

Adsorption Equilibrium Study Of Dyestuff from Petroleum Industry Effluent Using the Biomass and Activated Carbon Of The Prop Root Of *Rhizophora Mangleplamt*

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ABSTRACT : The comparative equilibrium adsorption study of three different types of dyestuff effluent on the biomass and activated carbon prepared from wastes of rhizophora mangle root has been carried out as a function of initial concentration, contact time and pH variations. The sorption processes which were examined by means of Freundlich and Langmuir models revealed the effectiveness of both BRR and ACRR adsorbents in uptaking the dyes investigated by the level of agreement of the adsorption constants. Acidic and disperse dyes show higher adsorption at higher pH whereas basic dyes showed higher adsorption at lower pH. The binding capacity experiments revealed the following amounts of dyestuff bound per gram of adsorbent (mg/g): 2.67 BG4, 4.97 DB6 and 1.30 DB26 on biomass and 2.16 BG4, 3.73 DB6 and 6.78 DB26 on carbon. The separation factor (S_F), values obtained for the three dyes showed that the interactive processes on both adsorbents were a mixture of physisorption and chemisorption mechanisms. A single factor analysis of variance (ANOVA) showed that there is no significant difference in the sorption behaviour of the three dyes between the two adsorbents. The study also revealed that the rhizophora based adsorbents compared favourably with commercially available grades. The optimum conditions obtained in this investigation are relevant for the optimal design of a dyestuff effluent treatment column.

KEYWORDS: Dyestuff Adsorbent, Biomas, Activated Carbon, Effluent, Petroleum

I. INTRODUCTION

The products of the petroleum industry are major contributors to our present standard of living. The activities of the upstream and downstream petroleum industry can impact the environment and the greatest impact arises from the release of wastes into the environment in concentrations that are not naturally found. These wastes which are organic and inorganic in nature include hydrocarbons such as traces of crude oil, solids contaminated with hydrocarbons such as heavy metals and a wide variety of chemicals including dye-stuff. Dyes are coloured substances that can be used to produce a significant degree of coloration when dispersed in or reacted with other materials. The primary use for dyes is textile coloration, although substantial quantities are consumed for coloring such diverse materials as leather, paper, Plastics, petroleum products and food (James, 1962). In the petroleum industry, solvent dyes and azo dyes are used to colour or "mark" petroleum products like gasoline, diesel, kerosene, and lubricants etc. solvent dyes are economical, easy to use, have high and low flash point and are stable. They are designed to provide an outstanding easy brand or grade identification, leak detection and fraud detection in some countries. Dyes are also used as traces to identify poor producing zones of a dual-completed well. Azo dyes can give about 22 aromatic amines as their degradation products which may be carcinogenic. This means that they constitute a health risk. Although environmental authorities have regulated industrial discharges for many years, considerable quantities of azo dyes may have accumulated in the environment as a result of refinery effluent discharged in Nigeria. Unless this colour is removed by chemical or physical means, it may lead to pollution of water. The presence of dyes in the effluent impart high biochemical Oxygen demand (BOD) load to the liquid waste.

When dissolved oxygen reduces below a certain level, the aquatic life is affected adversely. This is because strong colour could result in high turbidity leading to reduction in light penetration, thus, affecting the growth of animal and plant life in the water. Studies by Crips and Bumpus (1990) revealed that dry biomass of marine plants can decolorize certain pigments and dyes in water. This actually informed the choice of the biomass of root of *Rhizophora mangle* plant as bio-adsorbent for the removal of dyes used to colour petroleum products in this study. Various methods used for the treatment of colour effluent are coagulation, flocculation and precipitation (Cooper, 1993), adsorption (Yeh and Thomas 1995), biological treatments (Laszlo, 1994) and membrane technology (Churchley, 1994). Out of these methods, adsorption at solid/liquid interface is one of the most economical and effective treatment methods for removal of dyes and has an edge over other methods due to its sludge-free clean operation. This actually informed the choice of the biomass and activated carbon of the *rhizophora mangle* plant as a low-cost land biodegradable adsorbent used for the treatment of coloured effluent by adsorption technique in this investigation. This paper presents the adsorption equilibrium of dyes as a function of initial concentration, contact time and pH, conducted at laboratory scale using synthetic dye waste water of acidic, basic and disperse dyes. The effect of dye structure on adsorption capacity is also discussed.

II. EXPERIMENTAL

2.1 Preparation of Biomass and Activated Carbon of *Rhizophora* root

The detailed experimental procedure for sample preparation and activation has been published elsewhere (Horsfall and Abia 2003, Jadhav and Vanjara, 2004). The bark of the *rhizophora* root was air dried for 5 days and then oven dried at 90°C for 24 hours to constant weight then ground and screened to 2.36mm size with Tyler screen to obtain granules of biomass. 500 grams of the finely divided granules of biomass was soaked in excess 0.3M HNO₃ for 4hrs to remove any metals and soluble biomolecules followed by washing thoroughly with deionized water until a pH of 7 was attained and then air dried. This air dried Biomass was then washed with deionized water and centrifuged at 3000 xg for five minutes using a portable refrigerated test tube centrifuge model Pr-2. The supernatant obtained was discarded whereas the biomass was collected and spread on filter paper for air drying and it was ready for use as adsorbent. The activated carbon was prepared from the biomass of *rhizophora* root by incinerating the biomass in an iron tubing of 30mm diameter using the furnace carbolite equipment (GallenKamp model OV-160 England). The tubing was heated in an oxygen deficient atmosphere for 2hours and at 500°C. This was to eliminate most of the volatile matter in the biomass. The carbon was then physically activated by partial gasification in limited supply of air using CO₂ gas as the gasification agent at 900°C. This was to develop the porosity and the surface area (Wauquier, 1995). The activated carbon was then stored in stoppered bottle after sieving to particle size of 2.36mm through the appropriate mesh tyler screen. The biomass of *rhizophora* root (BRR) and the activated carbon of *rhizophora* root (ACRR) were the two adsorbents used in this study.

2.2 CHARACTERIZATION OF THE BRR AND ACRR ADSORBENTS

The adsorbent used in this study were characterized through FTIR spectroscopy to ascertain some of the important functional groups responsible for their behaviour during the adsorption process using the SHIMADZU I. R. PRESTIGE-21 (200VCE) model. The samples were prepared in KBr pellet. The porosity of the adsorbents was determined using the Pore- 200 manually operated Gas porosimeter.

The analysis and characterization of both BRR and ACRR adsorbents is given in table 1.

Table 1: Analysis and characterization of BRR and ACRR

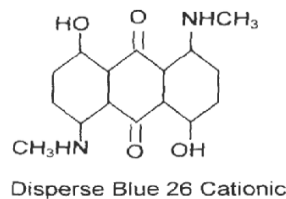
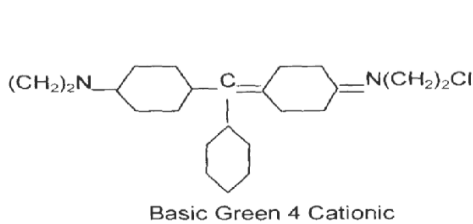
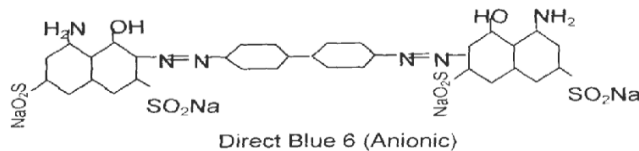
	BRR	ACRR
Apparent Density (g/m ³)	0.32	0.37
Particle size (mm)	2.36	2.36
Porosity (%)	17.90	19.62
FTIR Analysis		
Frequency (cm⁻¹)	Groups	
At 3400 in BRR	-C-H Stretching from CH ₂ groups	
At 1600 in BRR	C=O Stretching from – COOH	
At 3300 in BRR	-OH stretching from – COOH	
At 1700 in ACRR	Normal Carbonyl Groups	
At 1565 in ACRR	Conjugated hydrogen bonded carbonyl groups	

2.3 EXPERIMENTAL PROCEDURE

The details of the batch experimental procedure to determine dye stuff binding on biomass and activated carbon as a function of initial concentration, contact time and pH were essentially the same as those described elsewhere (Jadhav and Vanjara, 2004; Gardea-Torresdey et al 1998; Horsfall and Spiff, 2005) but which were suitably modified and adapted. Three types of dyestuff were used in all the experiments i.e. Acidic (DB6), Basic (BG4) and Disperse (DB26). The details of dyes used are given in table 2. The concentration of the dye in each solution was determined using a spectrophotometer with a glass cell of 1.0cm path length. All measurements were made at the wavelength corresponding to maximum absorbance (γ_{max}) of each dye. For adsorption experiments, a constant mass of 0.5g of each of the adsorbents was in the different experiments, added to an Erlenmeyer flask containing 50ml of dye solution. The system was equilibrated for a time period of 6 hours in a flask shaker. The time period of 6 hours was sufficient for equilibration. Residual dye concentrations at equilibrium were then determined spectrophotometrically. All the equilibrium studies were carried out at the natural pH of the dye solutions used: DB6-7.2; BG4-4.0; DB26-6.5.

