



**Pelagia Research  
Library**

## **Pelagia Research Library**

Der Chemica Sinica, 2015, 6(12):41-54



**Pelagia Research  
Library**  
ISSN: 0976-8505  
CODEN (USA) CSHIA5

### **Kinetic and thermodynamic study of dye removal by carbonized eucalyptus bark and its surface derivatives**

**Ekta Khosla<sup>a</sup>, Satindar Kaur<sup>b</sup> and Pragnesh N. Dave<sup>\*c</sup>**

<sup>a</sup>Department of Chemistry, Hans Raj Mahila MahaVidyalaya, Jalandhar(Punjab), India

<sup>b</sup>Department of Food Sciences and Technology, Guru Nanak Dev University, Amritsar(Punjab), India

<sup>c</sup>Department of Chemistry, Krantiguru Shyamji Krishna Verma Kachchh University, Mundra Road, Bhuj(Gujarat), India

---

#### **ABSTRACT**

*Adsorption of basic dye on carbonized Eucalyptus bark and its surface derivatives has been investigated. Several experiments have been carried out by using batch adsorption technique. Basic violet 10(Rhodamine B) has been used as a model dye and the effects of process variables like effect of adsorbent dosage, pH, contact time, temperature; initial dye concentration has been evaluated. The adsorption of basic violet 10 was found to take place at  $pH > pHz_{pc}$  for all the adsorbents. Thermodynamic parameters like  $\Delta G^{\circ}$ ,  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  are determined and the processes were found to be entropy driven in nature. The study highlights the application of low cost carbons for the removal of dyes from aqueous medium by the ion exchange process. The kinetics followed was first order and Langmuir and Freundlich isotherm fitted the data well. Scanning electron microscopic analysis and Fourier transform infra red spectroscopy (FTIR) reveals a noticeable surface morphology change with electrostatic complexation after surfactant modification.*

**Key words:** Carbonized Eucalyptus bark, surfactant modification, kinetics, thermodynamics

---

#### **INTRODUCTION**

Sorption of pollutants from waste water is an age old process. Rapid growth and industrialization has led to increase the pollutants in the form of dyes, toxic heavy metals, organics, surfactants salts etc. Most of the industries liberate waste chemicals in outlet water stream. Dyes constitute a major class of pollutants as the presence of dyes in waste water is unpleasant and unhealthy as some dyes are toxic and even carcinogenic (Namasivayam et al.,2002). Colored water can affect ecosystem by penetration through hydrosphere. Textile industries use a huge volume of water and chemicals during wet processing stages and thus produces elaborate amount of effluent containing color. Dyes are apparent even at concentrations i.e. even below 1 ppm (Robinson et al.,2001). Most of the dyes are resistant to aerobic digestion and stable to heat, light and oxidizing agents (Sun et al., 2003). Several methods are in practice for dye removal from waste water. The common strategies involves flocculation and coagulation ( Judkins et al., 1978; Bhattacharya et al.,2006; Kang et al., 2007) membrane separation (Cheremisinoff., 2002; Al Bastaki., 2004; Petrinic et al., 2007) ion exchange(Eliassen et al.,1967; Crini., 2006; Ghobarkar et al.,1999) oxidation (Hempfling., 1997; Kim et al.,2004; Zhu et al.,2008) adsorption(Malik et al.,2007; Ali et al.,2007; Al-Degs et al.,2007) biosorption(Wong et al.,2004; Slokar et al.,1998; Mittal et al.,1996) irradiation (Rela et al.,2000) ultrasonication ( Suzuki et al., 2000) etc are the techniques in practice. Adsorption is simple, technically feasible and procedure of choice in batch and column method. The designing of batch reactor involves optimization of variables like time, temperature and nature of material used as adsorbent. In the last decade several low cost adsorbents like bottom ash and deoiled soya(Gupta et al.,2006) alunite (Ozacara et al.,2003) cotton waste (Mc Kay et al.,1981) tea waste ( Tamezuddin et al., 2009) peat (Mc Kay et al.,1981) maize cob( El Geunidi et al.,1992) soy meal hull (Arami et al.,2005) hazelnut shell (Ferro., 2007) orange and banana peel (Annadurai et al.,2002) grass waste (Hameed., 2009)

tree fern (Ho et al.,2005) orange peel (Ardejani et al., 2007) coir pith (Namasivayam et al.,2001) date stone (Mahmoodi et al.,2010) sunflower stalk (Sun et al.,1997) sewage sludge( Dave et al., 2011) eucalyptus bark (Morais et al.,1999; Dave et al., 2011) etc. have been used for the removal of color from synthetic waste water. The use of plant waste for color removal is beneficial because the materials are usually locally available, low cost, and are biodegradable. Many researchers have carbonized (Namasivayam et al., 2002) the plant material for deriving adsorbent with properties of activated carbon which is supposed to be best adsorbent. Due to its high cost and difficult regeneration of activated carbon adsorbent substitutes are being designed. In the present work Eucalyptus bark (EB) is carbonized and its efficiency is evaluated for the removal of a model dye Basic Violet 10 (BV-10). The Eucalyptus bark carbon (EBC) is treated with anionic, cationic and non ionic surfactant and evaluated for dye removing efficiency. We have studied the specific characterization of EBC, SDS-EBC (Sodium dodecyl sulfate modified EBC), CPC-EBC (Cetylpyridinium chloride modified EBC) and TX-EBC (Triton X-100 modified EBC) for the removal of BV-10. SDS, CPC and TX are anionic, cationic and non ionic surfactants respectively and are used as model surfactants belonging to different classes. Numerous parameters like effect of pH, temperature, contact time and initial dye concentration are evaluated and isotherm and kinetic models are investigated. This is assumed that after adsorption the carbon generated from biomass degrades naturally leaving behind a very small volume of sludge.

## MATERIALS AND METHODS

### 2.1 Materials

Basic violet 10 (Rhodamine B) a xanthene based cationic dye, C.I.45170 ( $C_{28}H_{31}ClN_2O_3$ ) was supplied by Thomas Baker company. Sodium hydroxide, hydrochloric acid, sodium dodecyl sulphate (SDS), cetylpyridinium chloride (CPC), triton X-100 (TX), sulphuric acid and sodium bicarbonate were of analytical grade and were used as received. The structure of Basic violet-10, SDS, CPC and TX-10 are given in Figure 1. BV-10 (Basic violet 10) is a fluorescent cationic dye used in textile dyeing because of its more rigid structure than other organic dyes. Due to its cationic structure, it can apply for anionic fabrics which contain negative charges such as polyester fibers, wool, silk, and acrylic fibers. The dye is brilliant and most fluorescent among other synthetic dyes.

### 2.2 Adsorbent Preparation

Eucalyptus bark (EB) was collected in autumn 2010 from adult trees from the Eucalyptus cloning centre in Philaur, Punjab, India. The collected bark was washed with distilled water several times to remove the dirt particles and water soluble materials. The bark was cut into chips. EB chips were carbonized (Preethi et al.,2006) with 98% sulphuric acid (20 g of EB chips were soaked in 50 mL of sulphuric acid for 48 h. The material was then washed thoroughly with water and dipped in 1000 mL of 1%  $NaHCO_3$  for 24 h followed by washing with distilled water till the wash was neutral and conductance was  $< 0.05$  mS with no evident color. The material was then completely dried in an oven at 353 K for 24 h. The dried EBC was then crushed, and sieved to eliminate fine particles ( $< 0.25$  mm). Finally, surfactants SDS, CPC and TX-100 modifications were carried out to get the surface derivatives. 5.0 g of EBC is mechanically stirred in 100 mL of  $2 \times 10^{-2}$  M SDS, 100 mL of  $10^{-3}$  M CPC and 100 mL of  $2 \times 10^{-2}$  M Triton X-100 for 3 hours at 303 K. It is assumed that the treatment given by surfactant below its critical micellar concentration (CMC) changes the surface behavior by forming monolayer of adsorbed surfactant on the surface. The modified EBC was filtered and washed with double distilled water thrice and the material was dried in hot air oven at 343 K for 24 h. FTIR Spectra of EBC and its surface derivatives was carried out to confirm the surface modifications using Perkin Elmer spectrophotometer. The pH of dye solutions and  $pH_{zpc}$  were determined by using pH meter by Toshvin (TMP-85). An auto arranging conductivity meter TCM+15, provided with temperature compensator made by Toshnival, India was used for determination of surfactant characteristics and nature of the filtrate of bark and its derivative washings. The weighing were carried out on a digital weighing balance of accuracy up to 0.1 mg by citizen Co. Shimadzu 2101 PC UV –Visible spectrophotometer was used for the determination of residual dye concentration in the medium. The sample was also characterized by X-ray diffractometry using an X'PERT PRO PANalytical with  $Cu-K_{\alpha}$  radiation.

