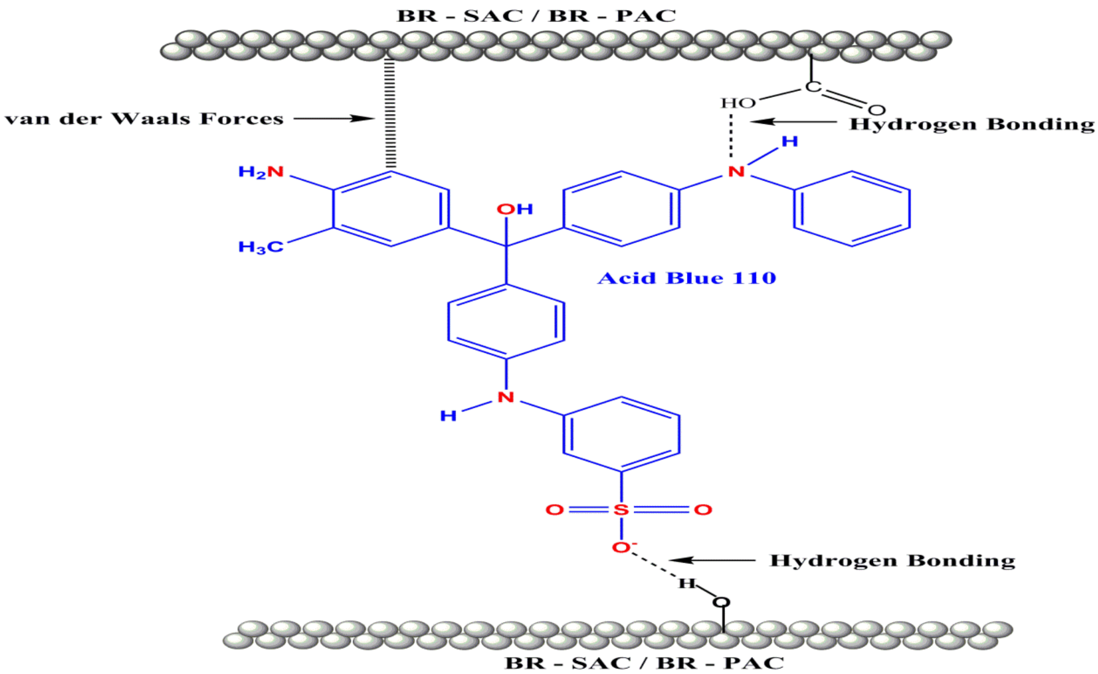

Figure 96 Mechanism of Adsorption of RB5 Dye onto BR-SAC/BR-PAC

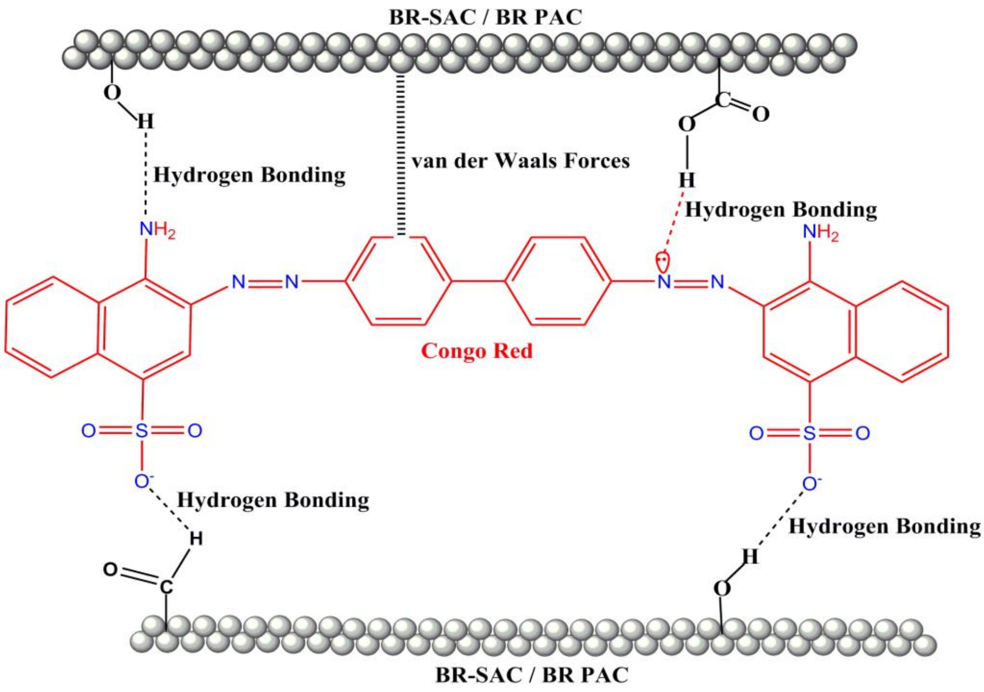

Figure 97 Mechanism of Adsorption of CR Dye onto BR-SAC/BR-PAC

4.12 Energy Dispersive X-ray Analysis (EDX)

The results of EDX analysis of the adsorbents BR-SAC and BR-PAC are presented in **Tables 58 & 59.** The K-ratio is the ratio of the intensity (number of X-ray counts) in the filtered peak for an element of interest in the sample to the intensity in the filtered peak for the standard assigned to that element. Z, the atomic number of the element, A and F indicates the absorbance and fluorescence values to compensate for the X-ray peak interaction **(Kibami *et al.*, 2017).**

An adsorbent with highest amount of carbon and lowest amount of oxygen is considered to be most effective for the recovery of dyes from aqueous solution **(Kibami *et al*., 2017; Elavarasan *et al*., 2018; Bello, 2017).** The elemental composition of the two adsorbents BR-SAC and BR-PAC obtained from EDX studies are shown in **Tables 58, 59 & Figures 98 – 101.** The adsorbent BR-PAC has the highest amount of carbon by weight (62.29%) compared to the adsorbent BR-SAC (55.88%), clearly indicates that the adsorbent with rich carbon content (BR-PAC) acts as an efficient adsorbent for adsorption of dyes from aqueous solution as well as from dyeing industry effluent. EDX mapping of BR-PAC adsorbent also reveals uniform distribution of carbon surface which may the reason for the higher dye uptake from aqueous solution and also from dyeing industry effluent. The presence of other elements (Al, Si, Na &Cd) indicated in the EDX mapping might be from the adsorbent raw material.