Table 2: Details of Dyes Used

C.1.Name of Dyes	C.1 No	Molecular weight	Ionic nature	λ_{max} (nm)
Direct Blue 6 (DB6)	22610	932.20	Anionic	585.0
Basic Green 4 (BG4)	42000	927.02	Cationic	617.5
Disperse Blue 26 (DB26)	63305	310.39	Cationic	570.0



2.4 DATA ANALYSIS

The amount of dyestuff sorbed by both biomass and activated carbon of *rhizophora* root during the series of batch investigations was determined using a mass balance equation (Chu and Hashim, 2001) expressed as in eq. (1).

$$q_e = \frac{v}{m}(c_o - c_e) \dots\dots\dots (1)$$

Where q_e = Concentration of the sorbate on the sorbent (mg/g) at equilibrium

C_e = Concentration of sorbate in solution (mg/l) at equilibrium

C_o = Initial sorbate concentration in solution (mg/l)

M = Mass of sorbent used (g)

V=Volume of initial dyestuff solution used (L)

The percentage of adsorbate sorbed on the adsorbent is calculated using the equation:

$$\% \text{ adsorbed} = \frac{C_o - C_e}{C_o} \times 100 \dots\dots\dots($$

2)

2.4.1. LANGMUIR AND FREUNDLICH MODELS:

Sorption equilibrium provides fundamental physicochemical data for evaluating the applicability of phytosorption processes as a unit operation usually described by isotherm models whose parameters express the surface properties and affinity of the sorbent at fixed conditions. Two models were used to fit the experimental data, the Langmuir and Freundlich models. The Langmuir equation is chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface and expressed by

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \dots\dots\dots$$

(3)

Where:

K_L (md^3/g) is a constant related to the adsorption energy
 q_{\max} (mg/g) is the maximum sorption upon complete saturation of the adsorbent surface.

The linearized form of the above equation (3) after rearrangement is given as

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \dots\dots\dots(4$$

)

The experimental data are fitted into equation (4) for linearization by plotting C_e/q_e against C_e .

The Freundlich model was chosen to estimate the adsorption intensity of the sorbate 1Thards the sorbent and is represented in equation (5)

$$q_e = K_F C_e^{\frac{1}{n}} \dots\dots\dots($$

5)

Where

- q_e = The amount adsorbed per unit mass of adsorbent at equilibrium
- $\frac{1}{n}$ = Adsorption intensity
- C_e = Concentration of sorbate in solution at equilibrium
- K_F = Experimental Constant related to the sorption energy

The value of n indicates the affinity of the sorbent towards the adsorbent. Equation (5) conveniently used in linear form by taking logarithm of both sides as

$$\ln q_e = \ln K_F + \frac{1}{n} C_e \dots\dots\dots($$

6)

A plot of $\ln C_e$ against $\ln q_e$ in equation (6) yielding a straight line indicates the confirmation of the Freundlich adsorption isotherm.

ANALYSIS OF VARIANCE

Due to the bias resulting from experimental errors, the internal structures not accessible at first glance of the amount adsorbed (q_e values) for the different adsorbates in the various tables of experimental results were determined by single factor analysis of variance (ANOVA). This helps to describe the relationship between the two adsorbents (BRR and ACRR) to adsorb the different contaminants.

SEPARATION FACTOR

The shape of the Langmuir isotherm can be used to predict whether a sorption system is favourable or unfavourable in a batch adsorption process (Poots et al 1978). Accordingly, the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant called the equilibrium parameter or separation factor, SF which is defined by the following relationship.

$$S_F = \frac{1}{1 + K_L C_o}$$

...(7)

Where

- SF = Dimensionless Separation Factor
- C_o = Initial Adsorbate Concentration (mg/l)
- K_L = Langmuir Constant related to the apparent energy (dm³/mg)

The parameter, SF indicates the shape of the isotherm and nature of the sorption process as given below:

If S_F > 1, this implies unfavourable isotherm (there is an unfavourable interaction between adsorbate and adsorbent and therefore, adsorbate may not be possible) If S_F = 1, this implies linear isotherm (there is a linear relation between adsorbate and adsorbent interaction and the possible interactive process is a mixture of physisorption and chemisorption mechanism. When 0 < S_F < 1, this implies favourable isotherm (there is a favourable interaction between sorbate and sorbent, and the predominant mechanism is physisorption).

If SF=0, this implies irreversible isotherm (there is an indefinite stoking between sorbate and sorbent and the predominant mechanism is chemisorption).

III. RESULTS AND DISCUSSION

3.1 Characterizations of the Biomass and Activated Carbon Adsorbents

The adsorbents used in this study were characterized to ascertain some of the important function groups, porosity, apparent density and particle size using appropriate instrumentation as described in section 2.2. Table 1 shows the results for the characterization of BRR and ACRR. The FTIR analysis carried out on both adsorbents confirmed the presence of some important functional groups by correlating their known wavelength or wave-number values with the actual peaks in the respective infrared spectral (Fig1 and 2). The reference material used for interpreting the spectral is (David, 1989).