### 3.0 Adsorption Studies

A stock solution of 500 ppm was prepared by dissolving required amount of BV-10 in distilled water and further dilutions were made to get the particular concentration of dye in batch experiment using distilled water. The series of experiments were conducted by placing 50 mL of dye solution in an Erlenmeyer flask and adding the required amount of adsorbent to that in water bath incubator shaker made by orbitech India. Ltd. The pH of different solutions was attuned with 0.1 N HCl and 0.1 N NaOH. After attainment of equilibrium the aqueous phase was analyzed for residual dye concentration using UV visible spectrophotometer. From the absorbance data  $q_e$  ( $mg \cdot g^{-1}$ ) was determined using equation 1.

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

Where  $C_0$  is initial dye concentration,  $C_e$  is final dye concentration and  $V$  is volume of dye in liters and  $W$  is mass of adsorbent in g. Duplicate experiments were performed to get concordant results and the average results were reported. The kinetics of dye removal was studied using 250 ppm BV-10 solution. The samples were withdrawn at regular intervals and residual concentration was analyzed after centrifugation using ultracentrifugation at 1000 rpm. The isotherms were studied by using 50 mL of dye solution within concentration range of 100 ppm to 250 ppm for EBC and surfactant modified EBC at 303 K, 313 K and 323 K. After the attainment of equilibrium the residual dye concentration was analyzed spectrophotometrically.

### 3.1 Statistical analysis

The statistical analysis of the data obtained for kinetics and isotherms was evaluated by using SPSS 17.0 software. The best fit on the model is estimated by calculating correlation coefficient  $R$ .  $n$  is number of pairs of data. This is assumed that if  $x$  and  $y$  have strong positive correlation then the value of  $R$  approaches to 1.000. The correlation coefficient greater than 0.95 is assumed to be good for the present set of data.

$$R = \frac{n \sum xy - (\sum x)(\sum y)}{\sqrt{n(\sum x^2) - (\sum x)^2} \sqrt{n(\sum y^2) - (\sum y)^2}}$$

Second parameter which is calculated to find the best fit of the model is standard error of the estimate (SEE). For a linear regression SEE is given by the following relationship

$$\sigma_{est} = \sqrt{\frac{\sum (Y - Y_{est})^2}{N}}$$

$Y$  is the actual value and  $Y_{est}$  is the estimated value of the parameter. SEE helps to make judgment about the size of standard error of estimate from scatter plot.

Third parameter measured for the significance is Residual sum of squares. It is sum of explained sum of squares and residual sum of squares. RSS is expressed as

$$RSS = \sum_{i=1}^n (Y_i - Y_{est})^2$$

RSS is the measure of amount of variance in data that is not explained by regression model.

The model is said to be fit in a better way only if  $R$  is high and higher than 0.95 and SEE and RSS is low.

## RESULTS AND DISCUSSION

### 4.1 Characterization of the adsorbent

Surface chemistry of the EBC such as specific surface area and pore volume were measured using nitrogen gas adsorption technique with micromeritics surface area analyzer with liquid nitrogen at 77 K. The acidity and basicity of the adsorbent were determined by the Boehm titration method (Bohem *et al.*, 1966; Fabish *et al.*, 1984) as reported elsewhere. The zero point charge of the activated EBC and derivatives was determined by solid addition technique (Srivastava *et al.*, 2011). Scanning electron micrograph of the adsorbent eucalyptus bark was carried out to find out the morphological characteristics of EBC and its derivatives. The characteristics of EBC are given in Table 1. The chemical analysis of Eucalyptus bark before carbonization suggests that cellulose, hemicelluloses and lignin are the main components (Khosla *et al.*, 2012). SEM of EBC and modifications reveal rough and porous surface texture with judicious changes upon treatment with surfactants as shown in Figure 2. The X-ray diffraction analysis of the EBC was carried out and shown in Figure 3, revealed the crystalline nature of the sample. The XRD spectra of adsorbents suggest that the coherence length is determined by using Debye-Scherrer equation

$$L = \frac{0.9\lambda}{\beta \cos \theta}$$

Where  $\lambda$  is wave length ( $1.5406 \text{ \AA}$  Cu-K $\alpha$ ),  $\theta$  is diffraction angle and is full width half maximum (FWHM). The coherence length is estimated from molecular size and is significantly larger than molecular size. The d-spacings are calculated and found that after carbonization the d-spacings decrease. The d-spacing of EB decreases from  $4.108 \text{ \AA}$  to  $3.0316 \text{ \AA}$ . FTIR spectra (Figure 4) revealed that the adsorbent mainly has cellulose as all the samples presented a band at  $3367\text{-}3370 \text{ cm}^{-1}$  due to O-H stretching and C-H stretching bands at  $2922\text{-}2924 \text{ cm}^{-1}$ . In surfactant modified EBC additional shoulder appeared at  $2851\text{-}2852 \text{ cm}^{-1}$ . The bands at  $1035\text{-}1038 \text{ cm}^{-1}$  suggests the presence of C-O stretching in cellulose. The bands at  $1610\text{-}1618 \text{ cm}^{-1}$  suggests the  $\beta$ -glycosidic linkages between sugar units of cellulose and the bands between  $1500\text{-}1530 \text{ cm}^{-1}$  reveals that aromatic ring vibrations are also existing (Owen *et al.*, 1989). The carbonization temperature was below 373 K thus the functional groups remained same but particle size and surface area changed as is evident from XRD and surface area analysis. Based on these results, it is suggested that the dehydration for developing micropores proceeds with increasing carbonization temperature. It was assumed that the pyranose ring ( $1200\text{-}1225 \text{ cm}^{-1}$  and  $1379\text{-}1431 \text{ cm}^{-1}$ ) is formed during dehydration at the primary carbonization step because these vibrational modes do not exist in the eucalyptus bark samples (Khosla *et al.*, 2012).

Table 1- Physicochemical properties of EBC

Surface area ( $\text{m}^2\text{g}^{-1}$ )	17.3242
Bulk density ( $\text{g mL}^{-1}$ )	0.3566
Pore volume ( $\text{cm}^3\text{g}^{-1}$ )	8.7
Pore size distribution (nm)	100-500
Zero point charge (pHpzc)	7.8
Total surface acidity ( $\text{mmol g}^{-1}$ )	0.613
Total surface basicity ( $\text{mmol g}^{-1}$ )	0.296
Loss on ignition (%)	92.0
Total moisture (%)	2.2

Table 2- Adsorption capacities of BV-10 on various adsorbents

Adsorbent	qm (mg/g)	Reference
Sugarcane dust	3.24	49
Fly ash	2.33	50
Iron chromium oxide (ICO)	2.98	51
Tamarind fruit shells activated carbon	3.94	52
Coir pith	2.56	53
Raw orange peel	3.23	54

Table 3- Freundlich and Langmuir parameters for adsorption of BV-10 over EBC and its derivatives at different temperatures

Temperature(K)	KF	n	$Q_s(\text{mol/g})$	$b(\text{L/mol})$
<b>EBC</b>				
303	10.136	3.498	0.0764	54.368
313	13.131	3.712	0.0828	100.394
323	11.727	2.567	0.1055	74.119
<b>SDS-EBC</b>				
303	6.961	2.379	0.1073	21.754
313	10.765	2.883	0.1049	38.533
323	10.995	2.715	0.1053	49.002
<b>CPC-EBC</b>				
303	11.105	3.836	0.0776	48.976
313	9.788	3.064	0.0909	38.243
323	9.135	2.666	0.1049	32.250
<b>TX-EBC</b>				
303	0.852	1.174	8.196	1.416
313	1.065	0.938	4.439	3.356
323	0.844	1.185	8.867	5.667

Table 4-Values of thermodynamic parameters for adsorption of BV-10 over EBC and its derivatives at different temperatures

Temperature(K)	$\Delta G^\circ$ (KJ mol <sup>-1</sup> )	$\Delta H^\circ$ (KJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
<b>EBC</b>			
303	-10.065		
313	-11.994	-26.105	+0.1003
323	-11.563		
<b>SDSEBC</b>			
303	-7.758		
313	-9.502	-32.773	+0.0757
323	-10.451		
<b>CPCEBC</b>			
303	-9.803		
313	-9.483	+16.942	+0.0236
323	-9.328		
<b>TXEBC</b>			
303	-0.8762		
313	-3.150	-57.7	+0.1759s
323	-4.658		