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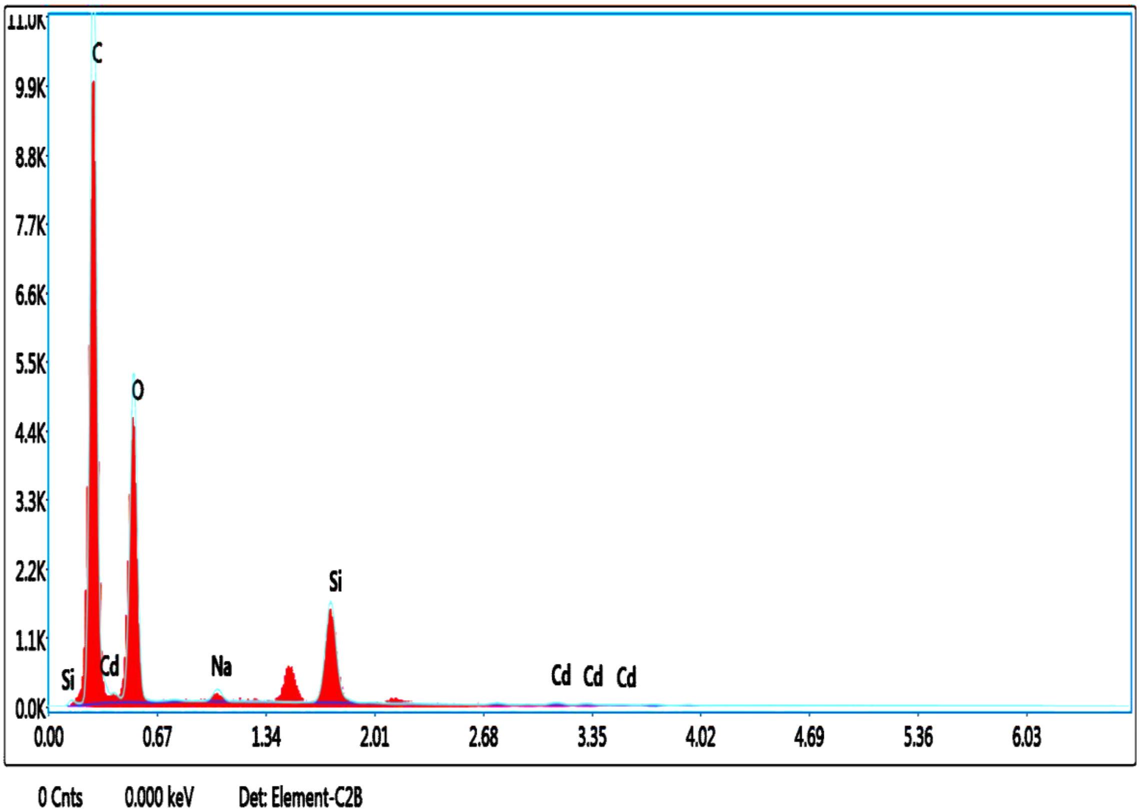
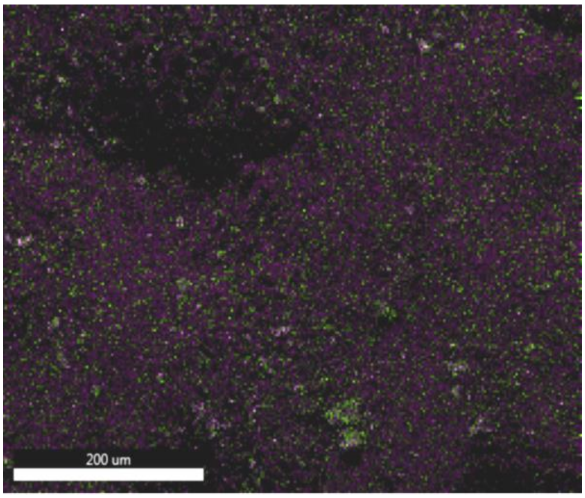


Figure 98 EDX Spectra of BR-SAC

Table 58 Elemental Composition from EDX of BR-SAC Adsorbent

Element	Weight%	Atomic%	K ratio	Z	A	F
C K	55.88	65.82	0.3291	1.0411	0.5656	1.0000
O K	32.47	28.71	0.1264	0.9827	0.3962	1.0000
Na K	1.08	0.66	0.0069	0.8795	0.7267	1.0019
Si K	9.20	4.63	0.0766	0.8705	0.9542	1.0032
CdL	1.37	0.17	0.0085	0.5886	1.0589	0.9996