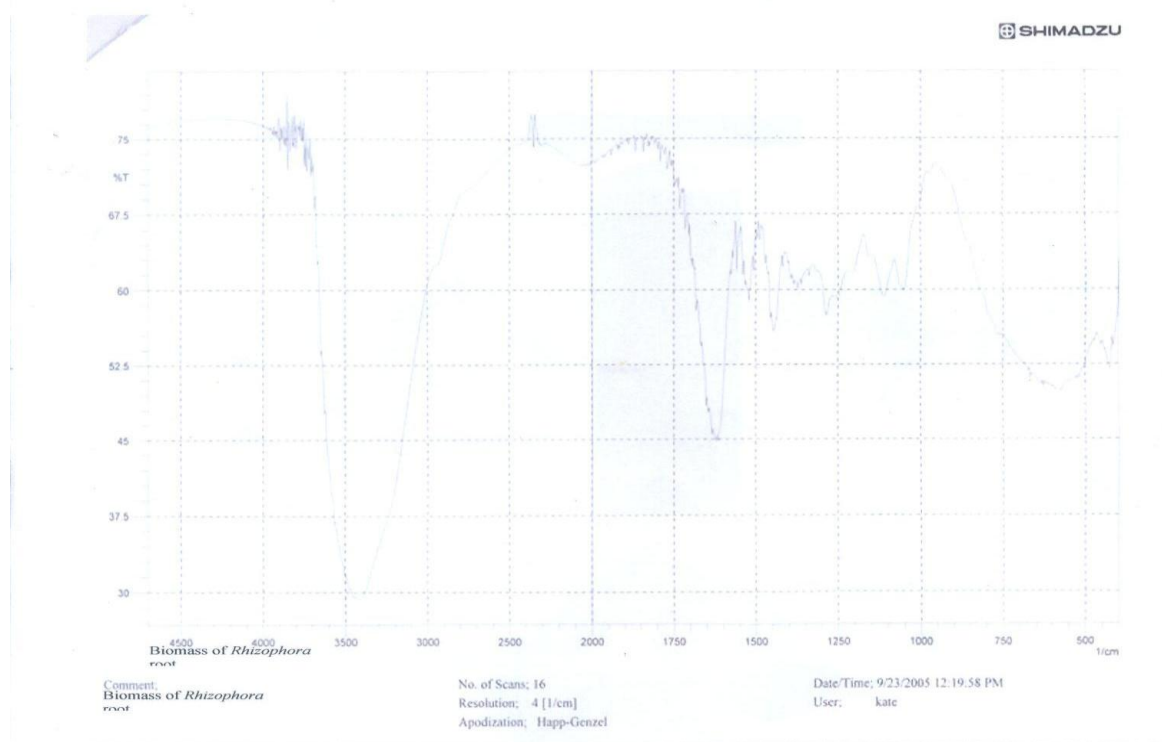


Figure 1: The FTIR Spectrum of Biomass of Rhizophora Root

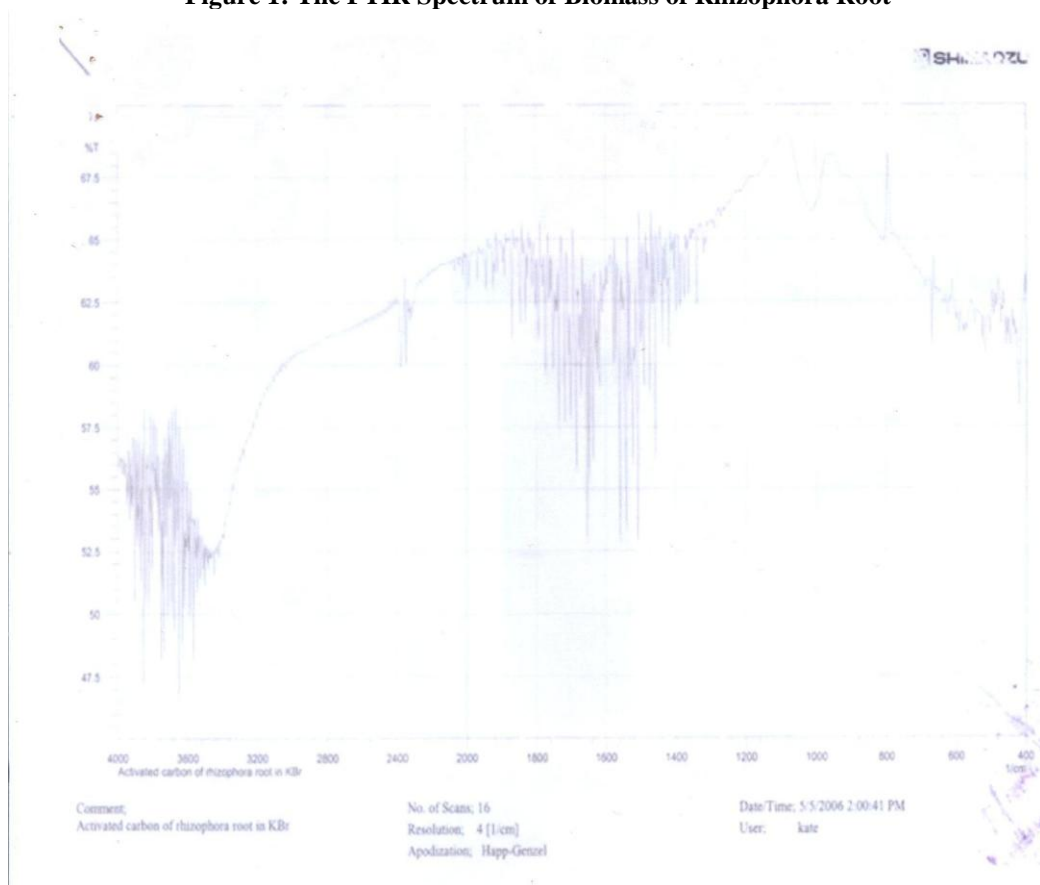


Figure 2: The FTIR Spectrum of Activated Carbon of Rhizophora Root in KBr pellet

EQUILIBRIUM ADSORPTION STUDIES

Results of the adsorption of dye stuff on the adsorbents as function of concentration and pH are shown in figures 3-8.

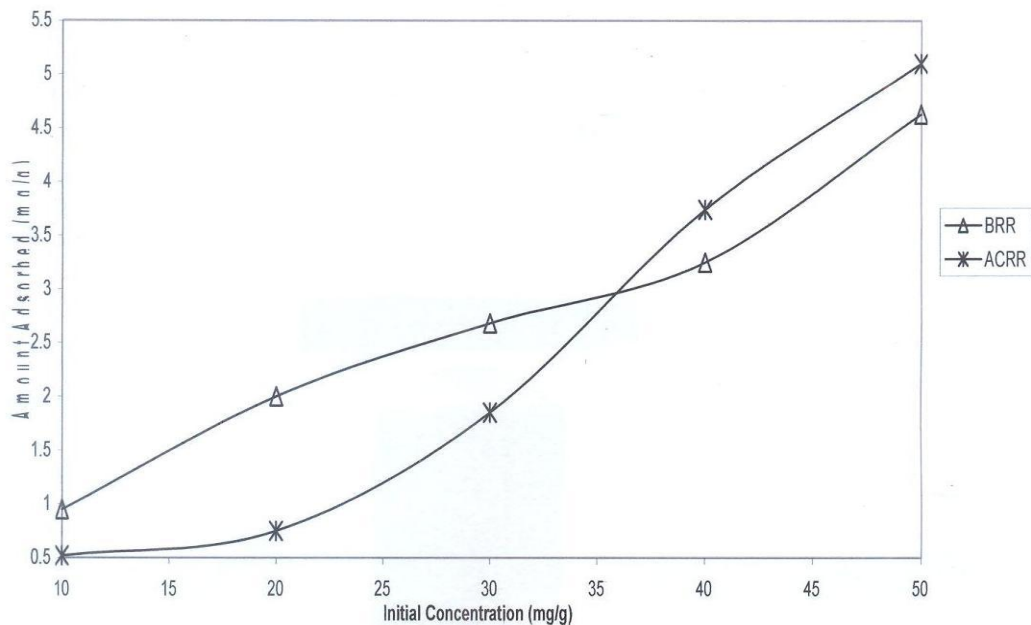


Figure 3: Comparative plots of Effect of Concentration on the adsorption of DB26 on ACRR using pH Values

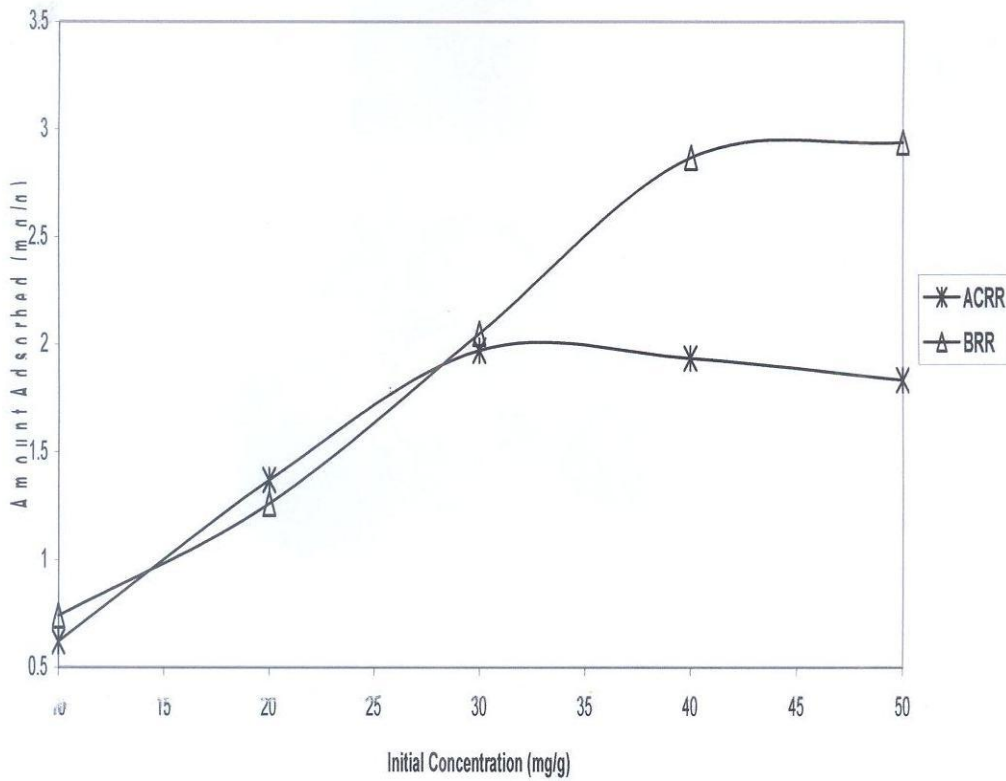


Figure 4: Comparative plots of Effect of Concentration on the adsorption of BG4 on ACRR and BRR using pH Values

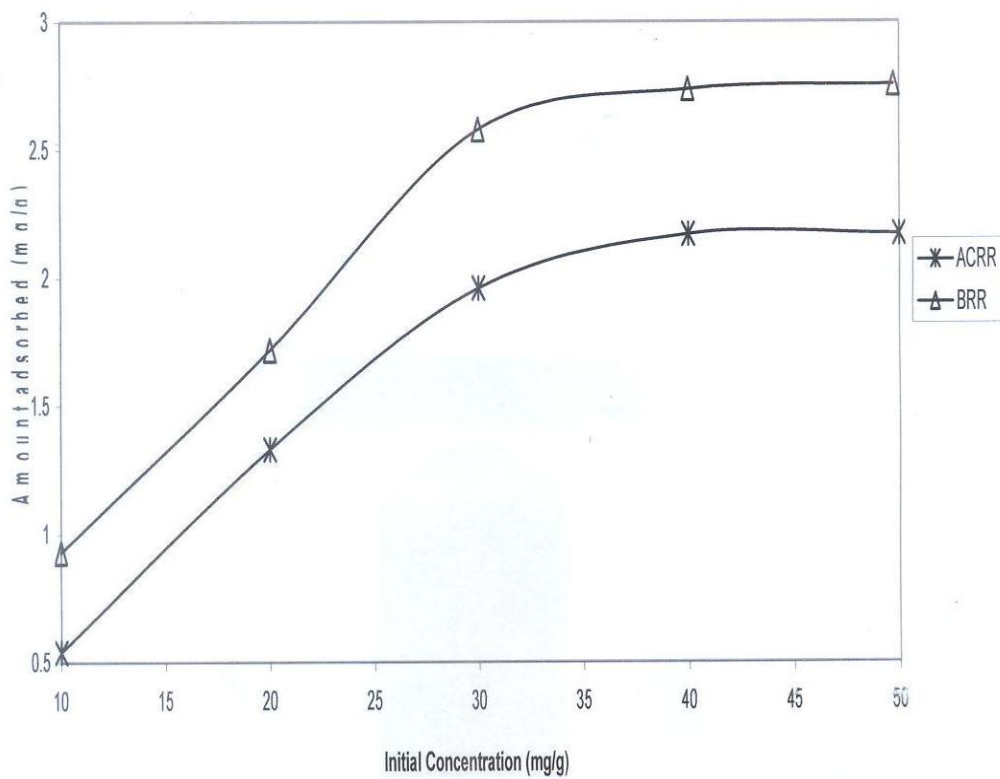


Figure 5: Comparative plots of Effect of Concentration on the adsorption of DB6 on ACRR and BRR using pH Values

