



A Comparative Adsorption Study with Different Activated Carbons as Adsorbents for the Removal of Cationic Dye from Aqueous Solution

N. Kannan¹ and R. Pagutharivalan²

¹Centre for Research and Post-Graduate studies in Chemistry,
Ayya Nadar Janaki Ammal College (Autonomous), Sivakasi 626 124, Tamil Nadu, India.

²Department of Chemistry, H.H.The Rajah's College (Autonomous),
Pudukkottai- 622 001, Tamil Nadu, India.

E-mail: dr_n_kannan@yahoo.co.in, paguthuchem@gmail.com

ABSTRACT

A carbonaceous adsorbent prepared from plant material like Emblica Officinalis Bark Carbon (EOBC) was found to show good porosity, appreciable surface area and consequently adsorbs dyes to an appreciable extent. Effect of various experimental parameters have been investigated using batch adsorption technique at room temperature ($30\pm 1^\circ\text{C}$) and the adsorption of Rhodamine B (RB) on carbonaceous adsorbent confirms to Langmuir equation, is a first-order process and pore diffusion controlled. The efficiency of carbonaceous adsorbent was evaluated by comparing the results with those obtained on a Commercial Activated Carbon (CAC). It was found that prepared carbonaceous adsorbent exhibits dye removal efficiency that is about 86–96% of that observed with CAC. FT-IR spectra of the adsorbents were recorded to explore the number and position of functional groups available for the binding of dye onto adsorbents. SEMs of the native and exhausted (CAC and EOBC) were recorded to explore the morphology of the adsorbent.

Keywords: Rhodamine B , , Emblica Officinalis Bark Carbon , Freundlich and Langmuir isotherms, Kinetics of adsorption.

INTRODUCTION

Color is one of the characteristics of an effluent, which is easily detected and readily traced back to its source. Most of the dyes normally have a complex aromatic molecular structure which makes them more stable and more difficult to biological degradation [1]. Many industrial processes use different synthetic chemical dyes for various purposes. Some frequent users of these chemicals include paper and pulp manufacture, dyeing of cloth, leather treatment, printing etc. Most of the used solutions containing such dyes are discharged as effluents [2]. Large quantities of colored effluents are discharged into receiving water each year. It affects the aesthetic nature but also interferes with the transmission of sunlight into waters and therefore reduces photosynthetic activity [3]. Wastewater offer considerable resistance for their biodegradation due to the presence of these heat and light stable dyes, thus upsetting aquatic life [4]. Thus, pollution caused by industrial wastewater has become a common problem for many countries [5]. It is estimated that 10–15% w/w of this capacity is discharged in effluents.

From environmental point of view, the discharge of dyes into natural water bodies represents a serious problem because of their persistence and non-biodegradable characteristics [5]. Highly colored effluents containing dyes can affect aquatic life present in natural water bodies by decreasing sunlight penetration or even leading to direct poisoning of living organisms [6-10]. In order to avoid these problems, effluents containing dyes must be treated for their removal before disposal. For this task some processes can be employed like: (i) photochemical degradation, which is not an efficient process due to the high stability of most dyes in front of light and (ii) chemical or anaerobic digestion, which are not suitable for dyes elimination because their intrinsic resistance [11]. The application of the adsorption technique has assumed remarkable importance in the treatment of contaminated waters and effluents, especially if the adsorbent employed presents low cost and does not require any treatment before its utilization [12,13]. Adsorption process using activated carbons is widely used to remove pollutants from wastewaters. However, commercially available activated carbon which is widely used as adsorbent is expensive [14].

Earlier adsorbents used include banana pith [15], wheat straw [16], sawdust [17], powdered waste sludge [18], babul seed [19] wheat shells [20], wheat bran [21] and hen feathers [22], Peat moss and rice hulls [23], coconut husk [24], fly ash [25], *emblica officinalis* bark [26], *moringa oliefera* bark [27], zea mays dust carbon [28] and tamarind seed powder [29] have also been reported as efficient adsorbent for removing colour.

Rhodamine B dyes are generally toxic, and are soluble in water, methanol and ethanol [30]. It is widely used as a biological stain [31]. RB is used for dyeing of various products including cotton [32], silk [33], paper [34], and finds a variety of applications in the analytical and photo-chemical fields, especially in the extraction, spectrophotometric and fluorometric analysis of uranium [35-37]. Hence, it may be found in wastewater of many industries and chemical, biomedical and photochemical laboratories. In the present study removal of RB on EOBC was studied by batch adsorption model.

MATERIALS AND METHODS

Preparation of Activated Carbon

The raw material *Emblica Officinalis Bark* (EOB) were collected locally, washed, dried, cut into small pieces, carbonized at 300-400°C and thermally activated with sodium bicarbonate at 700-900°C to produce CO₂ inert atmosphere at this temperature, which avoids ash formation. The obtained carbon was ground well to a fine powder and sieved (Jeyant Sieve, India) into discrete particle size (90, 125, 150, 180, 210 and 250 micron) and stored. 90 micron size carbon was activated by acid digestion (4N HNO₃; 2hr at 80°C) and dried in an air oven at 120°C for 2 hr. The resulting carbon washed with distilled water until a constant pH of the slurry reached.

Adsorption Experiments

An accurately weighed quantity of the rhodamine B dye was dissolved in double distilled water to prepare the stock solution (1000 mg/l). The percentage purity of the dye was taken into consideration while preparing the stock solutions. Adsorption experiments were carried out at room temperature (30 ± 1°C) under batch mode [38]. Experimental solutions of desired concentration were obtained by successive dilution. All the other chemicals used in this study were of reagent grade and obtained commercially. Double distilled water was employed for preparing all the solutions and reagents. Thermostatic incubator shaker (Neolab, India) was used to maintain the temp (30 ± 1°C). The concentrations of the RB solution was analyzed by measuring its absorbance at $\lambda_{\text{max}} = 544 \text{ nm}$ using UV-Visible Spectrophotometer (ELICO Semi Micro Spectrophotometer, (Model, no: 207) India. Exactly 50 ml of dye solution of known initial concentration (C_i) was shaken at constant agitation speed (200 rpm) with required dose of adsorbent of a fixed particle size (90 micron) for a specific period of contact time (Table 2). The pH of the dye solution was adjusted by adding either 1 M HCl or 1 M NaOH solution and the pH values of dye solutions were noted with digital pen pH meter (Hanna instruments, Portugal). After equilibration, the final concentration (C_f) of RB was measured. The values of percentage removal of dye and amount adsorbed (q in mg g^{-1}) were calculated using the following relationships:

$$\text{Percentage removal} = 100 (C_i - C_e)/C_i \quad (1)$$

$$\text{Amount adsorbed (q)} = (C_i - C_e)/m \quad (2)$$

Where C_i and C_e are the initial and equilibrium (final) concentration of dye (in mgL^{-1}), respectively and m is the mass of adsorbent, in gL^{-1} .