Table-5-Pseudo first order rate constants for the removal of BV-10 by EBC and its derivatives at 303 K

	K1(s <sup>-1</sup> )	qe(mg g <sup>-1</sup> )	R
EBC	5.3x10 <sup>-3</sup>	18.12	0.9850
SDSEBC	1.9x10 <sup>-3</sup>	20.58	0.9743
CPC EBC	1.2x10 <sup>-3</sup>	25.09	0.9898
TX EBC	6.9x10 <sup>-4</sup>	9.44	0.9669

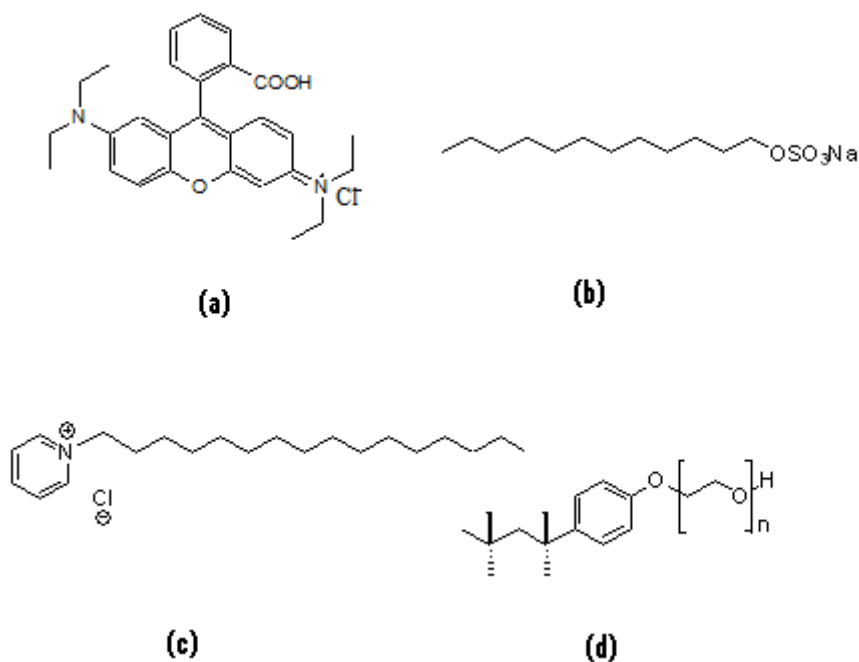


Figure:1a. Structure of Basic violet 10

Figure: 1b. Structure of SDS

Figure: 1c. Structure of CPC

Figure: 1d. Structure of TX-100

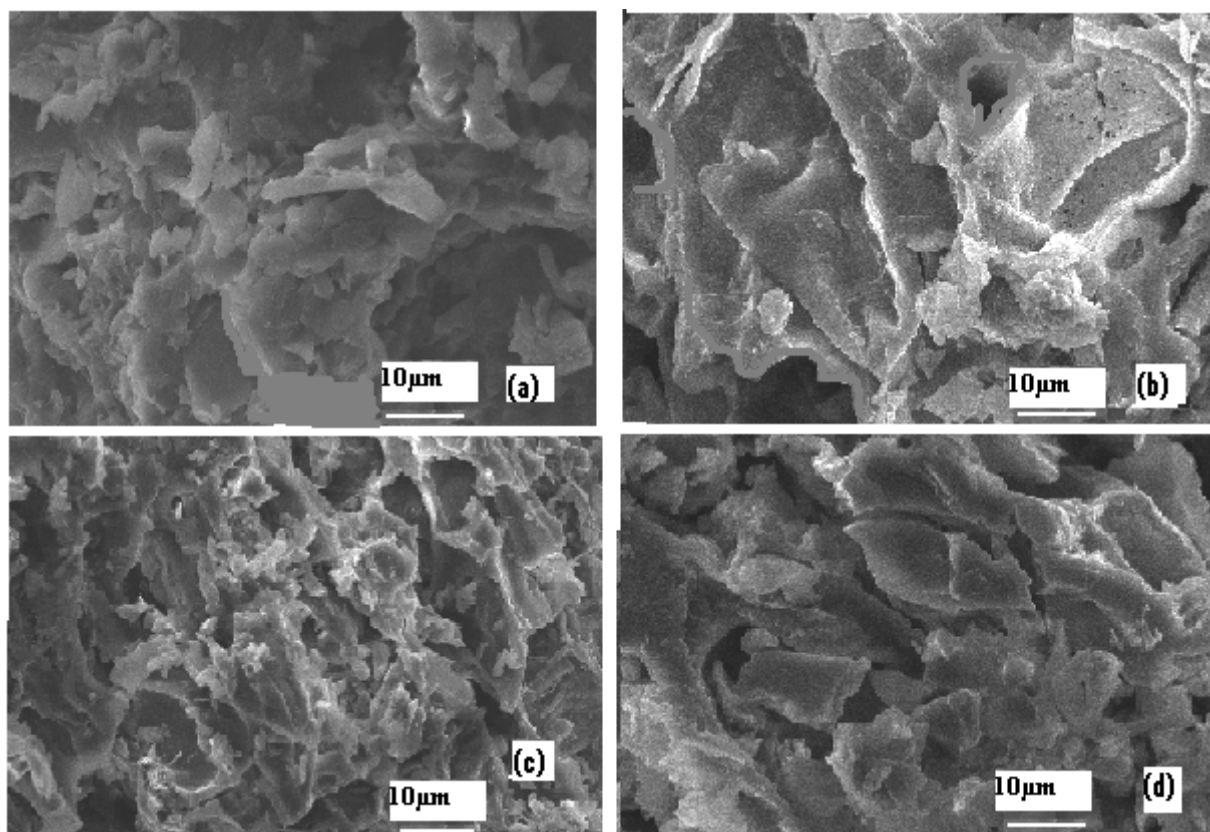


Figure: 2a. SEM of EBC  
Figure: 2b. SEM of SDS-EBC  
Figure: 2c. SEM of CPC-EBC  
Figure: 2d. SEM of TX-EBC