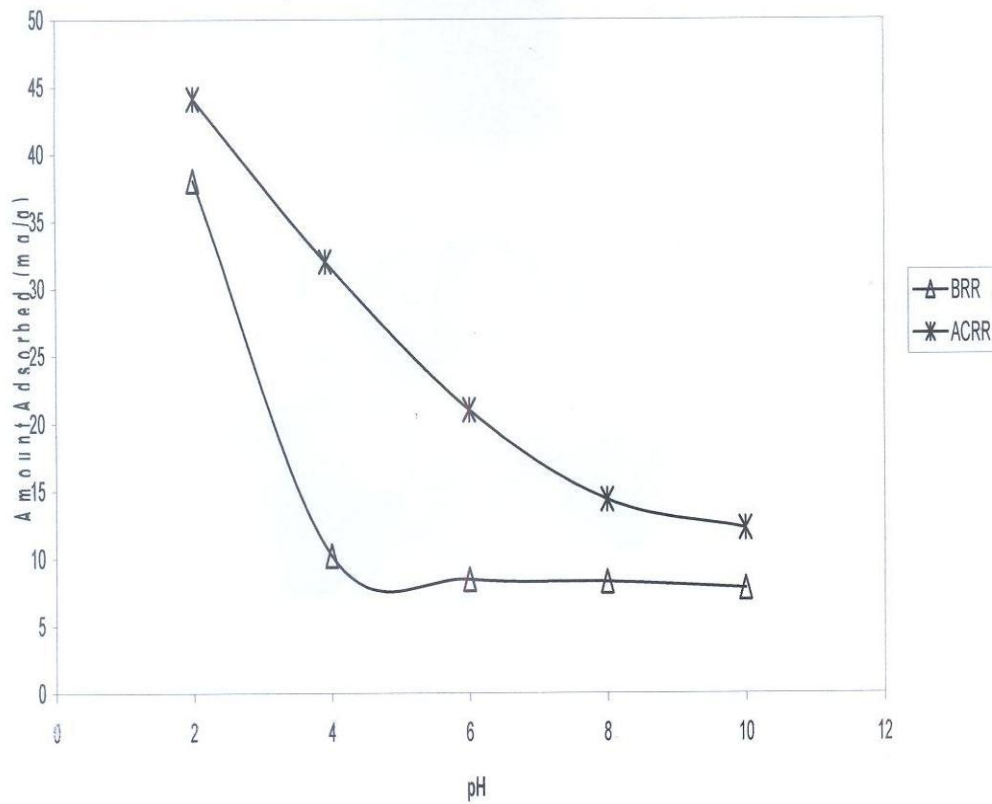


Figure 6: Comparative plots of Effect of pH on the adsorption of DB6 on BRR using pH Values

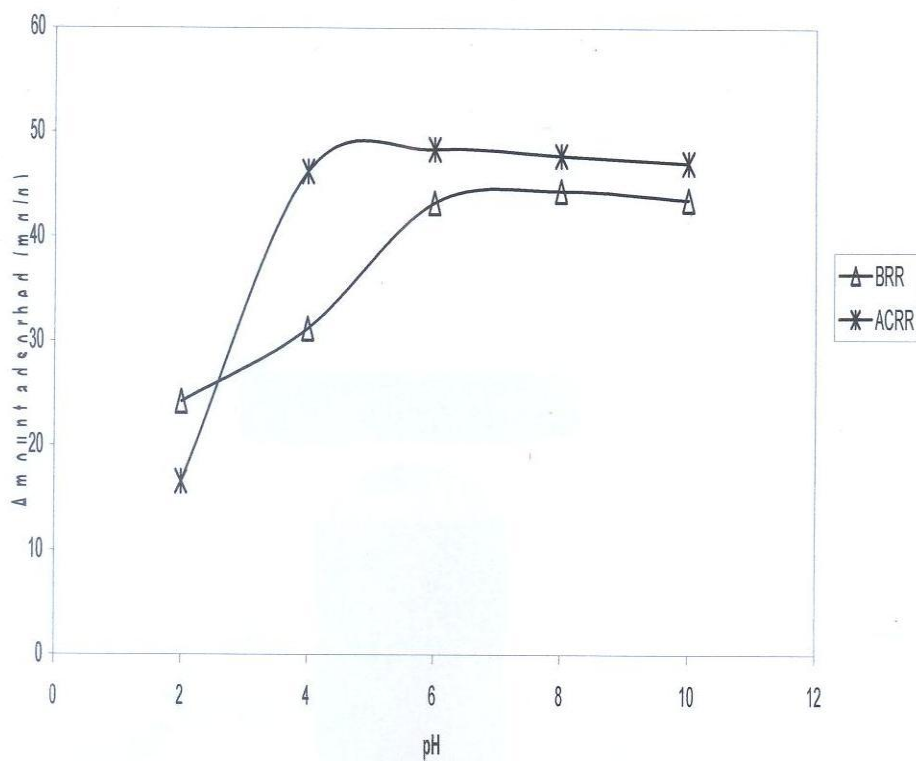


Figure 7: Comparative plots of Effect of pH on the adsorption of BG4 on ACRR and BRR using pH Values

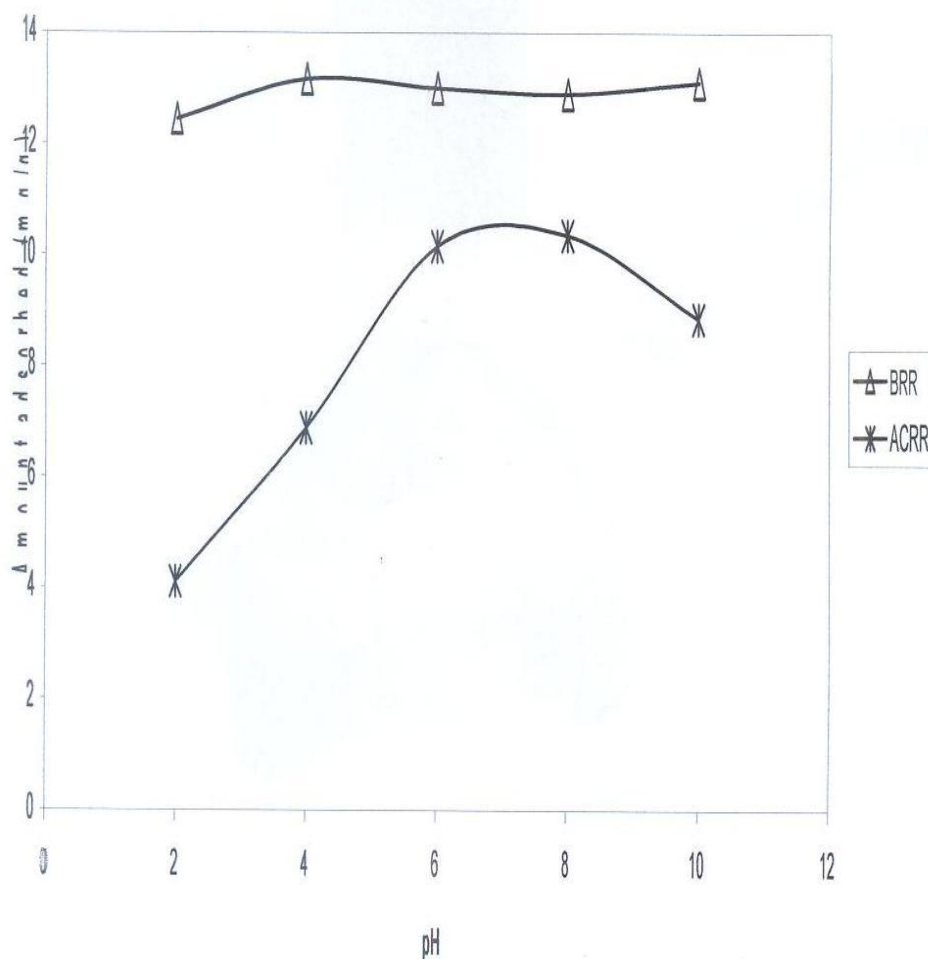


Figure 8: Comparative plots of Effect of pH on the adsorption of DB26 on ACRR and BRR using pH Values

EQUILIBRIUM ADSORPTION STUDIES

Results of the adsorption of dye stuff on the adsorbents as a function of concentration and pH are shown in figure 9-21. The results show that the amount of cationic (BG4) and anionic (DB6) dyes adsorbed increased with increase in concentration of dye until saturation occurred. It was also observed that the adsorption of dispersed dyes (DB26) increased with increase in concentration and no saturation was observed in the concentration range studied. This is an indication that under the prevailing experimental conditions, there was no formation of complete monolayer of DB26 molecules covering the surface of the adsorbent.

The biomass (BRR) contains cellulose which in aqueous solution exhibits negatively charged species (Khattri and Singla, 1988). The cationic dyes (DB26, BG4) in aqueous solution adsorb on the surface of negatively charged biomass through electrostatic interaction. The activation of biomass carbon at 900°C exhibits amphoteric properties (Faust, 1992) which showed lower level of adsorption of cationic dyes. Dispersed dyes have very low solubility in aqueous solution (Jones, 1984). Therefore the adsorption of DB26 on the surface of the biomass and carbon might have occurred through physical interaction, i.e. hydrophobic interaction with the hydrophobic part of the cellulose in the biomass. In the case of activated carbon, the presence of surface carbonyl group enhanced adsorption of aromatic compounds with the formation of the donor-acceptor complex involving the π electrons of benzene ring with the partial positive charge on the adsorption of low soluble hydrophobic species.