RESULTS AND DISCUSSION

Scanning Electron Microscope (SEM) study gives useful informations regarding the textural/morphological characteristics of the adsorbents [39]. The SEM images of pure CAC and EOBC (Figure.1-A, C) show the porosity of the structure. After dye adsorption, a significant change is observed in the surface morphology of these adsorbents (Figure. 1-B, D). The adsorbents have a rough surface and pores containing a new shiny and bulky particles. It also shows that the particles can be included to account for the irregularities. At higher magnification, the globules are distinctly visible and they appear to be quite uniform with internal porous

structures. The size of the particles of used adsorbents were **90 microns**. From the SEM picture we find well aligned uniform pore net work is developed upon activation and pore shape is spherical layer structure [40].

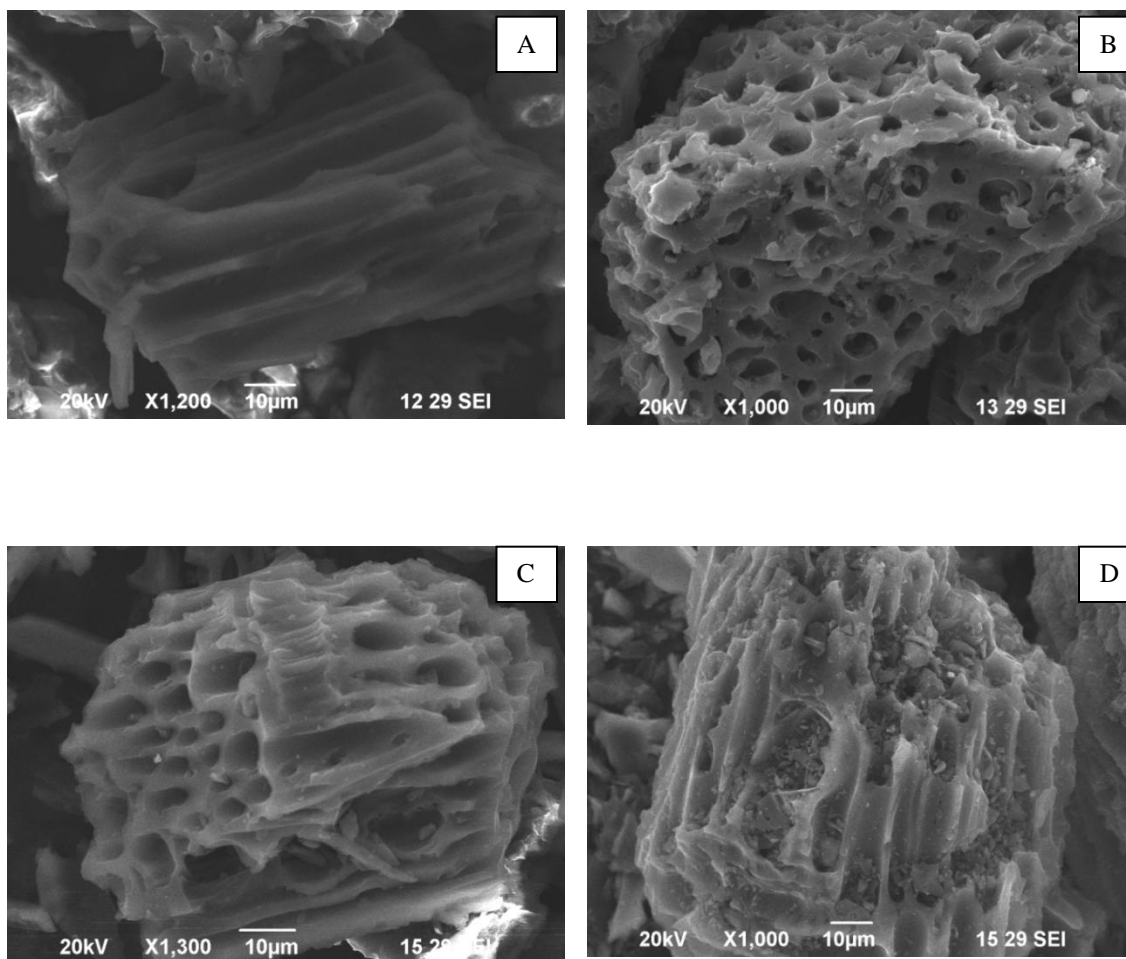


Figure 1. SEM images of before (A, C) and after (B, D) adsorption of RB on CAC and EOBC.

The FT-IR spectra of CAC and EOBC before and after adsorption of RB were used to determine the frequency changes in the functional groups in the adsorbents. FT-IR spectra of the adsorbent displays number of absorption peaks, indicating the complex nature of studied adsorbent [41]. Table -1. Presents the fundamental peaks of the adsorbent before and after use.

Table 1. FT-IR Spectroscopic characteristic frequencies ($\bar{\nu}$ in cm^{-1}) of CAC and EOBC before and after adsorption of RB.

Adsorbents	O-H stretching	C-H stretching	>C=O stretching	>C=C< bending	C-O stretching	-CN = stretching
CAC	3446-3454	2424-2432	1631-1660	1612-1550	1119-1121	----
CAC-RB	3437-3440	2969-2719	1631-1657	1380-1385	1118-1123	1526-1532
EOBC	3385-3448	2924-2938	1708-1891	1611-1600	1032-1082	---
EOBC-RB	3444-3448	2244-2253	1733-1893	1444-1458	1037-1084	1560-1568

The peak around 3385.9 cm^{-1} and 1708.5 cm^{-1} represented bonded hydroxyl group and C=O stretching. The peak observed at 1708.5 cm^{-1} corresponds to C=O stretching. The peaks around 1614.7 cm^{-1} corresponds to the C=C stretching and at 1037.4 cm^{-1} corresponds to C-O band. The observed peak of -OH, C=O and C-O bands are shifted to 3448 , 1891 and 1082 cm^{-1} when CAC and EOBC are loaded with RB (Figure 2). It seems that these functional groups participate in dye binding on the surface of CAC and EOBC.

