

Spring 6-12-2014

# Equilibrium, kinetic and thermodynamic study of adsorption of rhodamine B from aqueous solution by activated carbon from *Peltophorum Pterocarpum* leaf

B. Jeyaraj  
*Loyola College*

Y. Subbareddy  
*Loyola College*

C. Jayakumar  
*Loyola College*

K.S. Nagaraja  
*Loyola College*

S. Valliammai  
*Loyola College*

Follow this and additional works at: [http://dc.engconfintl.org/wbtr\\_i](http://dc.engconfintl.org/wbtr_i)

 Part of the [Environmental Engineering Commons](#)

---

## Recommended Citation

B. Jeyaraj, Y. Subbareddy, C. Jayakumar, K.S. Nagaraja, and S. Valliammai, "Equilibrium, kinetic and thermodynamic study of adsorption of rhodamine B from aqueous solution by activated carbon from *Peltophorum Pterocarpum* leaf" in "Wastewater and Biosolids Treatment and Reuse: Bridging Modeling and Experimental Studies", Dr. Domenico Santoro, Trojan Technologies and Western University Eds, ECI Symposium Series, (2014). [http://dc.engconfintl.org/wbtr\\_i/39](http://dc.engconfintl.org/wbtr_i/39)

This Conference Proceeding is brought to you for free and open access by the Proceedings at ECI Digital Archives. It has been accepted for inclusion in Wastewater and Biosolids Treatment and Reuse: Bridging Modeling and Experimental Studies by an authorized administrator of ECI Digital Archives. For more information, please contact [franco@bepress.com](mailto:franco@bepress.com).

# Equilibrium, Kinetic and thermodynamic study of adsorption of Rhodamine B from aqueous solution by activated carbon from *Peltophorum Pterocarpum* leaf

**B.Jeyaraj, Y.Subbareddy, C.Jayakumar, K.S.Nagaraja, S.Valliammai**

**Department of Chemistry, Loyola Institute of Frontier Energy,**

**Loyola College(Autonomous),**

**College of Excellence(CE), Chennai-34.**



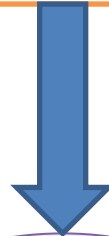
**Wastewater and Biosolids Treatment and Reuse, to be held from  
June 8-14, 2014, in Otranto, Italy**

# INTRODUCTION

- Pigments and dyes are widely used in the textiles and leather dyeing, paper, printing, pharmaceutical and cosmetic industries.
- There are nearly 10,000 dyes with an annual production of  $8 \times 10^5$  tones.
- Approximately 15% of the dyestuffs are lost in the industrial effluent during manufacturing and processing operations.
- Nearly, there are 756 dyeing industries in and around Thirupur and Erode Districts in Tamilnadu, India
- 8500 acres of land are being polluted.

.