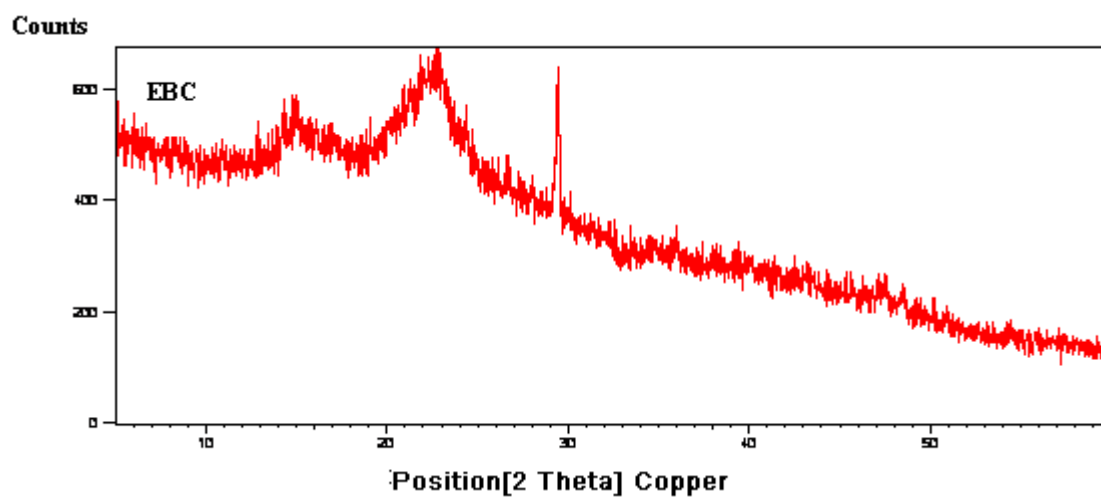


Figure: 3. XRD of EBC

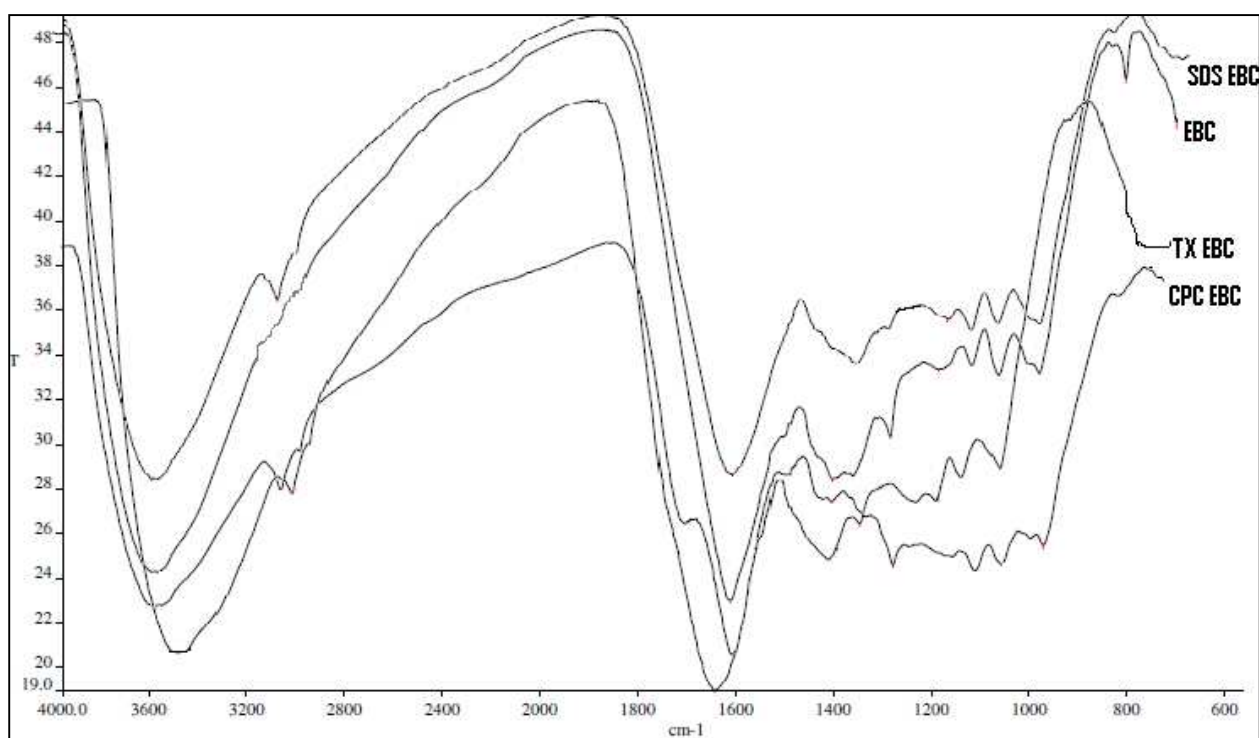


Figure: 4 FTIR spectra of EBC and its derivatives

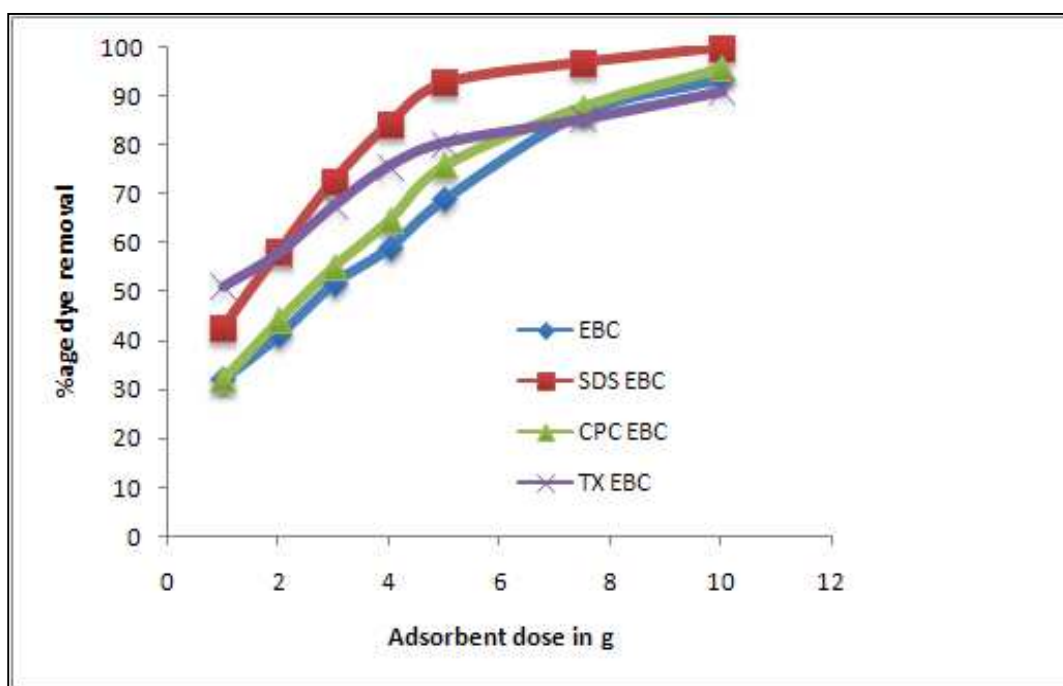


Figure: 5 Effect of adsorbent dose on dye removal, dye concentration 250 ppm, 303 K, 200 rpm

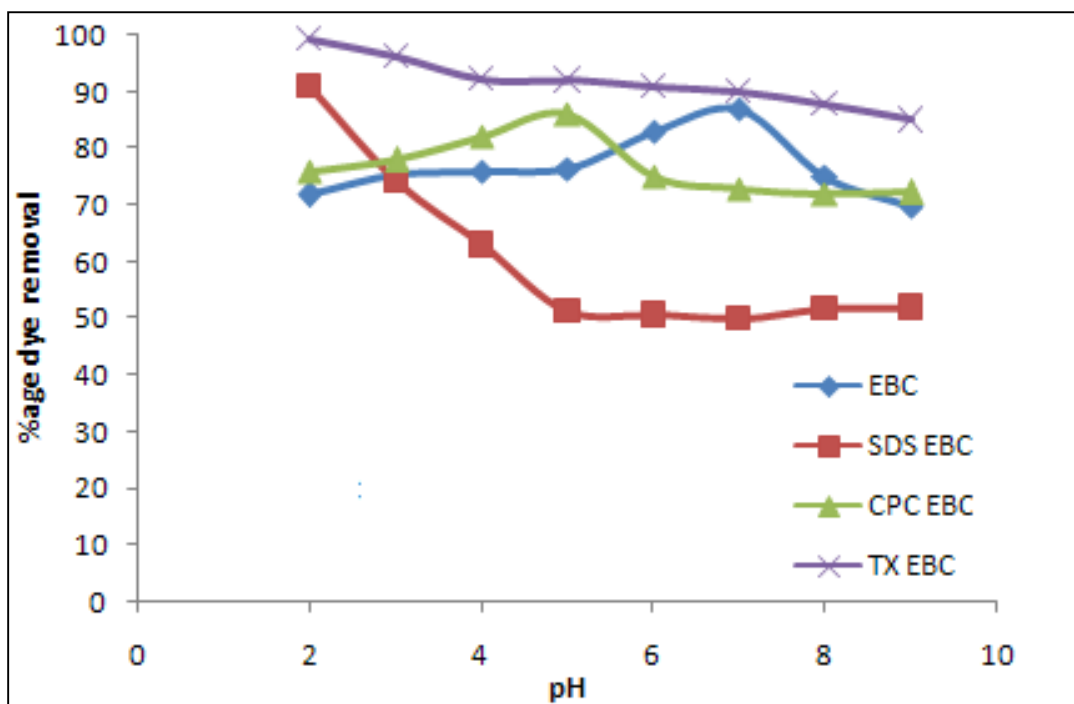


Figure: 6 Effect of initial pH on dye removal, dye concentration 250 ppm, 303 K, 200 rpm