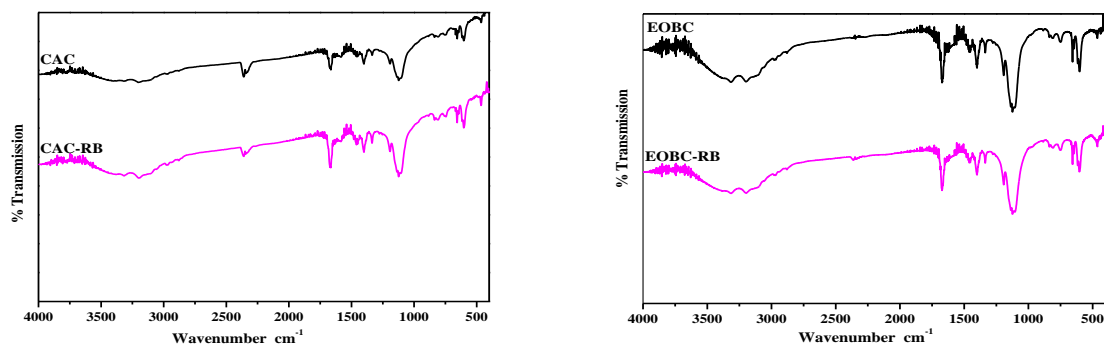


Figure 2. FTIR spectrum of before and after adsorption of RB on CAC and EOBC.

Effect of initial concentration

Effect of initial concentration on the extent of removal of RB (in terms of percentage removal and amount adsorbed) on CAC and EOBC were studied. The initial concentration provides an important driving force to overcome all mass transfer resistance of dye anions between the aqueous and solid phases [42]. The relevant data are given in Table 2. The percentage removal is found to decrease exponentially, while the amount of RB adsorbed increases exponentially with the increase in initial concentration of RB (Figure 3). This indicates a decrease in adsorption, which is attributed due to the lack of available active sites required for the high initial concentration of RB. Similar results have been reported in literature on the extent of removal of dyes [43-45], metal ions [46-49] and carboxylic acid [50, 51].

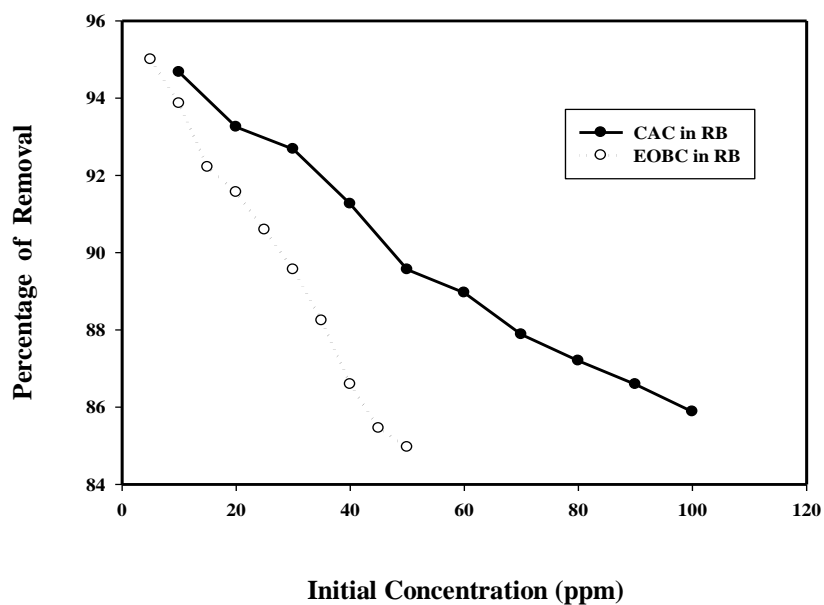


Figure 3. Effect of Initial concentration for the removal of RB onto CAC and EOBC

Table 2. Effect of process parameters on the extent of removal of RB by CAC and EOBC at $30 \pm 1^\circ\text{C}$

Variation	Adsorbents	Initial concentration (ppm)	Contact time (min)	Dose of ACs (g/l)	Initial pH	Particle size (μ)
Initial concentration	CAC	10 – 190(90*)	30	2	7.5	90
	EOBC	10 – 100(50*)	30	4	7.5	90
Contact time	CAC	90	5-50	2	7.5	90
	EOBC	50	5.50	4	7.5	90
Dose of ACs	CAC	90	30	1 - 2	7.5	90
	EOBC	50	30	3.5 - 4.4	7.5	90
Initial pH	CAC	90	30	2	2-11	90
	EOBC	50	30	4	2-11	90
Particle size	CAC	90	30	2	7.5	45-250
	EOBC	50	30	4	7.5	45-250

* Optimum Initial Concentration

Table 3. Effect of process parameters on the extent of removal of RB and amount adsorbed by CAC and EOBC at 30 ±1°C

Variation	Parameters*	CAC	EOBC
Initial concentration	% R	93.00-80.63	97.25-86.50
	Q	21.16-38.65	22.95-34.53
Contact time	% R	89.26-99.650	88.26-99.11
	Q	23.73-30.25	22.56-28.78
Dose (g l ⁻¹)	% R	84.56-99.28	80.83-98.56
	Q	18.19-27.15	28.13-32.89
Initial pH	%R	84.22-99.20	86.59-99.83
	Q	24.43 -34.56	23.56-35.56
Particle size (μ)	%R	-	90.25-99.23
	Q	-	25.35-34.45

Adsorption Isotherms:

In order to determine the adsorption potential, the study of adsorption isotherm is essential in selecting an adsorbent for the removal of dyes. The adsorption data were analyzed with the help of Freundlich and Langmuir isotherms.

$$\text{Freundlich isotherms: } \log q_e = \log K + (1/n) \log C_e \quad (3)$$

$$\text{Langmuir isotherms: } (C_e/q) = (1/Q_0 b) + (C_e/Q_0) \quad (4)$$

Where, K and 1/n are the measures of adsorption capacity and intensity of adsorption, respectively. q is the amount dye adsorbed per unit mass of adsorbent (in mg g⁻¹) and C_e is the equilibrium concentration of dye (in mgL⁻¹ or ppm); Q₀ and b are Langmuir constants, which are the measures of monolayer adsorption capacity (in mgg⁻¹) and surface energy (in g L⁻¹), respectively.