DYE INDUSTRIES



Solid waste

Types of Pollutants

Water pollution



RIVER NOYYAL



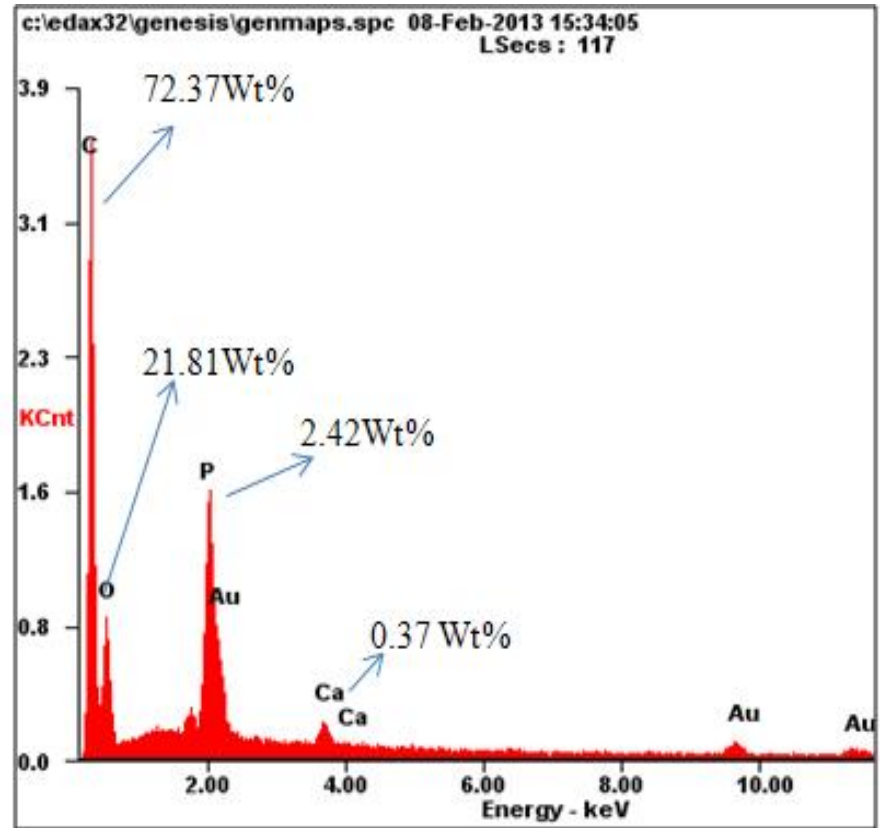
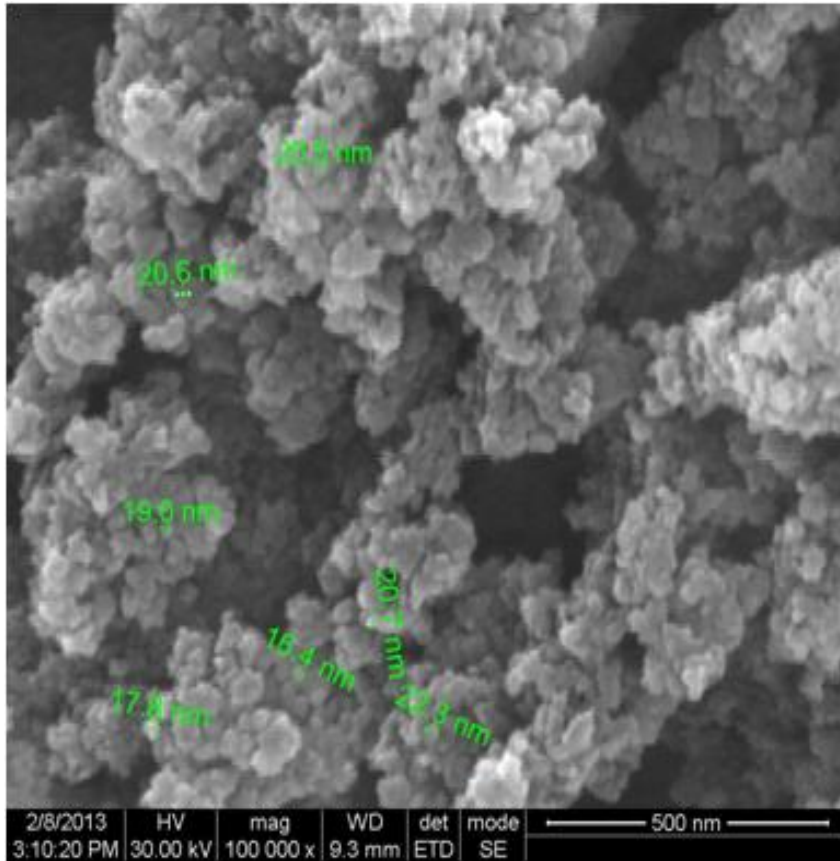
# EFFECTS OF EFFLUENT

1. Imparts color to water bodies.
2. Reduces light penetration and photosynthesis
3. Dyes increase BOD of effluent thereby affecting aquatic life.
4. When it is released into rivers or lakes, it is toxic to fish & microbial organisms.
5. Rhodamine B (RB) is widely used as a colorant in textiles and food stuff. RB is carcinogenic and also harmful to the environment.
6. It is important to remove RB from textile effluent.