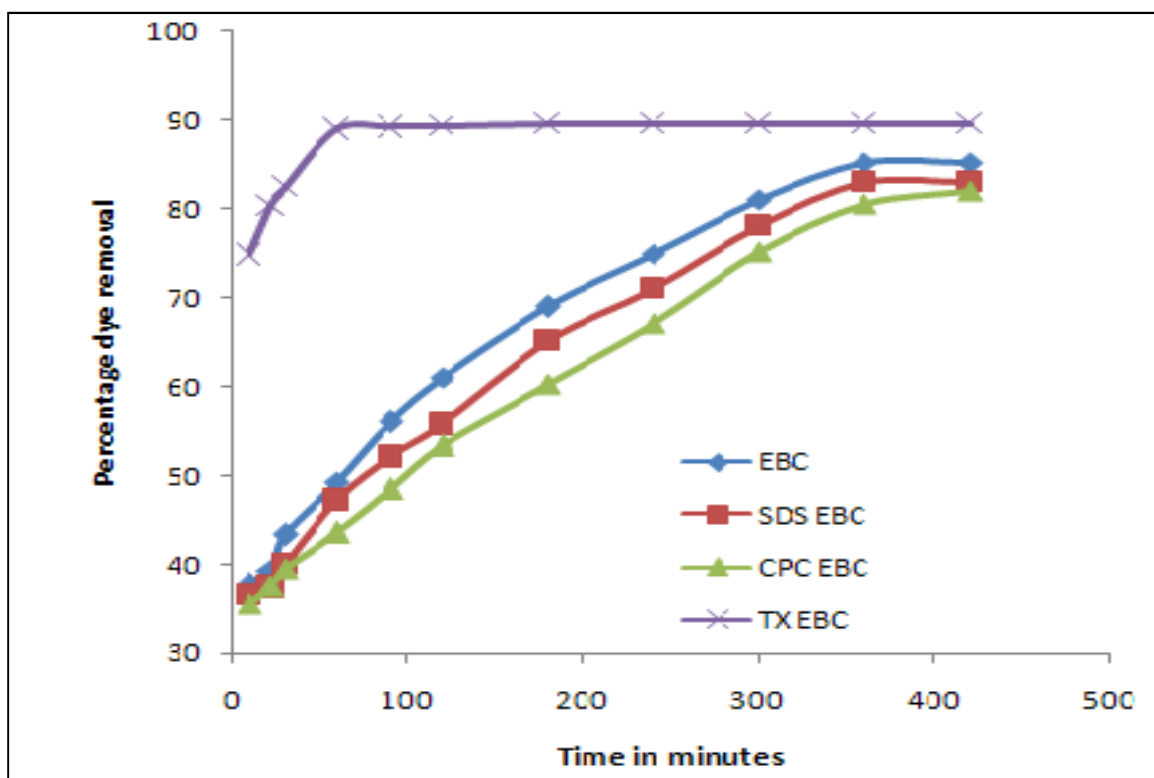


Figure: 7 Effect of contact time on percentage dye removal, dye concentration 250 ppm, 303 K, 200 rpm