The values of Freundlich and Langmuir constants obtained from the linear correlation between the values of (i) log q_e and log C_e (ii)(C_e/q_e) and C_e. They are found to be linear (Figure 4A, 4B). The applicability of Langmuir isotherm indicates the formation of mono-layer and also nature of adsorption process. The values of adsorption isotherm constants along with the correlation co-efficients are presented in Table 4. In order to compare the validity of each model a normalised standard deviation, Δq(%) is calculated using the following equation:

$$\Delta q (\%) = 100 \times [(\sum [(q_t^{\text{exp.}} - q_t^{\text{cal.}}) / q_t^{\text{exp.}}]^2) / (n - 1)]^{1/2} \quad (5)$$

Where the superscripts, exp. and cal. are the experimental and calculated values of q_t viz., the amount adsorbed at different time t and n is the number of measurements. The Δq (%) values are also given in Table 4. Based on the low values of Δq (%), it is concluded that the adsorption of RB can best be described by the Langmuir adsorption isotherm. This indicates the applicability of Langmuir isotherm and the mono-layer coverage on adsorbent surface. The mono-layer adsorption capacities (Q_0) of the adsorbents are found to be of the order: EOBC < CAC

Adsorption capacity of EOBC is better and nearer to CAC. Further, the essential characteristics of the Langmuir isotherm can be described by a separation factor, R_L , which is defined by the following equation:

$$R_L = [1 / (1 + bC_i)] \quad (6)$$

Where, R_L is the separation factor, C_i and b are the initial concentration of dye (in mg L^{-1} or in ppm) and Langmuir constant (in g L^{-1}). The value of R_L , indicates the shape of the isotherm and nature of the adsorption process as given below;

R_L value	Nature of adsorption process
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

In the present study, the value of R_L (0.127 and 0.132) indicates that the adsorption process is favourable for this low cost adsorbent.

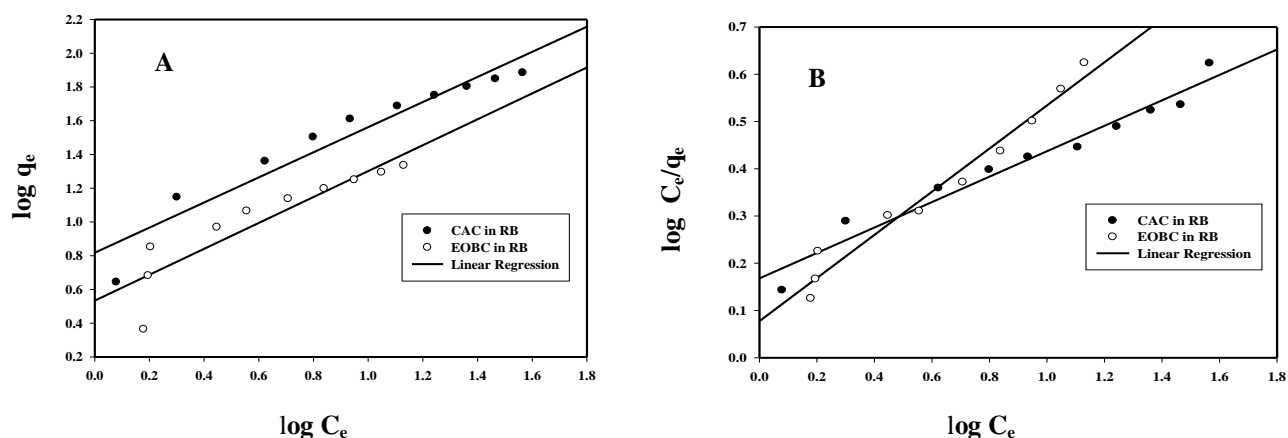


Figure 4. (A) -Freundlich and (B)-Langmuir adsorption isotherms for the removal of RB onto CAC and EOBC

Table 4. Freundlich and Langmuir parameters of adsorption isotherms for the removal of RB by CAC and EOBC at 30 ±1°C.

S. No	Parameters	Adsorbents	
		CAC	EOBC
1	Freundlich isotherm		
	Slope(1/n)	0.862	0.572
	Intercept (log k)	54.65	5.451
	Correlation coefficient (r)	0.996	0.987
	$\Delta q(\%)$	0.015	0.007
2	Langmuir isotherm		
	Slope(1/Q _o)	0.040	0.188
	Intercept (1/Q _o b)	0.175	0.678
	Correlation coefficient (r)	0.996	0.991
	Q _o (mg/g)	34.538	22.47
	b (g/L)	0.597	0.345
	R _L	0.127	0.132
	$\Delta q(\%)$	0.007	0.004

Effect of contact time

The effect of contact time on the amount of RB adsorbed is observed at the optimum initial concentration of RB. The relevant data are given in Table 2.0. The extent of removal of RB by these adsorbents is found to increase exponentially and reach a maximum value with increase in contact time (Figure 5). The relative increase in the extent removal of RB after 35min., of contact time is not significant and hence it is fixed as the optimum contact time. Similar results have been reported in literature for the removal of dyes [12,43-46,52]. The contact time experiments are useful to investigate the influence of system parameters on the rate and extent of adsorption.

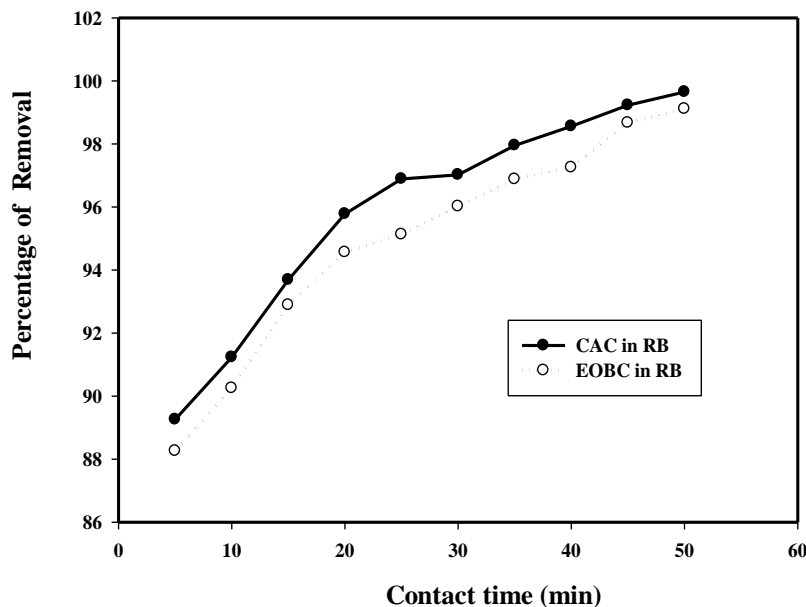


Figure 5. Effect of contact time for the extent removal of RB onto CAC and EOBC

Kinetics of adsorption

The kinetics and dynamics of adsorption of RB these two adsorbents have been studied by applying the various first order kinetic equations, proposed by Natarajan-Khalaf-as cited by Kannan and Vanangamudi [45], Lagergren-as cited by Trivedi, and Bhattacharya- Venkobachar .