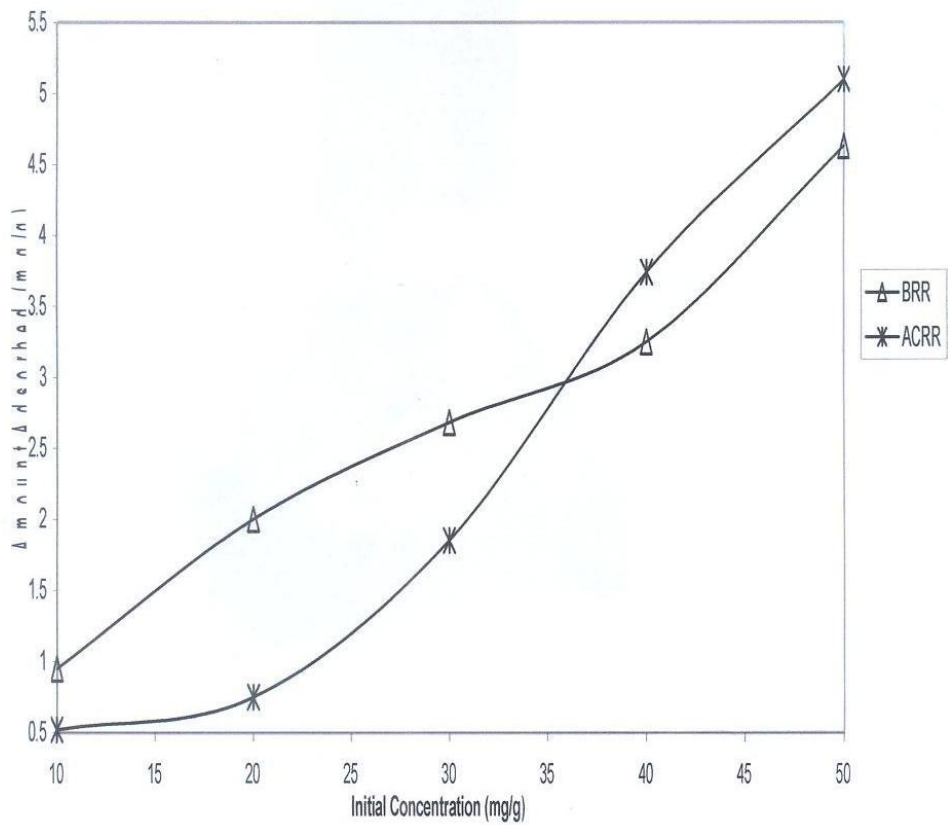


Figure 9: Comparative plots of Effect of Concentration on the DB26 on ACRR using pH Values

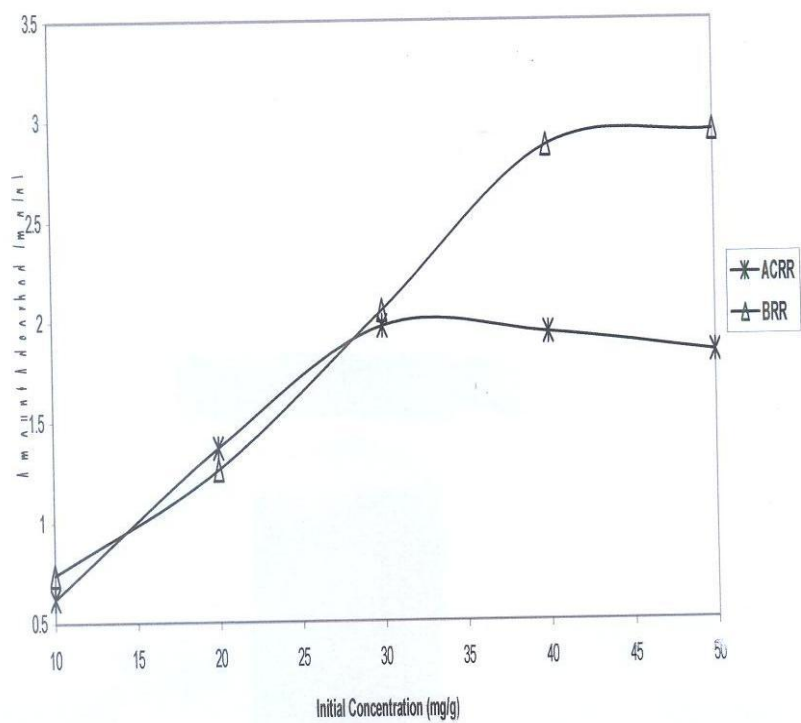


Figure 10: Comparative plots of Effect of Concentration on the adsorption of BG4 on ACRR and BRR using pH Values

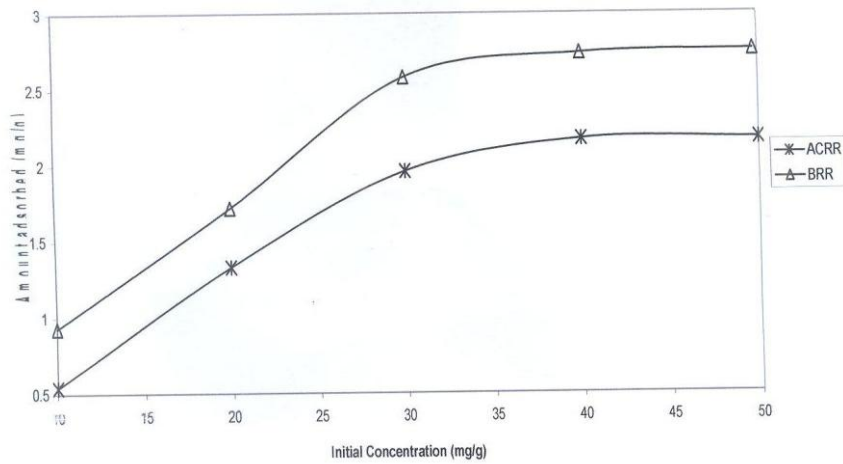


Figure 11: Comparative plots of Effect of Concentration on the adsorption of DB6 on ACRR and BRR using pH Values

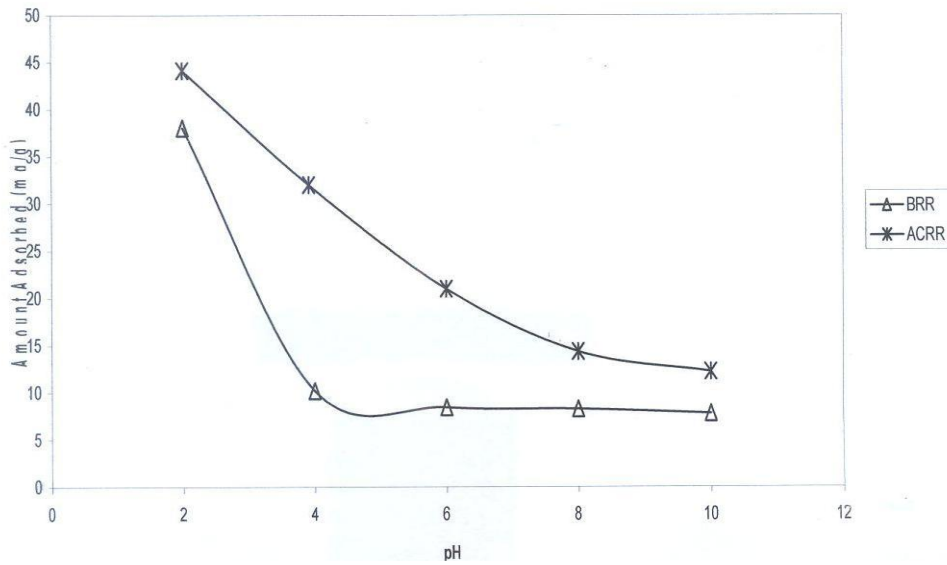


Figure 12: Comparative plots of Effect of pH on the adsorption of DB6 on BRR using pH Values

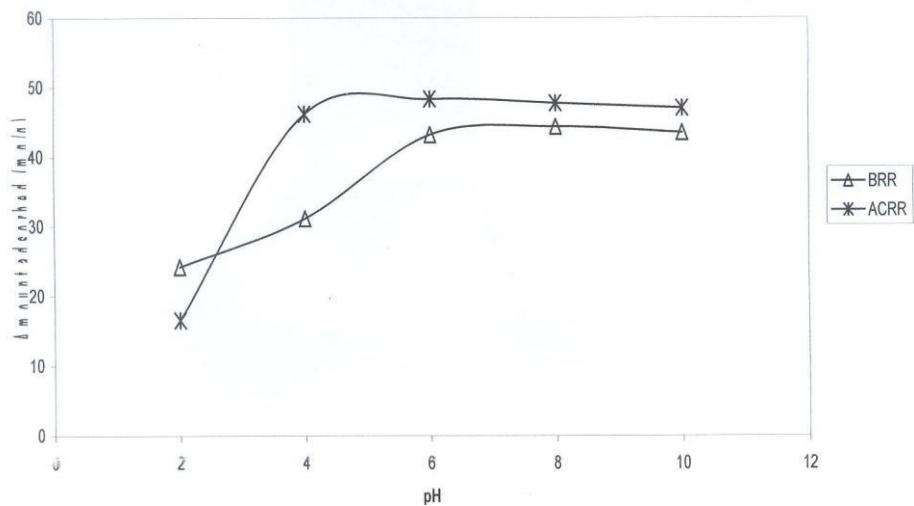


Figure 13: Comparative plots of Effect of pH on the adsorption of BG4 on ACRR and BRR using pH