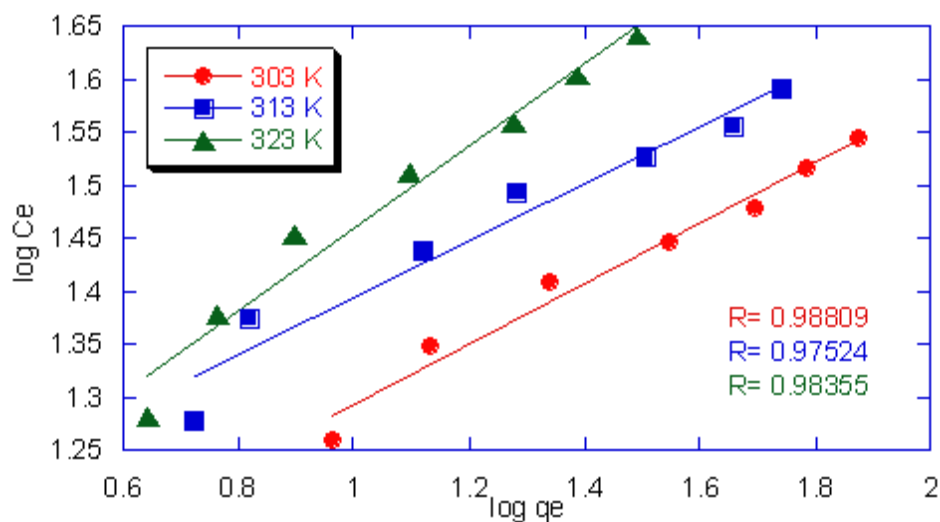


Figure: 8a Freundlich plots for sorption of dye on EBC

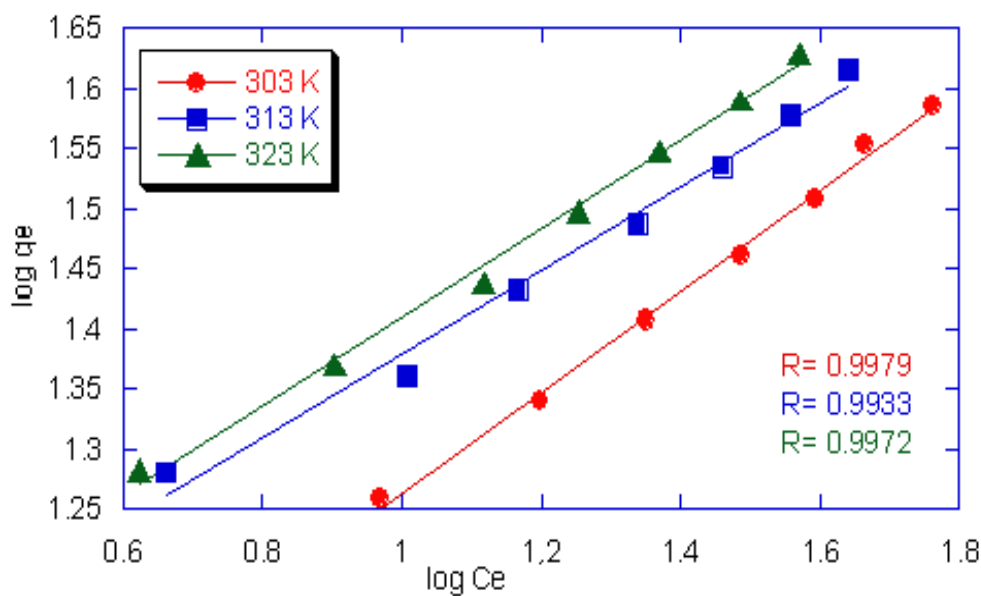


Figure: 8b Freundlich plots for sorption of dye on SDSEBC

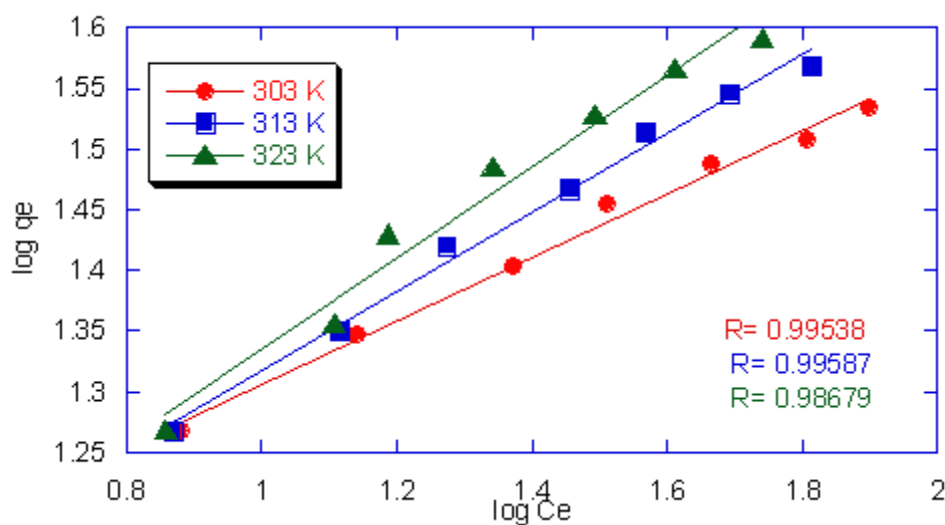


Figure: 8c Freundlich plots for sorption of dye on CPC EBC

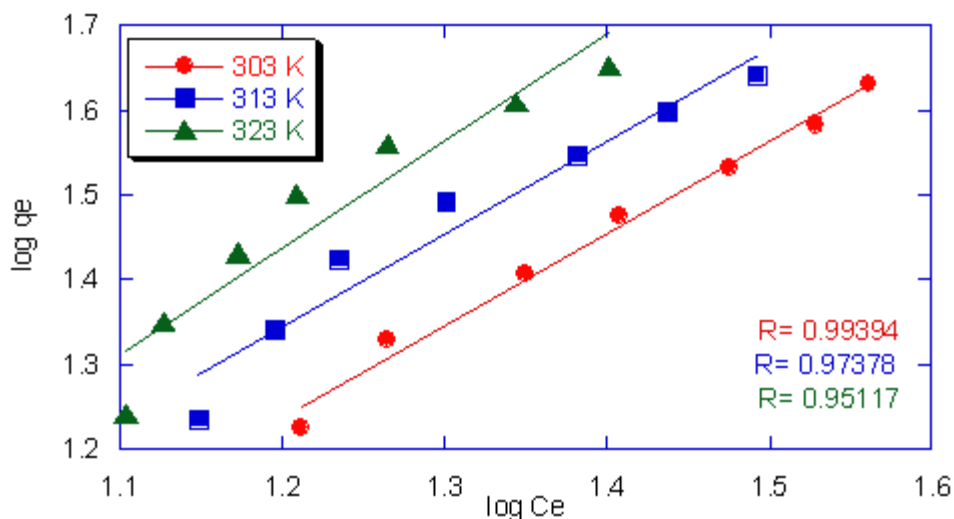


Figure: 8d Freundlich plots for sorption of dye on TX EBC

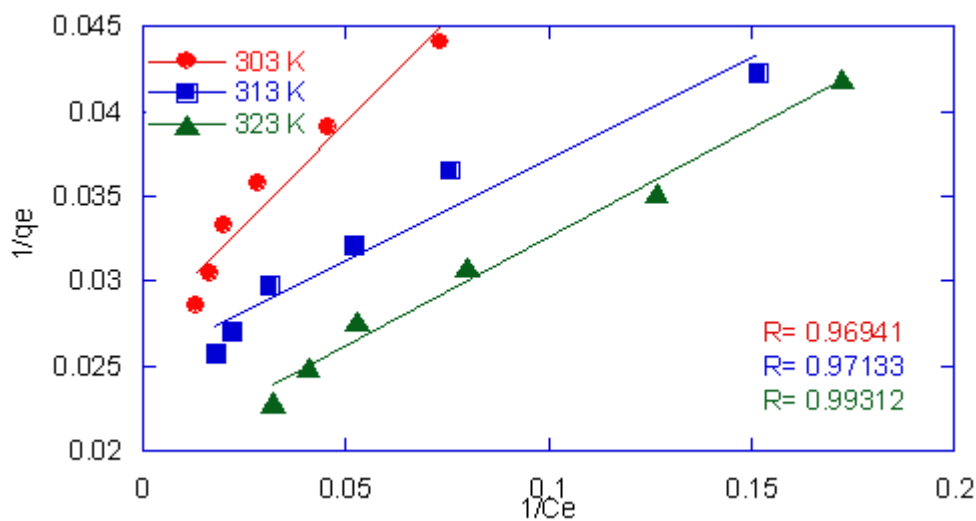


Figure: 9a Langmuir plots for sorption of dye on EBC

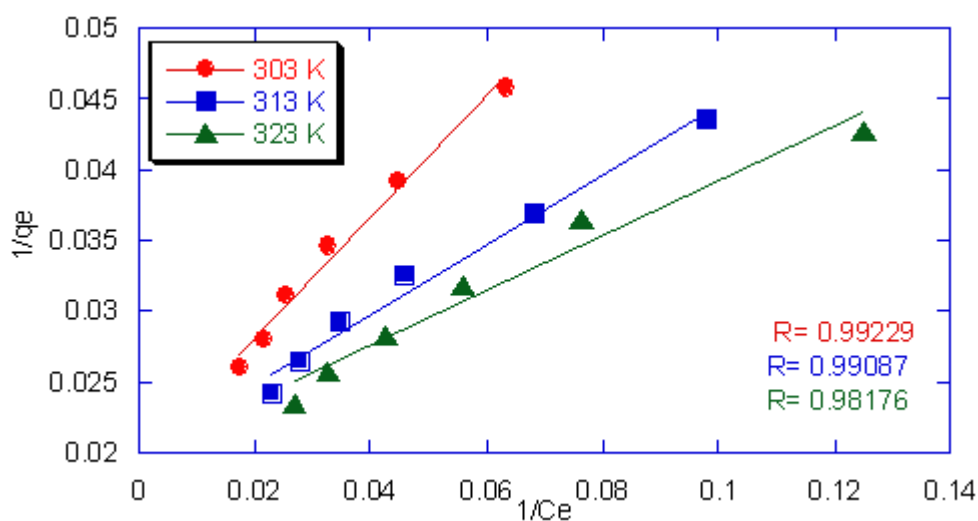


Figure: 9b Langmuir plots for sorption of dye on SDSEBC

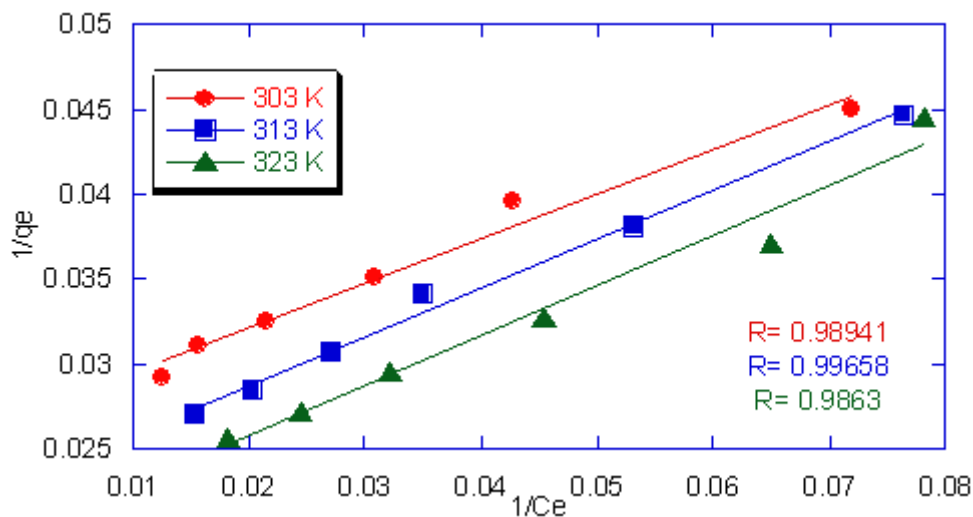


Figure: 9c Langmuir plots for sorption of dye on CPC EBC

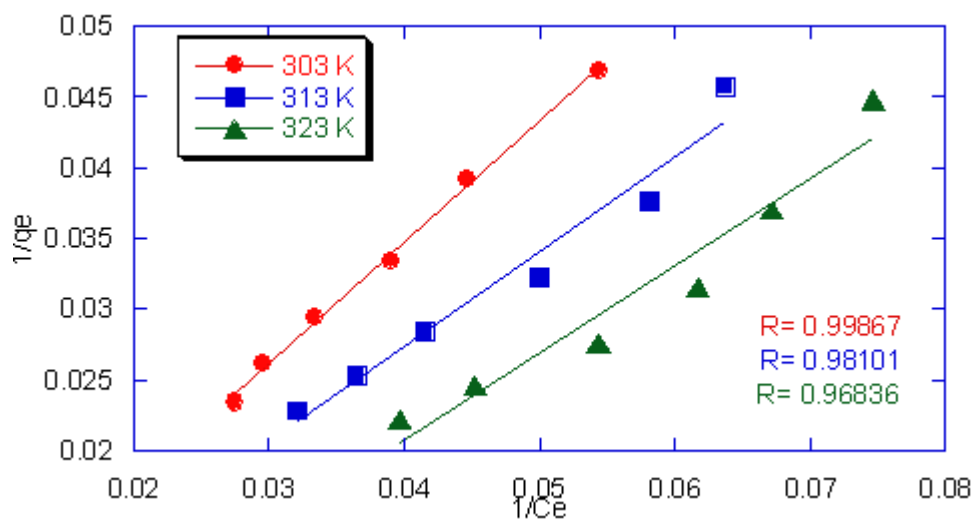


Figure: 9d Langmuir plots for sorption of dye on TX EBC

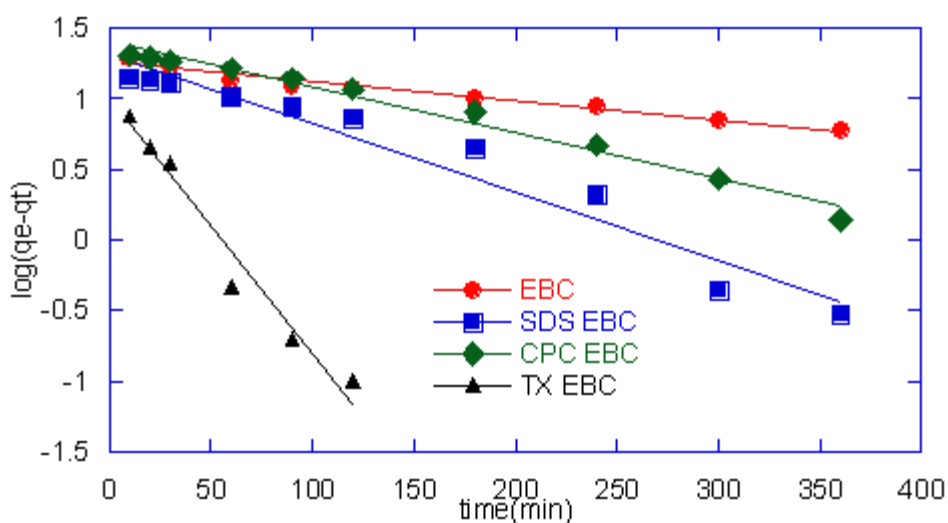


Figure: 10 First order kinetic model for the adsorption of BV-10 on EBC, SDSEBC, CPC EBC and TX EBC at 303 K