Natarajan and Khalaf equation:

$$\text{Log } (C_i / C_t) = (k / 2.303) t \quad (7)$$

Lagergren equation:

$$\text{Log } (q_e - q_t) = \text{log } q_e - (k / 2.303) t \quad (8)$$

Bhattacharya and Venkobachar equation:

$$\text{Log } [1 - U(T)] = - (k / 2.303) t \quad (9)$$

Where k is the first order rate constant (min^{-1}) for adsorption of RB. C_i and C_t are the concentration of dye (in mg L^{-1} or ppm), at time zero and at time t respectively; q_e and q_t are the amount of dye adsorbed per unit mass of the adsorbent (in mg g^{-1}) and at time t respectively,

$$U(T) = [(C_i - C_t) / (C_i - C_e)] \quad (10)$$

Where C_e is an equilibrium concentration of RB (mg L^{-1}).

The values of (i) $\log(C_i/C_t)$, (ii) $\log(q_e - q_t)$ and (iii) $\log[1-U(T)]$ are linearly correlated with time (t). The values of first order rate constant (k), Δq (%) and correlation co-efficient (r -value) are given in Table 5. All the linear correlations are found to be statistically significant, indicating the applicability of these kinetic equations and the first order nature of the adsorption process of RB on these adsorbents.

The rate of adsorption (k-value) for CAC and EOBC are obtained from Lagergren equation and it is found to be almost equal with the value obtained from Bhattacharya and Venkobachar equation. Hence any one of these kinetic equations could be used in future to calculate k-value for the adsorption of dyes. Lagergren plots are shown in Figure 7(A), based on the high r-values, which are close to unity and low Δq (%) values, it is concluded that the Lagergren equation is applicable to the kinetics of adsorption of RB.

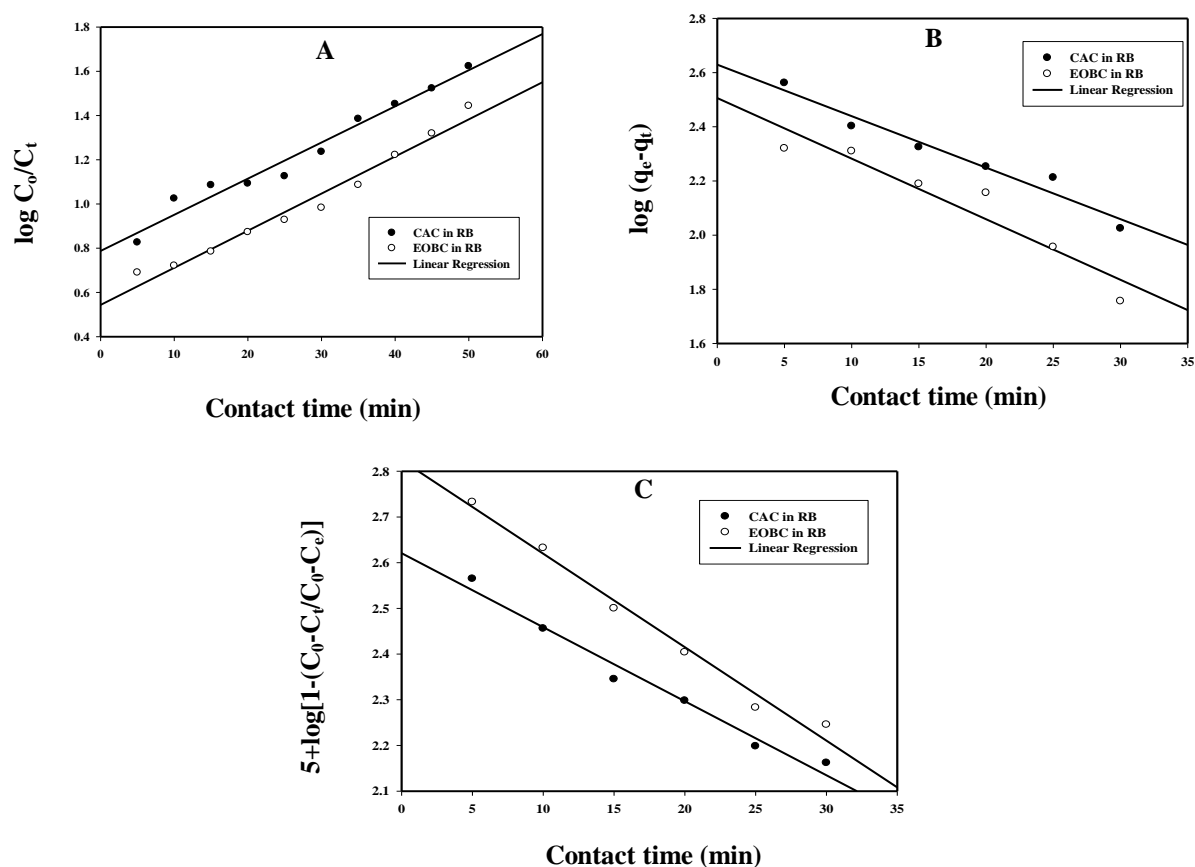


Figure 7. (A)- Natarajan & Khalaf, (B)- Lagergren and (C)- Bhattacharya &

Intra particle diffusion model

The adsorbate species (dye RB) are most probably transported from the bulk of the solution into the solid phase through intra particle diffusion / transport process, which is often the rate limiting step in many adsorption processes, especially in a rapidly stirred batch reactor. The possibility of intra particle diffusion process was explored by using the Weber and Morris intra particle diffusion model [54]:

$$q_t = k_p t^{1/2} + C \quad (11)$$

Where q_t is the amount of dye adsorbed (in mg g^{-1}) at time t ; C is the intercept and k_p is the intra-particle diffusion rate constant (in $\text{mg g}^{-1} \text{min}^{-1/2}$).