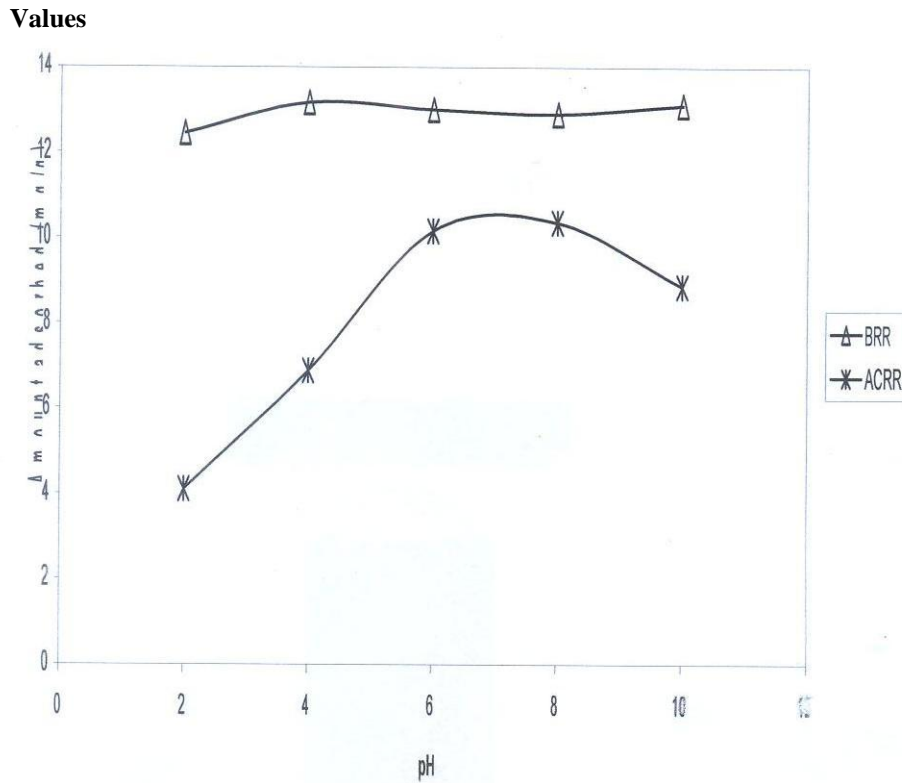


Figure 14: Comparative plots of Effect of pH on the adsorption of DB26 on ACRR and BRR using pH Values

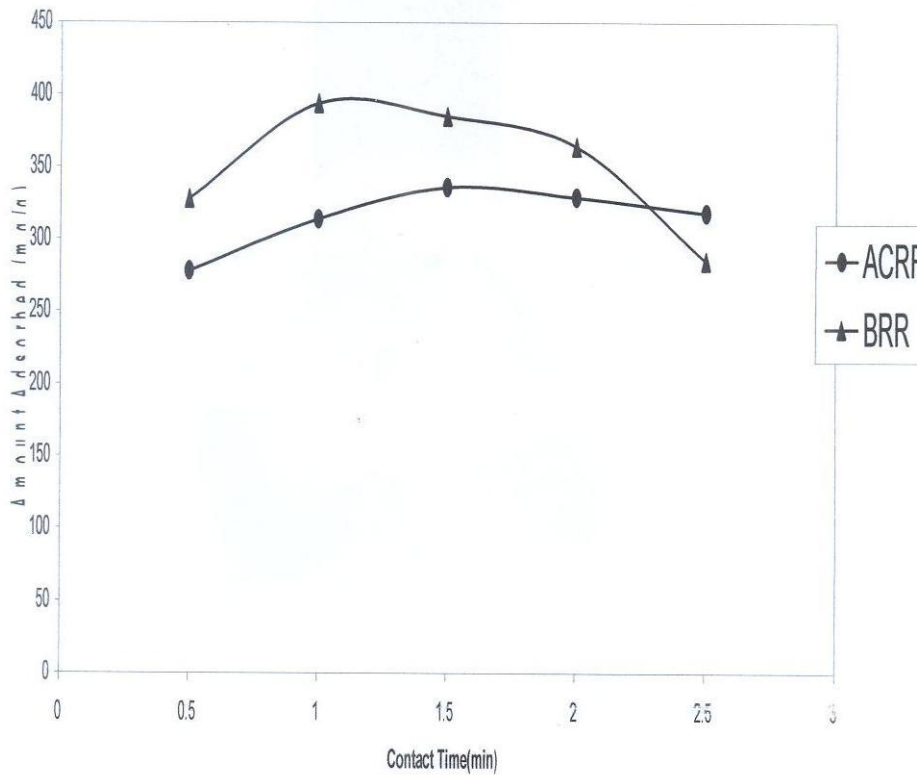


Figure 15: Comparative plots of Effect of Contact time on the adsorption of DB6 on ACRR and BRR using pH Values

The adsorption of the three dyes DB6, BG4 and DB26 on the two adsorbents (BRR and ACRR) was tested by using the Freundlich and Langmuir models (figs 9-21)