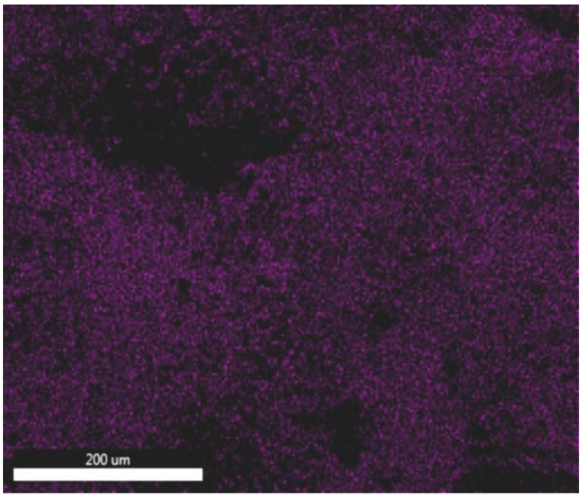


Figure 99 a **Figure 99 b**

Element Overlay and Carbon Surface of the Adsorbent BR-SAC

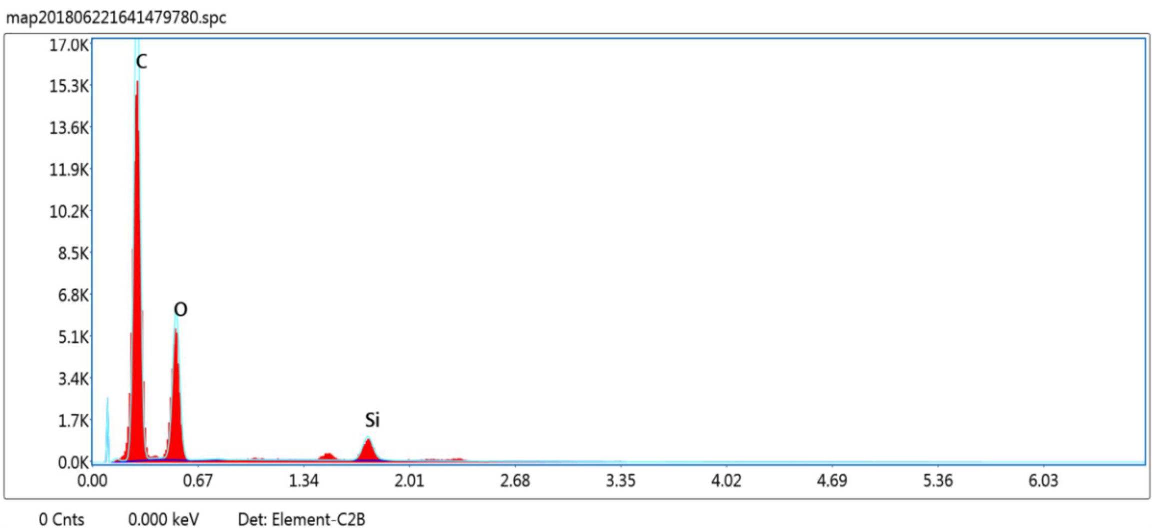


Figure 100 EDX Spectra of BR-PAC

Table 59 Elemental Composition from EDX of BR-PAC Adsorbent

Element	Weight%	Atomic%	K ratio	Z	A	F
C K	62.29	70.17	0.4280	1.0278	0.6684	1.0000
O K	31.96	27.03	0.1200	0.9697	0.3871	1.0000
Al K	1.58	0.79	0.0123	0.8428	0.9189	1.0056
Si K	4.17	2.01	0.0343	0.8583	0.9547	1.0036

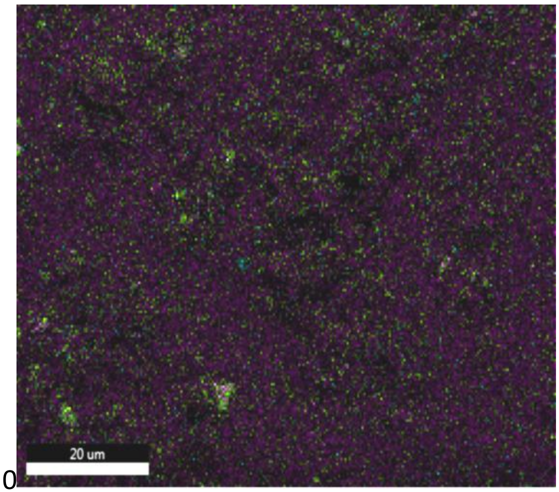


Figure 101

Element Overlay of BR-PAC

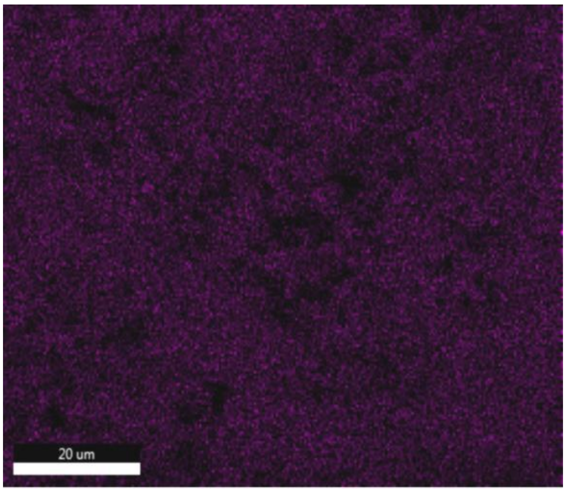


Figure 101 a

Carbon Surface of BR-PAC

4.13 Statistical Analysis

To study the significance of correlation coefficient and validity of the experimental data of the research work, statistical tests are used **(Achla Kaushal and Singh, 2017).** Karl Pearson's correlation coefficient (r) is a very helpful statistical formula that measures the linear relationship between any two variables.