The values of q_t are found to be linearly correlated with values of $t^{1/2}$ (Figure 8-A). The k_p values were calculated by using correlation analysis (Table 5.). The r -values are found to be close to unity, this reveals the presence of intra particle diffusion process [62], [57]. Based on the calculated values of k_p ($\text{mg g}^{-1} \text{min}^{-1/2}$) for EOBC, indicates that the EOBC has more porous like CAC. The large values of intercept (Table 5.0) give an idea about the boundary layer thickness *i.e.* larger the intercept, greater is the boundary layer effect⁴⁴. The intercept (C) value of CAC is more and EOBC is less, indicating the boundary layer effect is maximum in CAC and minimum in EOBC.

The correlation of the values of \log (% removal) and \log (time) also resulted in linear relationship (Figure 8.0-B). This indicates that the process of intra particle diffusion also taking place in this adsorption system (Table 5). The divergence in the values of slope from 0.429-0.414, indicates the presence of intra particle diffusion process as one of the rate limiting steps, besides many other processes controlling the rate of adsorption, all of which may be operating simultaneously [43,44,52].

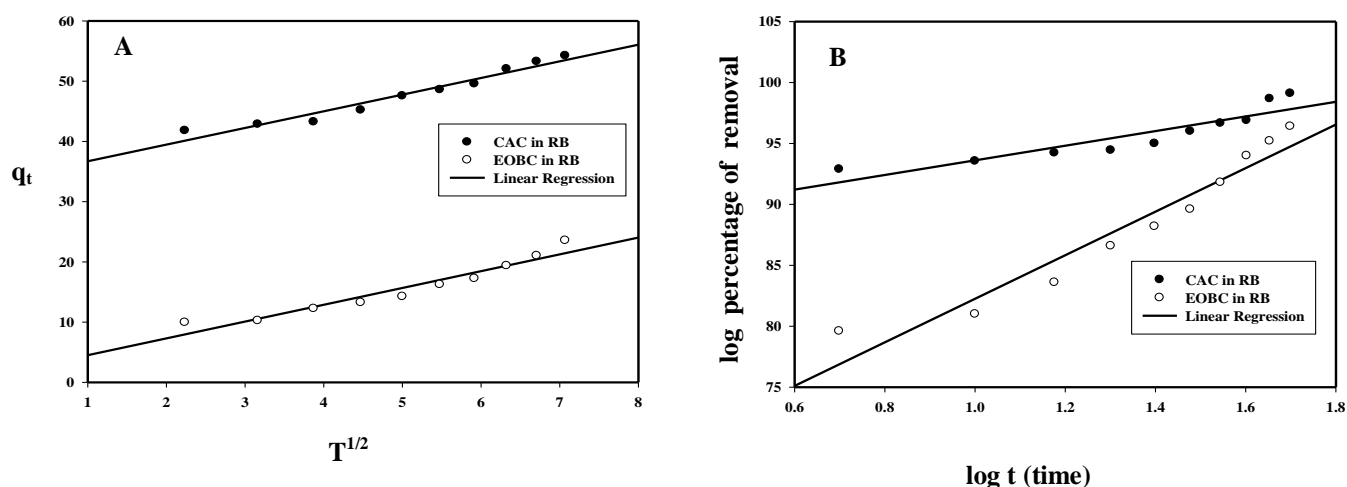


Figure 8. (A) - Intra-particle diffusion model, (B) - log Intra-particle diffusion Plot.

Table 5. Kinetics and dynamics of adsorption of RB by adsorption on CAC and EOBC at $30 \pm 1^\circ\text{C}$.

S.No	Parameters	CAC	EOBC
01	Natarajan & Khalaf equation.		
	Correlation Coefficient (r)	0.997	0.934
	$10^2 k$ (min^{-1})	9.108	0.523
	Δq (%)	8.562	37.25

02	Lagergren equation. Correlation Coefficient (r) 10^2k (min^{-1}) Δq (%)	0.999 15.128 2.892	0.956 7.598 11.035
03	Bhattacharya and Venkobachar equation. Correlation Coefficient (r) 10^2k (min^{-1}) Δq (%)	0.998 15.619 6.782	0.983 8.205 17.12
04	Intra Particle diffusion Model. Correlation Coefficient (r) k_p ($\text{mg g}^{-1} \text{min}^{-1/2}$) Intercept (C) Δq (%)	0.928 178.5 76.28 1.256	0.986 3.976 2.369 0.019
05	Log (% removal) Vs log (time) Correlation Coefficient (r) Slope (m) Δq (%)	0.989 0.429 18.36	0.936 0.414 34.04

Effect of dose

The effect of dose of adsorbent on the amount of RB adsorbed has been studied (Table 2.0). The value of amount adsorbed (q) is observed to decrease exponentially with increase in dose of adsorbent. This may be due to the increase in availability of surface active sites resulting from the increased dose and conglomeration of the adsorbent [2840, 43,45,55]. The value of percentage removal of RB (Table 2) increase exponentially with increase in dose of adsorbent (Figure 9). This suggests that the adsorbed species (dye) may either block the access to the internal pores or causes particles to aggregate and there by resulting in the availability of active sites for adsorption. Similar observations have been noticed for the removal of dyes [12,43-45,53].

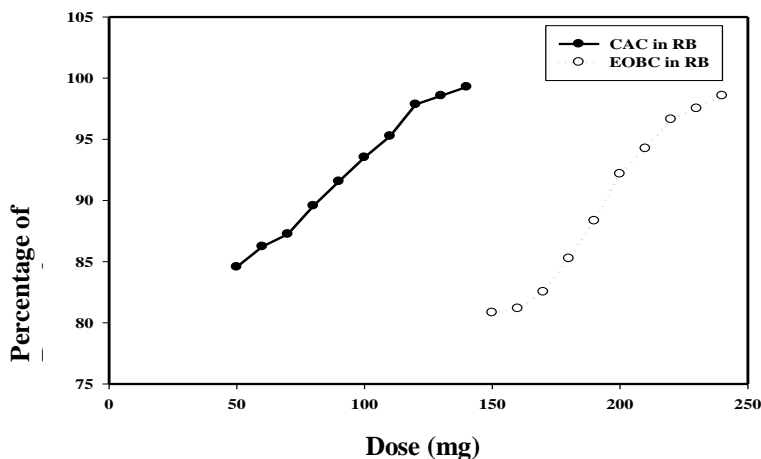


Figure 9. Effect of dose for the removal of RB onto CAC and EOBC

Effect of initial pH

The effect of initial pH of the dye solution on the amount of dye (RB) adsorbed has been studied by varying the initial pH, under constant conditions of other process parameters (Table 2.0). The pH value changes slightly after adsorption and a decrease in pH value is noted ($\Delta\text{pH} = \text{pH}_{\text{final}} - \text{pH}_{\text{initial}}$). The optimum pH value is fixed as 7.5. The results are shown in (Figure10.0).The increase in initial pH almost linearly increases the amount of RB adsorbed. The change in initial pH values of dye solution significantly affect the adsorption characteristics of basic dye indicating that removal of RB (basic dye) is enhanced by basic solution. This result is in harmony with the literature reports for basic dye [28,40,43,46,53].