# Preparation of Activated carbon

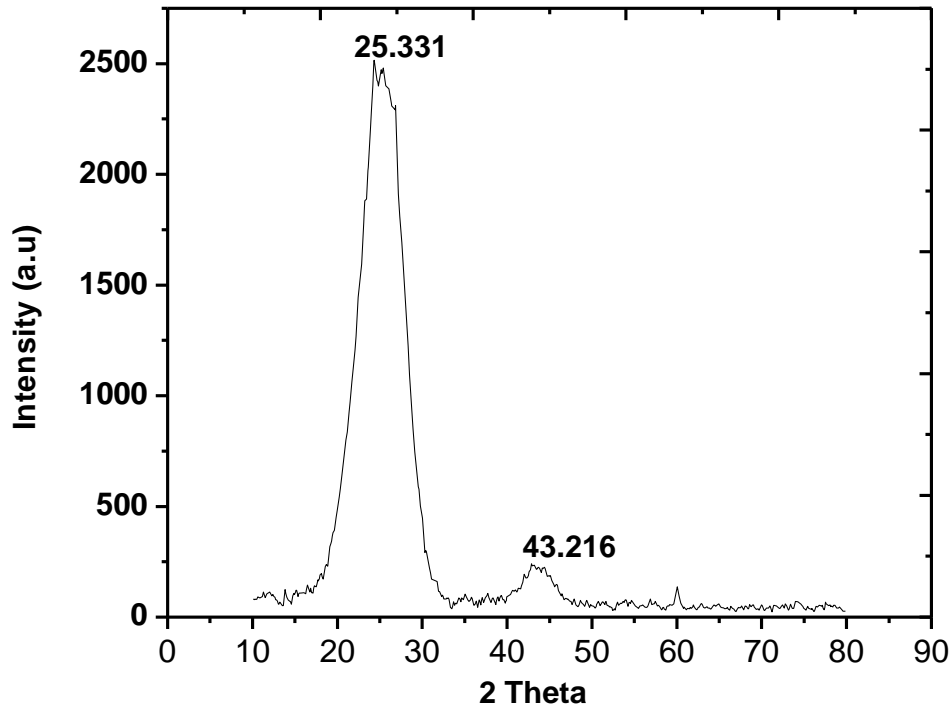
- ❖ *Peltophorum Pterocarpum* leaves were dried at room temperature.
- ❖ After grinding to a fine powder, the mass was oven dried at 110 °C for 2h. The dried mass was impregnated with H<sub>3</sub>PO<sub>4</sub> (85 wt. %) in the ratio of 5:1 (g H<sub>3</sub>PO<sub>4</sub> /g *Peltophorum pterocarpum* leaves powder) and allowed to carbonize at 450 °C in a muffle furnace for 1h.
- ❖ The obtained carbon material was washed with distilled water and dried overnight at 110°C.

# 1. SEM and EDAX Analysis of PAC



The surface morphology of the activated carbon observed by SEM indicated the presence of various sizes of pores on its surface ranging between 16.4 nm to 22.3 nm. It can be concluded that the synthesized activated carbon is nanomaterial in nature. **These nano pores allow the molecules of the dye to be adsorbed**

## 2. XRD Pattern of PAC



- The two diffraction peaks centered at  $2\theta$  of  $25.331^\circ$  and  $43.216^\circ$  were attributed to 002 and 101 planes of the graphitic carbon.
- The inter layer spacing ( $d_{002}$ ) was calculated using the Bragg's law