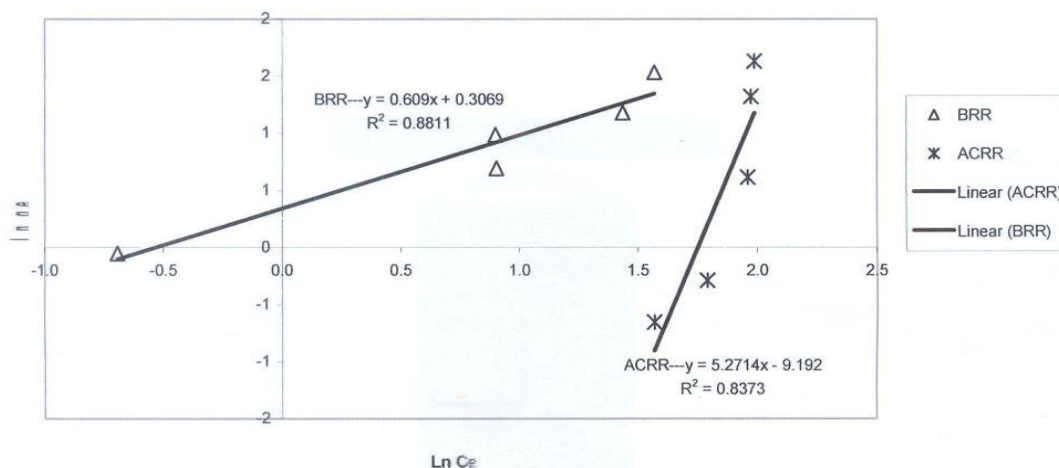


Figure 16: Plots of Freundlich Model for DB26

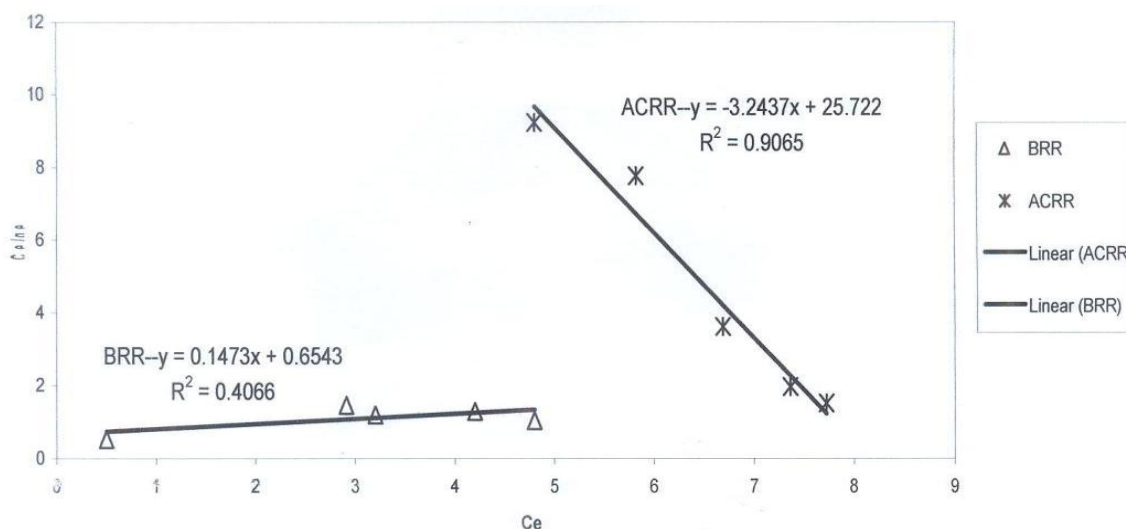


Figure 17: Plots of Langmuir Model for DB26

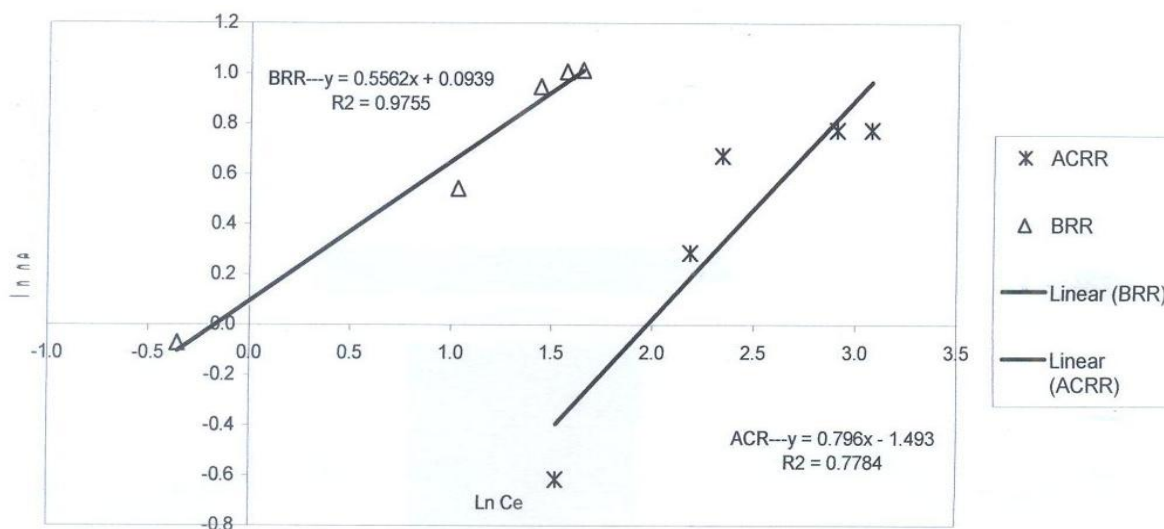


Figure 18: Plots of Freundlich Model for DB6

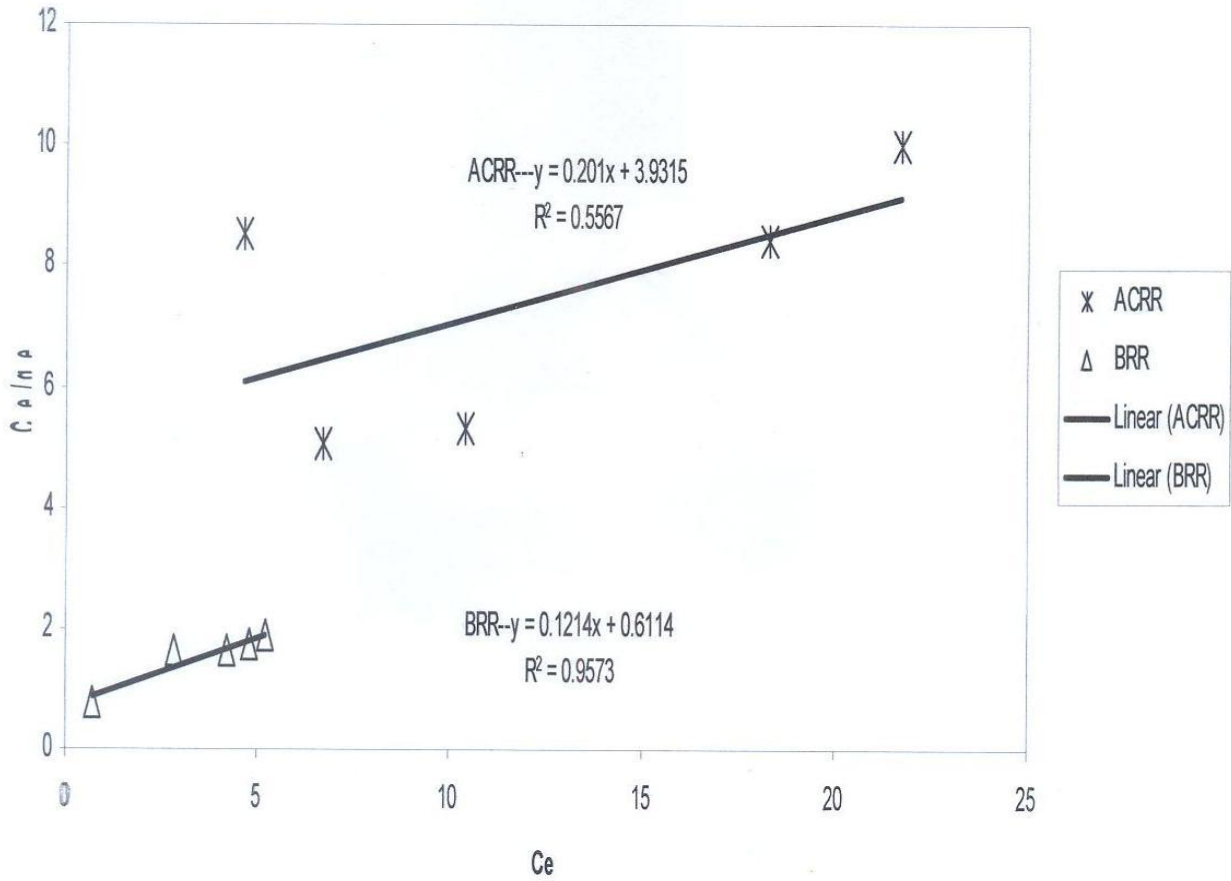


Figure 19: Plots of Langmuir Model for DB6

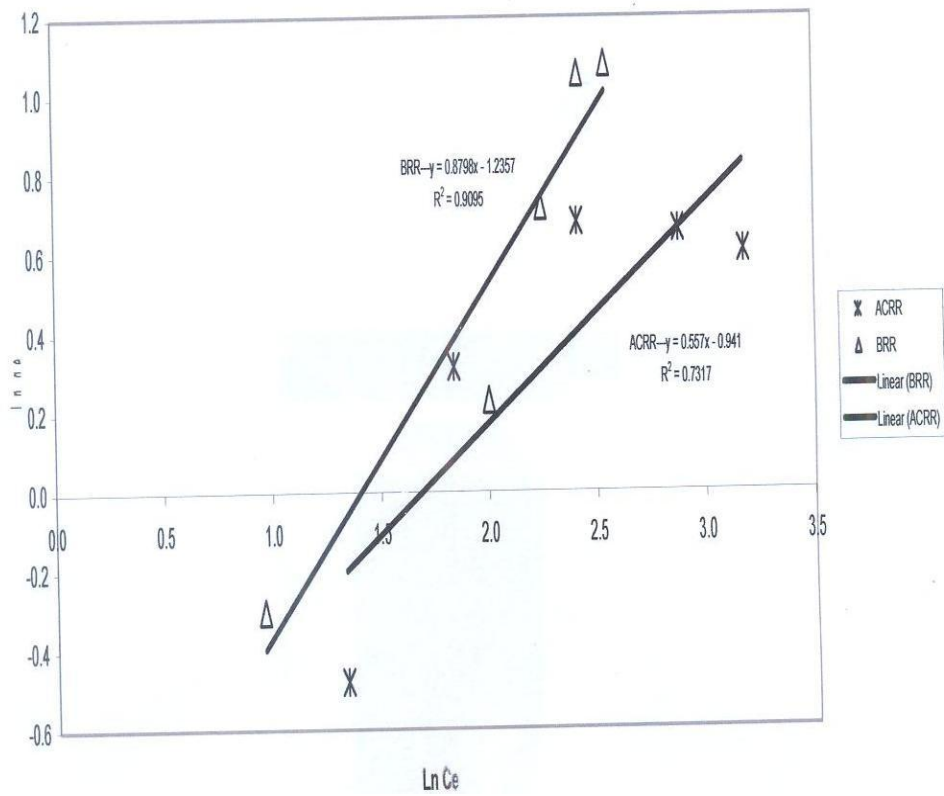


Figure 20: Plots of Freundlich Model for BG4

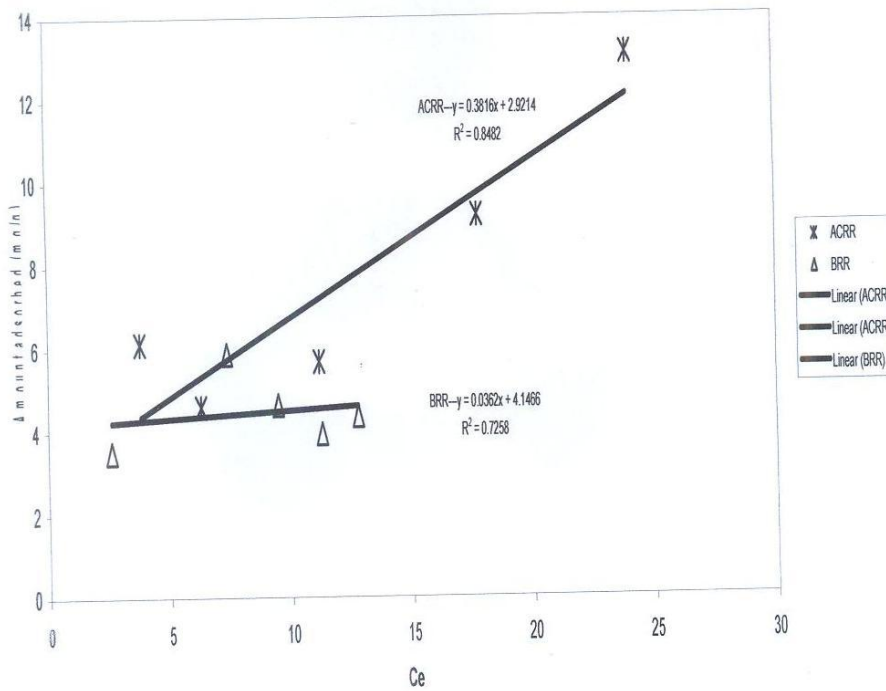


Figure 21: Plots of Langmuir Model for BG4

The various Freundlich and Langmuir constants for all the adsorbate-adsorbent systems calculated are shown in table 4.