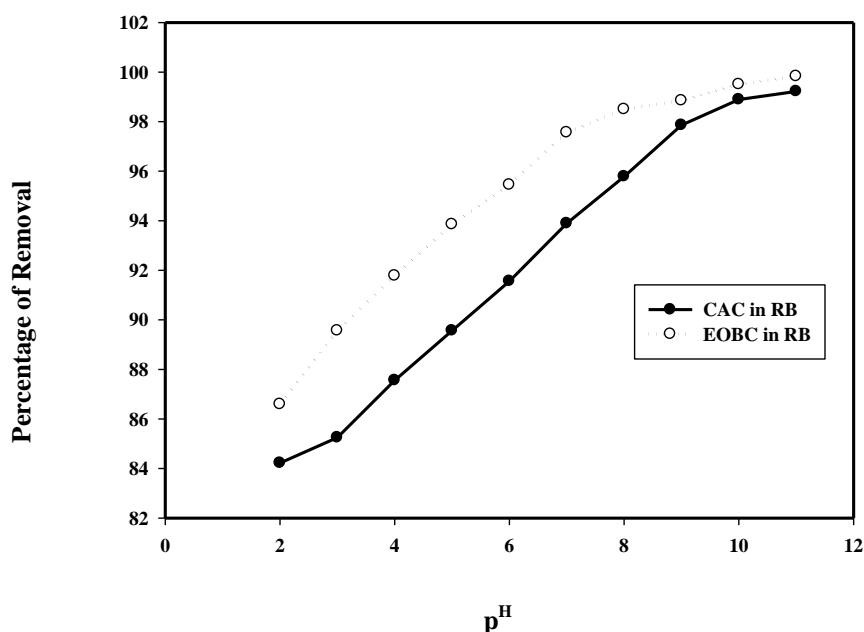


Figure 10. Effect of initial pH for the removal of RB onto CAC and EOBC

Effect of particle size

The amount of RB adsorbed increases linearly with the decrease in particle size of the adsorbent. This is due to the increase in available surface area with the decrease in particle size. The effect of particle size of EOBC (except CAC) on the amount adsorbed is shown in Figure 11.0. There exists a linear relationship between the amount adsorbed and particle size, as evidenced by the r-values close to unity (r-values for EOBC = 0.989). Similar observations have been reported for the adsorption of dyes [12,40,43-45,54].

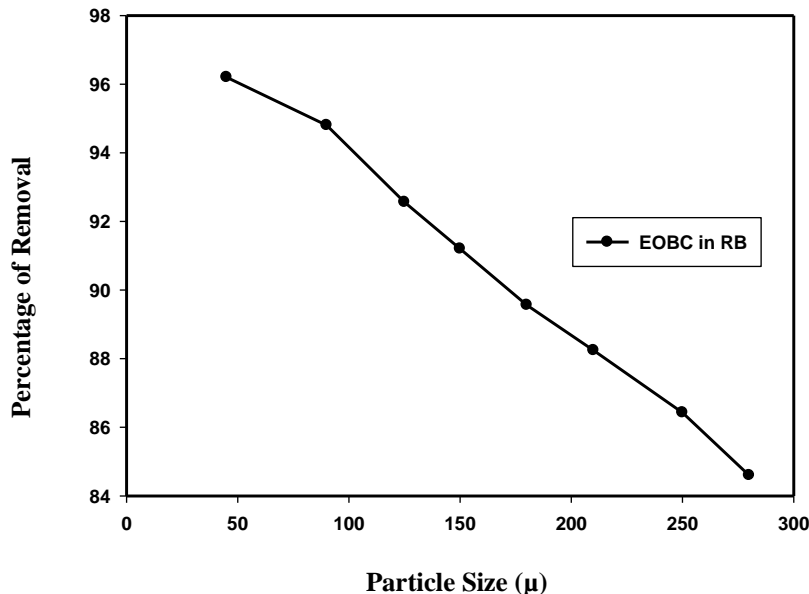


Figure 11. Effect of Particle size for the removal of RB onto EOBC

APPLICATIONS

The present study concludes that EOBC could be employed as low cost adsorbent as alternative to CAC for the removal of colour and dyes from water and wastewater in general and the data may be useful in construction, designing and fabrication of an economic treatment plant for the removal of Rhodamine B from wastewater. The results also helpful to design adsorption treatment systems and establishing a continuous treatment plant for water and wastewater.

CONCLUSION

The present study showed that *Emblica Officinalis Bark Carbon* (EOBC) can be used as an effective adsorbent for the removal of Rhodamine B dye from aqueous solution. The maximum adsorption capacity was observed (98.74%) by using carbonaceous *Emblica Officinalis Bark* at p^H of 7.5 with dose of 200 mg with agitation time of 30 minutes. The percentage removal of RB increases with decrease in initial concentration and particle size and increases with increase in contact time, initial pH and dose. The adsorption data are modeled with adsorption isotherms and first order kinetic equations. Adsorption process obeys Langmuir isotherm and Lagergren equation and proceeds with first order kinetics, with intra particle diffusion as one of the rate determining steps.

ACKNOWLEDGEMENT

The authors are thankful to the Management and the Principal of Ayya Nadar Janaki Ammal College, Sivakasi for providing facilities and support. The authors also thank the Director, Collegiate Education, Chennai and the Principal of H.H. the Rajah's College, Pudukkottai for providing permission to do Research work.