#### 4.2 Effect of adsorbent dose

To examine the effect of adsorbent dose on adsorption of dye on EBC and its surface derivatives, the experiments were conducted with adsorbent dose between 1.0 g/100 mL to 10.0 g/100 mL at 303 K. With the increase in the

adsorbent dose, the percentage dye removal increases. A noteworthy increase is observed at adsorbent dose of 5.0g/100 mL. This may be ascribed to the reason that with the increase in adsorbent dose number of active sites increases which makes the dye adsorption swift, The dye molecules first encounter the boundary layer effect and the porous structure of EBC makes physisorption possible and when surfactant is present on the surface the boundary layer effect changes to ion exchange due to adsorption desorption after surfactant modification the active sites become more available for dye removal, as at lower adsorbent dosage the number of dye molecules is relatively higher as compared to availability of adsorption sites. Thus it is justified that with the increase in adsorbent dose 100% dye removal takes place. The results are shown in Figure 5.

#### 4.3 Effect of pH

The effect of pH is studied in the range of 2-9 while initial concentration (250 ppm), adsorbent dose (5.0 g/100 ml) and temperature (303 K) were kept constant. The effect of initial pH on the dye removal is shown in Figure 6. The pHzpc of EBC, SDS-EBC, CPC-EBC and TX-EBC was found to be 7.8, 6.81, 3.5 and 6.92 respectively. This is usually observed that beyond pHzpc negative charge develops on the surface so cationic dyes are best adsorbed above their pHzpc but dye BV-10 contains a carboxylic group and two diethyl amino groups and one amino group is carrying positive charge, the dye upon increase of pH shows the zwitterions form in water may enhance the aggregation of BV-10 to form a dimer (Ramuthai *et al.*, 2009) and become unable to enter into the pore structure of the carbon surface. The greater aggregation of the zwitterionic form is due to the attractive electrostatic interaction between the carboxyl and xanthane groups of the monomer of dye. The adsorption capacity is highest for TX-EBC at pH 2; this may be attributed to the reason that the presence of non ionic surfactant causes no change in the charge of the surface of EBC; however the presence of surfactant causes additional functional groups on the porous carbon. The effect of change of pH is not prominent because of bipolar structure of dye, at low pH amino groups is protonated causing net positive charge on the dye and at high pH the carboxylic group is deprotonated causing no charge on the dye molecule.

#### 4.4 Effect of contact time

The effect of contact time was investigated in the batch mode at dye concentration 250 ppm and adsorbent dose of 5.0g/100 ml. The results have been shown in Figure 7 which suggests that the adsorption capacity of dyes increases with increasing contact time. Initially the rate of dye removal is higher due to high concentration gradient which decreases gradually due to decrease of dye concentration and blockage of active sites of the adsorbent. The equilibrium adsorption capacity is 38.4, 33.2, 36.26 and 44.8 mg/g for EBC, SDS-EBC, CPC-EBC and TX-EBC respectively. The adsorption capacity of different low cost adsorbents for BV-10 in literature (Khatri *et al.*, 1999; Khan *et al.*, 1999; Kannan *et al.*, 2007; Vasu *et al.*, 2008; Namasivayam., 2001; Namasivayam *et al.*, 1996) is very small due to its amphoteric nature of the dye though the presence of quaternary ammonium group makes this to be classified as a basic dye (Table 2). The adsorption is rapid for TX-EBC and relatively prolonged for EBC, SDS-EBC and CPC EBC. The equilibrium is obtained in 3 h for TX-EBC and 8h for EBC, SDS-EBC and CPC-EBC. The driving force is concentration gradient between solid and aqueous layer. This seems that the dye molecules first encounter the boundary layer effect and then follow the diffusion film mechanism. When a charged surfactant is present on the surface it takes relatively longer time for diffusion due to repulsive interaction of dye molecules with the surfactant on the surface. The dye molecules tend to arrange themselves as a least energetic conformation with minimum repulsions and maximum attractive forces before diffusion through the surface. The presence of different charges on the surface of EBC makes the process happening with different rates. This seems that the process is electrostatic complexation driven.

#### 4.5 Adsorption isotherms

The Freundlich and Langmuir isotherm models have been successfully applied to all of the above system at various temperatures 303 K, 313 K and 323 K and thermodynamic parameters calculated accordingly. For the equilibrium concentration of adsorbate ( $C_e$ ) and amount of dye adsorbed at equilibrium ( $q_e$ ), the following linear forms of Langmuir and Freundlich isotherms were studied.

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \quad (2)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

Where  $Q_0$  and  $b$  are Langmuir constants and  $K_F$  and  $n$  are Freundlich constants. The Freundlich and Langmuir isotherms gave straight lines and intercepts and slopes were used to determine the values of Freundlich and Langmuir parameters as given in Table 3. The RSS for Freundlich isotherm fit is found to be in the range 0.00824-.03609 and SEE is found to be in the range 0.001-0.012 suggesting good agreement with Freundlich isotherm. The

RSS for Langmuir isotherm fit is found to be in the range 0.001228-0.00755 and SEE is found to be 0.000 suggesting better fitting of Langmuir isotherm. The isotherms are shown in Figure 8-9. The changes in the adsorption parameters for EBC and its surface derivatives suggest the concise idea of the thermodynamic parameters which were also calculated from the above data using equations 4-6. The Gibbs free energy,  $\Delta G^0$  was found to be negative at all temperatures, indicating spontaneous process at all the temperatures for EBC and its surface derivatives while enthalpy  $\Delta H^0$ , was negative for EBC, CPC-EBC and TX-EBC suggesting exothermic and irreversible nature of the process and is positive for SDS-EBC. The positive value of entropy,  $\Delta S^0$  for EBC and its surface derivatives suggests that the randomness factor is increasing though its value is small, the process is entropy driven. The behavior of SDS-EBC is different from EBC, CPC-EBC and TX-EBC suggesting that the structural changes after adsorption of dye takes place on EBC up to different extent in the presence of different charged surfactants. The thermodynamic parameters were calculated using the following equations and the values of parameters are given in Table 4.

$$\Delta G^0 = -RT \ln b \quad (4)$$

$$\Delta H^0 = -R \left( \frac{T_2 T_1}{T_2 - T_1} \right) \ln \left( \frac{b_2}{b_1} \right) \quad (5)$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \quad (6)$$

Where  $b$ ,  $b_1$ ,  $b_2$  are Langmuir constants at 303 K, 313 K and 323 K respectively.

#### 4.6 Kinetic Studies

The rate of removal of BV-10 has been studied as a function of time on EBC and its surface derivatives as can be seen in Figure 7. The equilibrium was attained in 3 h for TX-EBC and 8h for EBC, SDS-EBC and CPC-EBC. The adsorption proceeds in three steps; in the first step rapid adsorption of dye takes place on the active sites of adsorbent followed by slow establishment of equilibrium under potential gradient. Adsorption rate constant study was carried out with the famous Lagergran rate equation (equation 7)

$$\log(q_e - q_t) = \log q_e - \left( \frac{k_1}{2.303} \right) t \quad (7)$$

The time versus  $\log(q_e - q_t)$  plots as shown in Figure 10 was found to be linear suggesting that the adsorption followed the first order kinetics. The slope of the plot gave the value of rate constant and it is given in Table 5. The rate constant decrease with surfactant modification in first order kinetics probably due to double layer potential set up on the EBC surface layer which reduce the probability of the diffusion film mechanism. Thus, this step is slow followed by fast steps like particle diffusion and adsorption of dye. RSS and SEE values for pseudo first order kinetic fit lies in the range 0.03127-0.16304 and 0.008-0.212 respectively suggesting superior fit.