TABLE 4: Freundlich and Langmuir Constants for the various Adsorbent/Adsorbate systems showing the R_L^2 , R_F^2 , K_L , K_F , q_{max} and n values from the isotherms. (The values given are average for different concentration)

Adsorbate	Adsorbent	K_F (mg/g)	K_L (dm ³ /g)	q_{max} (mg/g)	n	R_F^2	R_L^2
BG ₄	ACRR	0.29063	1.30	2.162	1.936	0.9095	0.0258
	BRR	0.39024	1.36	2.6205	1.79533	0.7317	0.8482
DB ₆	ACRR	0.1984	29.80	3.237	1.79791	0.9755	0.9573
	BRR	0.22440	25.11	4.9751	1.25628	0.7784	0.2567
DB ₂₆	ACRR	0.035	22.51	6.78887	1.64204	0.8811	0.4066
	BRR	0.100102	12.61	1.30829	0.18970	0.8373	0.9065

These values are similar to those obtained by (Jadhav and Vanjara, 2004)

The results for the pH dependence study as shown in shown in figs 8, 9 and 10, revealed that while the adsorption of DB6 and BG4 on both adsorbents change with change in pH of the solution, the adsorption of DB26 on the biomass (BRR) remained fairly constant with changes in pH. However, the adsorption of DB26 on ACRR had shown a strong dependence on pH of the solution (fig 11). DB6 showed higher adsorption levels at lower pH whereas BG4 showed higher adsorption levels at higher pH. This is because with decrease in pH the surface of the adsorbents got protonated. The negatively charged DB6 therefore, showed greater adsorption at lower pH because of positive-negative electrostatic interaction. Positively charged BG4 had lower adsorption at lower pH due to repulsion between positively charged adsorbents and positively charged adsorbate. Adsorption of DB26 on the biomass was not much affected by charge in pH suggesting that the interaction might be hydrophobic in nature. The average values of both Freundlich and Langmuir constants for the various adsorbent dye systems are shown in table 4. The optimum conditions for the adsorption dye stuff on BRR and ACRR based on the experimental results are shown in table 5.

Table 5: Optimum conditions for the adsorption of Crude Oil, Heavy Metals, and Dyes on BRR and ACRR.

Parameters	Pollutants	Adsorbents	
		ACRR	BRR
Heavy Metals			
Temperature (°C)	Ni	70	40
	Cd	70	40
	Pb	70	40
Contact Time (min)	Ni	30	15
	Cd	30	15
	Pb	45	30
pH	Ni	7	5
	Cd	5	5
	Pb	7	6
Crude Oil			
		ACRR	BRR
Concentration (ppm)		1600	2000
Contact time (min)		2	2
Temperature (°C)		38	30
Dyes			
		ACRR	BRR
Concentration (ppm)	Direct Blue 6 (DB6)	2	2
	Basic Green 4 (BG4)	5	6
	Disperse blue 26 (DB26)	5	Adsorption constant with pH change
Contact time (min)	Direct Blue 6	1.5	1.0
pH	Direct Blue 6 (DB6)	2	2
	Basic Green 4 (BG4)	5	6
	Disperse Blue 26 (DB26)	5.5	Constant

SINGLE FACTOR ANALYSIS OF VARIANCE (ANOVA)

The summary of results of statistical analysis for the single factor ANOVA applying Microsoft excel is presented in table 6.

Table 6: Analysis of Variance (ANOVA) using the Langmuir Plot values of q_e for the different Adsorbent/Adsorbate Systems Applying the Microsoft Excel at 95% confident level.

DYES: DISPERSED BLUE 26 (DB 26)

ANOVA: Single Factor

SUMMARY				
Groups	Count	Sum	Average	Variance
BRR	5	13.51	2.702	1.89507
ACRR	5	11.96	2.392	3.91117

ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.24025	1	0.24025	*0.0828	0.780908	5.317655
Within Groups	23.22496	8	2.90312			
Error	0.0044	7	6.29x10 ⁻⁴			
Total	23.46961	16				

DYES: BASIC GREEN (BG4)
ANOVA: Single Factor

SUMMARY				
Groups	Count	Sum	Average	Variance
BRR	5	9.86	1.972	0.94357
ACRR	5	7.73	1.546	0.32603

ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.45369	1	0.45369	*0.7147	0.422451	5.317655
Within Groups	5.0784	8	0.6348			
Error	0.00343	7	4.9x10 ⁻⁴			
Total	5.53552	16				

DYES: DIRECT BLUE 6 (DB6)
ANOVA: Single Factor

SUMMARY				
Groups	Count	Sum	Average	Variance
BRR	5	10.73	2.146	0.64458
ACRR	5	8.17	1.634	0.49253

ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.65536	1	0.65536	*1.1527	0.314303	5.317655
Within Groups	4.54844	8	0.568555			
Error	0.00335	7	4.79x10 ⁻⁴			
Total	5.20715	16				

*= There is no significant difference between the variables since F is less than F crit **=
There is a significant difference since F is greater than Fcrit

The single factor ANOVA results indicate that n significant difference was obtained for the adsorption of the three dye stuff (DB26, DB6) between the two adsorbents BRR and ACRR. This means that BRR can replace ACRR as adsorbent for any of the dyes investigated and statistically, the same level of efficiency can be achieved.

THE SEPARATION FACTORS (S_F)

To find a quantitative interpretation of the adsorbate/adsorbent interactions observed, the favourability or unfavourability of the adsorption system was predicted using an essential feature of the langmuir isotherm called the separation factor (S_F). Table 7 gives the calculated separation factors values for the different dry-adsorbent systems.

Table 7: The calculated separation factors (S_F) values of the different adsorbate/adsorbent systems

Adsorbate	Adsorbent	K_L (dm ³ /mg)	Values of S_F	Types of Isotherm	Predominant Adsorption Mechanism
Nil	ACRR	1.06x10 ⁻⁴	1	Linear	Physisorption and Chemisorption
	BRR	-4.6x10 ⁻³	1.198	Unfavourable	Adsorption may not be possible
Cd	ACRR	1.18x10 ⁻⁴	1	Linear	Physisorption and Chemisorption

Pb	BRR	6.51×10^{-3}	0.813	Favourable	Physisorption
	ACRR	1.68×10^{-3}	1	Linear	Physisorption and Chemisorption
BG4	BRR	8.6×10^{-4}	0.764	Favourable	Physisorption
	ACRR	1.3×10^{-3}	1	Linear	Physisorption and Chemisorption
DB6	BRR	1.36×10^{-3}	1	Linear	Physisorption and Chemisorption
	ACRR	2.98×10^{-4}	1	Linear	Physisorption and Chemisorption
DB26	BRR	2.51×10^{-4}	1	Linear	Physisorption and Chemisorption
	ACRR	2.25×10^4	1	Linear	Physisorption and Chemisorption
CRUDE OIL	BRR	1.26×10^{-4}	1	Linear	Physisorption and Chemisorption
	ACRR	3.2×10^{-3}	0.897	Favourable	Physisorption
	BRR	8.2×10^{-3}	0.772	Favourable	Physisorption

The interaction between each of the dyes and each of the adsorbents investigated appeared to be a linear relationship. The possible interactive process therefore might have been a mixture of physisorption and chemisorption mechanisms since the S_f values are unity, 1. The results obtained in this study were compared with those of Jadhav and Vanjara (2004), a commercial grade adsorbent. The comparison is shown in table 8.

Table 8: Comparing Freundlich Constants for Adsorption of dyes between Jadhav (2004) and Kinigoma, (2007).

Absorbate	Adsorbent	Jadhav & Vanjara (sawdust)			Kinigoma (bark of <i>Rhizophora</i> root)		
		K_F (mg/g)	n	R^2	K_F (mg/g)	n	R_F^2
DB ₆	BRR	0.131	0.941	0.982	0.224	1.256	0.778
	ACRR	2.530	2.599	0.947	0.198	1.797	0.975
BG ₄	BRR	0.015	0.621	0.945	0.390	1.795	0.731
	ACRR	3.842	2.045	0.879	0.290	1.936	0.909
DB26	BRR	0.375	1.295	0.968	0.100	0.189	0.837
	ACRR	0.410	1.458	0.811	0.035	1.642	0.881

The closeness in the values of Freundlich constants obtained in Kinigoma, 2008 and those of Jadhav and Vanjara, 2004, both using different plant based adsorbents, has that was no remarkable indication difference between the operational efficiency of the *rhizophora* based adsorbents and other established ones.

IV. CONCLUSIONS

- [1] The study has shown in comparative terms the effectiveness and efficiency of both biomass and activated carbon of the bark of *rhizophora* root as sorbent materials in uptaking dyestuff as petroleum industry effluent contaminants. This was validated by the level of agreement of the different adsorption constants and favourability factors.
- [2] The adsorption of BG4 and DB6 dyes on the biomass and activated carbon adsorbents and also the adsorption of DB26 on the carbon is influenced by change in pH of the solution, where as adsorption of DB26 on biomass is not affected by change in pH of solution.
- [3] A single factor analysis of variance (ANOVA) showed that there was no significant difference in the sorption behaviour of the three dyes on both adsorbents.
- [4] These novel adsorbents have been found to compared favourably with commercially available grades and can therefore serve as alternatives to the more expensive and imported conventional one.
- [5] The results obtained in this study are relevant for the optimal design of dye effluent treatment plant and also for the predication of model parameters of sorbate sorbent interactions.

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