REFERENCES

- [1] S. Seshadri, P.L. Bishop, A.M Agha, Waste Manage., **1994**, 15, 127-137.
- [2] S.B.Bukallah, M.A. Rauf, S.S. Alali, Dyes Pigments, **2007**, 74, 85-87.
- [3] C. Namasivayam, R. Radhika, S. Suba, Waste Management, **2001**, 21 38 - 387.
- [4] I.D. Mall, V.C. Srivastava, N.K. Agarwal, Dyes Pigments, **2006**, 69, 210-223.
- [5] O.J. Hamdaoui, J. Hazard. Mater., **2006**, 135, 264-273.
- [6] S.T. Ong, C.K. Lee, Zainal, Bioresour. Technol, **2007**, 98, 2792-2799.
- [7] S. Srivastava, S. Sin, S. Roy, Aquat.Toxicol, **2004**, 66, 319-329.
- [8] S.J. Culp, F.A. Beland, J. Am. Coll. Toxicol,**1996**,15, 219-238
- [9] A. A. Attia, B.S. Girgis, N.A. Fathy, Dyes Pigments, **2008**, 76, 282-289.
- [10] E. E. Baldez, N.F. Robaina, R.J. Cassella, J. Hazard. Mater., **2008**, 159, 580 - 586
- [11] G. McKay, A.G Sweeney, Water Air Soil Pollution, **1980**, 14, 3-11.
- [12] N. Kannan M. MeenakshiSundaram, Dyes and Pigments, **2001**, 51, 25 - 40.
- [13] N. Kannan, M.Meenakshisundaram, Water Air and Soil Pollution, **2002**, 138, 289-305.
- [14] N. Kannan, A.Vijayakumar, P. Subramanian, E- J Chem., **2010**, 7 (3),770 - 774.
- [15] C. Namasivayam, N. Kanchana, Chemosphere, **1992**, 25, 1691-1706.
- [16] T. Robinson, B.Chandran, P.Nigam, Water Res. **2002**, 36, 2824 -2830.
- [17] V.K. Garg, A. Moiranthem, K. Rakesh, G. Renuka, Dyes Pigments, **2004**, 63, 243-250.
- [18] O. Serpil, K. Fikret, J. Environ. Manage, **2006**, 81,307-314.
- [19] M. Sujatha, A. Geetha, P. Sivakumar, P.N. Palanisamy, E- J. Chem., **2008**, 5(4),742- 753.
- [20] Y. Bulut, N. Gozubenli, H. Aydın, J. Hazard. Mater., **2007**, 144, 300-306.
- [21] M. T. Sulak, E. Demirbas, M. Kobya, Bioresour. Technol, **2006**, 98, 2590-2598.
- [22] A. Mittal, L. Kurup, J. Mittal, J. Hazard. Mater., **2007**, 146, 243-248.
- [23] S. S. Nawar, H.S. Doma, Sci.Total Enviro., **1989**, 79, 271.
- [24] K.S. Low, C.K. Lee, Pertanika, **1990**, 13, 221-228.
- [25] S. K. Khare, K.K. Pandey, R.M. Srivasatava, V.N. Singh, J. Chem.Tech., **1987**, 38, 99-104.
- [26] N. Kannan, R. Pagutharivalan, Indian Journal of Natural Sciences, **2011**, 1, 349-364
- [27] S. Arivoli, V. Ramuthai, M. Nandhakumar, M. Thiruchelvi, V. Vijayakumar, E-J. Chem., **2009**, 6 (S1), 363-S373.
- [28] S. Arivoli, B.R.Venkatraman, P.K. Baskaran, E-J Chem., **2011**, 8(1), 9-18.
- [29] Himmanushu patel, R.T.Vashi, E-J Chem., **2010**, 7(3), 975 - 984.
- [30] Lata Hem, V.K. Garg, R.K. Gupta, Desalination, **2008**, 219, 250 - 261
- [31] R.K.Ward, P. N .Nation, M. Maxwell, C.L. Barker, R.H. Clothier, Toxicol. In Vitro, **1997**, 11, 633 - 636.
- [32] H. Lata, S. Mor, V.K. Garg, P.K. Gupta, J. Hazard Mater., **2008**, 153, 213-220.
- [33] D. K. Kearns, Chem. Rev., **1971**, 71, 395 - 427.
- [34] F. P. Schafer, (Ed.), Dyes Lasers. Springer, Berlin Snavely, B.B. In Organic Molecular Photo physics. ed., Borkes, J.B. Wiley, New York, **1973**.

- [35] F. D. Snell, Photometric and Fluorometric Methods of Analysis, Part 2: Metals Chapter, **1978**
- [36] Uranium, Rhodamine B, P.1319–1396; Chapter 50: Thorium, Thoron, and P.1835-1844. John Wiley & Sons, New York.
- [37] G. Clark, (Ed.), Staining Procedures, fourth ed Williams and Wilkins, Baltimore 1981.
- [38] S. K. Srivastava, R. Tyagi, N. Pal, D. Mohan, J. Env. Eng., **1997**, 123(9), 842.
- [39] S. D. Richardson, C.S. Wilson, K. A. Rusch, Ground Water., **2004**, 42 (5), 678-688.
- [40] N. Bhadusha, T. Anantha baskaran, E-J Chem., **2011**, 8(4), 1696-1707.
- [41] G. Socrates “IR Characteristics Group Frequencies” John Wiley & Sons, New York, **1981**.
- [42] T. Murugan, A. Ganapathi, R.Valliappan, E-J Chem., **2010**,7(3),669-676.
- [43] C. Namasivayam, N. Kanchana, R.T.Yamuna, Waste Management, **1993**, 13, 89-95.
- [44] P. K. Dutta, Indian J. Env., Prot **2003**, 14, 443-446.
- [45] N. Kannan, M. Meenakshisundaram, Water Air Soil Pollut., **2003**, 138, 289.
- [46] N. Kannan, A.Vanangamudi, Indian J. Env., Prot **1991**, 11, 241.
- [47] N. Kannan, A. Rajakumar, Fres. Environ. Bull., **2002**, 11, 160.
- [48] A. Ramu, N.Kannan, A. Srivathsan A, Indian J.Env.Health, **1992**, 34, 192.
- [49] N. Kannan, A. Xavier, Toxic. Environ. Chem., **2001**, 79, 95.
- [50] N. Kannan, Indian J. Env., Prot **1991**, 11 (7), 514 -518.
- [51] S. Murugavel, " Kinetics and Equilibrium studies on the removal of dyes by Adsorption”, Ph.D., Thesis, Madurai Kamaraj University, Madurai, India, **2007**.
- [52] N. Kannan, S.Murugavel, Global Nest Journal, **2008**, 10 (3), 395 - 403.
- [53] T .W. Weber, and R.K. Chakravorti, J. Am. Inst. Chem. Eng., **1974**, 2, 228.
- [54] G. Crank, The mathematics of diffusion. London, Clarendon Press, NewYork, **1933**, pp.1.