### CONCLUSION

This study shows that BV-10 can be successfully removed from the simulated effluent by adsorption on EBC as well as its surface derivatives. These adsorbents were found to be porous and effective treatment of colored water before and after surfactant modification. The following conclusions can be drawn from this study: The batch adsorption experiments show that the adsorption of the BV-10 over EBC and its derivatives is dependent on pH, amount of adsorbent, concentration, contact time, and temperature, and 100% dye removal at dye concentration <250 ppm could be accomplished. The thermodynamic parameters obtained in both cases confirm the feasibility of the process at each concentration. The Freundlich and Langmuir isotherms fitted the data well suggesting homogenous distribution of functional groups on the heterogeneous surface of adsorbent before the surfactant treatment. The results of kinetic experiments show that the adsorption proceeds via first order kinetics over all adsorbents. The eucalyptus bark carbon and its surfactant modified adsorbents are economical and can be used as commendable adsorbents.

### REFERENCES

- [1] Annadurai, G.; Juang, R.S.; Lee, D.J.; **2002**, *J. Hazard Mater.* 92, 263-274.
- [2] Ali, I.; Gupta, V.K.; **2007**, *Nature Protocols* 1, 2661-2667.

- [3] Al.Degs, Y.; Khraisheh, M.A.M.; Allen, S.J.; Ahmad, M.N.A.; **2001**, *Sep. SciTech.* 36, 91-111.
- [4] Al-Bastaki N.; Chem. **2004**, *Eng. Process* 43, 1561-1567.
- [5] Arami, M.; Limaee, N.Y.; Mahmoodi, N.M.; **2005**, Tabrizi, N.S.; *J. Hazar. Mater.* 135, 171-179.
- [6] Ardejani, F.D.; BadiiKhLimaee, N.Y.;Mahmoodi, N.M.; Arami, M.M.; Shafari, S.Z., Mirhabibi, A.R., **2007**, *Dyes and Pigments.* 73, 178-185.
- [7] Bhattacharya, A.K.; Mandel, S.N.; Res **2006**, *J. Chem. Environment.* 10(1), 13-16.
- [8] Boehm,H.P.,Advances in Catalysis, edited by EleyD.D.; Pines, H.; Weisz P.B.; Academic Press, New York, **1966**.
- [9] Cheremisinoff, N.P.; Handbook of water and waste water treatment technologies, Butter worth – Heinmann, Boston.**2002**.
- [10] Crini, G.; **2006**, *Bioreso Technol.* 97, 1061-1085.
- [11] Dave, P.N.; Kaur, S.; Khosla, E.; **2011**,*Indian J. Chem. Technol.* 18(3),220-226.
- [12] Dave, P.N.; Kaur, S.;Khosla E.; **2011**, *Ind. J. of Chem. Technol.* 18(1),53-60.
- [13] El Geunidi, M.S.;Aly,I.H.; **1992**,*Adsorption Sci. Technol.* 9,121-128.
- [14] Eliassen,R.; Bennet, G.E.; **1967**, *J. Water Poll. Control Fed.* 39, R-82, 97-104.
- [15] Fambish, T.J.; Schleifer D E.; **1984**, *Carbon* 22, 19-38.Ferrero, F.; **2007**, *J. Hazard Mater.* 142, 144-152.
- [16] Hameed, B.H.; **2009**,*J. Hazard Mater.* 166, 233-238.
- [17] Hempfling, C.; **1997**, *Environ. Prog.* 16, 164-170.
- [18] Ho, Y.S.; Chiang, T.H.; Hsueh, Y.M.; **2005**, *Biochem.* 40,119-124.
- [19] Ghobarkar, H.; Schaf, O.; Guth, U.; **1999**, *Solid State Chem.* 27, 29-73.
- [20] Gupta, V.K.; Mittal, A.; Gajbe,V.;Mittal, J.; **2006**, *Ind. Eng. Chem. Res.* 45, 1446-1453.
- [21] Judkins, J.F.; Hornsky, J.S.; **1978**, *J. Water Poll. Control Fed.* 50, 2446-2456.
- [22] Kannan, N.; Murugavel, S., **2007**, *EJEAFChem.* 6,1860-1868.
- [23] Kang, Q.; Gao, B.;Yue, Q.; Zhon, W.; Shen, D.; **2007**, *Colloids surf. A: Physiochem. Eng. Aspects.* 299, 45-53.
- [24] Khosla, E.; Kaur, S.; Dave, P.N.; **2012**, *J. Chem Eng Data* 57(7), 2004-2011.
- [25] Khatri, S.; Singh, M.K.; **1999**, *Adsorp Sci. Technolo.* 17, 269-282.
- [26] Khan, T.A.; Ali, I.; Singh, V.V.; Sharma, S.; J. **2009**, *Environ. Protect Sci.* 3, 11-22.
- [27] Kim, T.H.; Park, C.; Yang, J.M.; Kim, S.; **2004**, *J. Hazard. Mater.* 112, 95-103.
- [28] Mahmoodi, N.M.;Hayati, B.; Arani,M.; **2010**, *J. Chem. Engg. Data* 55,4638-4649
- [29] McKay, G.; Porter, J.F.; Prasad, G.R.; **1999**, *Water Air and Soil Poll.* 114, 423-438.
- [30] McKay, G.; Allen, S.J.; McConvey,I.F.; Otterburn, M.S., **1981**,*J. Colloid interface Sci.* 80, 323-339.
- [31] Malik, R.; Ramteko, D.S.;Wate, S.R.; **2007**, *Waste Manag.* 27, 1129-1138.
- [32] Mittal, A.K.; Gupta, S.K.; **1996**, *Water Sci. Technol.* 34, 81-87.
- [33] Morais, L.C.; Frietas, O.M.;Goncalves, E.P.; Vasconcelos, L.T.; **1999**,*Water research.* 33, 979-988.
- [34] Namasivayam, C.; Radhika, R.; Suba, S.; **2001**,*Waste Manage.* 21(4), 381-387.
- [35] Namasivayam, C.; Muniasamy, N.;Gayathri, K.; Rani, M.; Ranganathan, K. ; **1996**, *Bioresour. Technol.* 57, 37-43.
- [36] Namasivayam, C.;Kumar, D.M.; Selvi, K.; Ashruffunissa, B. R.; Vanathi, T.; **2001**, *Biomass Bioenergy* 21, 477-483.
- [37] Namasivayam, C.; Kavitha, D.; **2002**, *Dyes and Pigments* 54, 47-58.
- [38] Owen, N.L.; Thomas, D.W.; Infrared studies of hard and soft woods, *Applied Spectroscopy.* **1989**.
- [39] Ozacara, M.; Sengil, I.A.; **2003**, *J. Hazard. Mater.* 98, 211-224.s
- [40] Petrinic, I.; Andersen, N.P.R.;Sostar, T.S.; La Marechal, A.M.; **2007**, *Dyes and Pigments* 74, 512-518.
- [41] Preethi, S.; Sivasamy, A.; Sivanesan, S.; Ramamurthi, V.; Swaminathan, G., **2006**, *Ind. Eng. Chem. Res.* 45, 7627-7632.
- [42] Ramuthai, S.; Nandhakumar,V.; Thiruchelvi, M.; Arivoli, S.;Vijayakumaran, V.; **2009**, *E-J. Chem.* 6(S1), S363-S373.
- [43] Rela, P.R.; Sampa, M.H.O.; Duarte, C.L.; Costa, F.E.; Sciani, V.; **2000**, *Radiat. Phys. Chem.* 57, 657-660.
- [44] Robinson, T.; McMullan, G; Marchant, R; Nigam, P; **2001**,*BioresourceTechnology* 77,247-255.
- [45] Srivastava, V.; Weng, C.H.; Singh, V.K.; Sharma, Y.C.; **2011**, *J. Chem. Eng. Data* 56,1414-1422.
- [46] Slokar, Y.M.; Marechal, A.M.L.; **1998**, *Dyes Pigments* 37, 335-356.
- [47] Suzuki, Y.; Maezawa, A.; Uchida, S.; Jpn. **2000**, *J. Appl. Phys.* 39, 2958-2961.
- [48] Sun, G.; Xu, X.; Ind. **1997**, *Eng. Chem Res.* 36,808-812.
- [49] Sun, Q.; Yang, L.; **2003**,*Water Res.* 37,1535-1544.
- [50] Tamezuddin, M.; Islam, M.A.; Mahmud, S.; Rukanuzzaman, M.; **2009**, *J. Hazard. Mater* 164, 53-60.
- [51] Vasu, A.E.; **2008**, *E-J Chem.* 5(4), 844-852.
- [52] Wong, Y.C.; Szeto, Y.S.; Cheung, W.H.; Mckay, G.; **2004**,*Proc. Biochem.* 39, 693-702.
- [53] Zhu, M.X.; Wang, Z.; Zhou, L.Y.; **2008**, *J. Hazard Mater.* 150, 37-45.