The "r" values were calculated for Lagergren, Intraparticle diffusion and Elovich kinetic models and for Langmuir and Freundlich adsorption isotherm models. t- test was used to test the significance of the observed correlation coefficient "r" for all the equations used in describing the data for adsorption of CV, AB110,RB5 & CR dyes using BR-SAC and BR-PAC adsorbents **(Table 60).**

The "t" values obtained for kinetic models and adsorption isotherm models are at 1% level of significance. Thus the statistical results are in favour of the experimental data obtained in this research work.

Table 60 Statistical Analysis (t-test)

Equation	Adsorbent	Adsorbate	Correlation Coeffecient			
Lagergren	BR-SAC	CV	0.9634**	0.9825**	0.9722**	0.9691**
		AB110	0.9597**	0.9934**	0.9971**	0.9521**
		RB5	0.9942**	0.9910**	0.9880**	0.9831**
		CR	0.9917**	0.9828**	0.9974**	0.9835**
	BR-PAC	CV	0.9831**	0.9922**	0.9917**	0.9952**
		AB110	0.9852**	0.9811**	0.9912**	0.9873**
		RB5	0.9750**	0.9792**	0.9692**	0.9743**
		CR	0.9172**	0.9873**	0.9813**	0.9790**
Intraparticle Diffusion	BR-SAC	CV	0.8902**	0.9192**	0.9225**	0.9448**
		AB110	0.8650**	0.9022**	0.9081**	0.9243**
		RB5	0.8890**	0.9192**	0.9434**	0.9553**
		CR	0.9427**	0.9564**	0.9621**	0.9772**
	BR-PAC	CV	0.8959**	0.8747**	0.8364**	0.8580**
		AB110	0.9914**	0.9851**	0.9910**	0.9932**
		RB5	0.9781**	0.9660**	0.9742**	0.9580**
		CR	0.9680**	0.9255**	0.9337**	0.9010**
Elovich	BR-SAC	CV	0.9580**	0.9760**	0.9770**	0.9840**
		AB110	0.9590**	0.9750**	0.9790**	0.9850**
		RB5	0.9680**	0.9790**	0.9740**	0.9830**
		CR	0.9840**	0.9850**	0.9840**	0.9850**
	BR-PAC	CV	0.9550**	0.9450**	0.9320**	0.9460**
		AB110	0.9910**	0.9850**	0.9910**	0.9930**
		RB5	0.9780**	0.9960**	0.9740**	0.9580**
		CR	0.9940**	0.9810**	0.9830**	0.9660**

Equation	Adsorbent	Adsorbate	Correlation Coeffecient		
Langmuir Adsorption Isotherm	BR-SAC	CV	0.9781**	0.9820**	0.9780**
		AB110	0.9902**	0.9716**	0.9784**
		RB5	0.9950**	0.9912**	0.9845**
		CR	0.9852**	0.9895**	0.9783**
	BR-PAC	CV	0.9521**	0.9745**	0.9782**
		AB110	0.9930**	0.9880**	0.9710**
		RB5	0.9950**	0.9884**	0.9895**
		CR	0.9760**	0.9740**	0.9790**
Freundlich Adsorption Isotherm	BR-SAC	CV	0.9892**	0.9891**	0.9690**
		AB110	0.9951**	0.9921**	0.9968**
		RB5	0.9830**	0.9905**	0.9992**
		CR	0.9785**	0.9901**	0.9958**
	BR-PAC	CV	0.9851**	0.9702**	0.9760**
		AB110	0.9841**	0.9896**	0.9950**
		RB5	0.9860**	0.9814**	0.9956**
		CR	0.9954**	0.9880**	0.9871**

** Significance level 1%