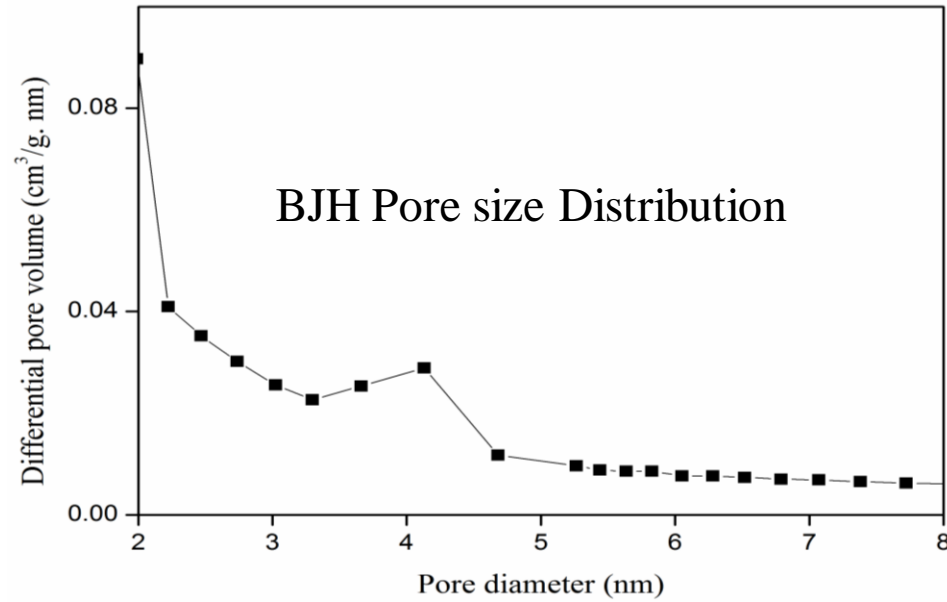
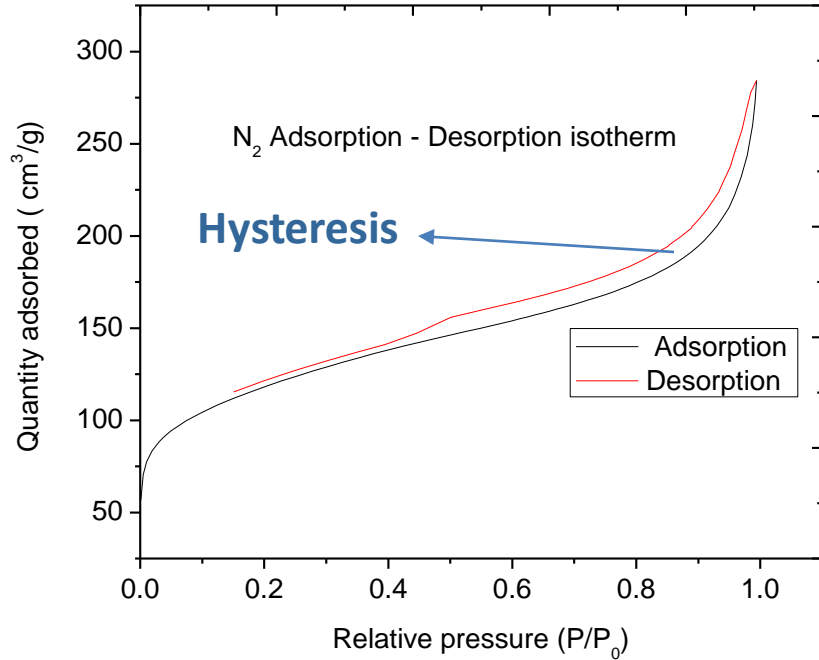
$$d = \frac{\lambda}{2 \sin \theta}$$

where,  $d$  is interlayer distance between two adjacent carbon sheets ( $d_{002}$ ),  $\lambda$  is wave length of X-rays and  $\theta$  is Bragg's angle.

The value of interlayer distance between two planes was found to be 0.351nm. The calculated interlayer spacing of PAC was near to the standard interlayer spacing of pure graphite carbon. **The activated carbon in the present study is graphitic and nanocrystalline in nature.**

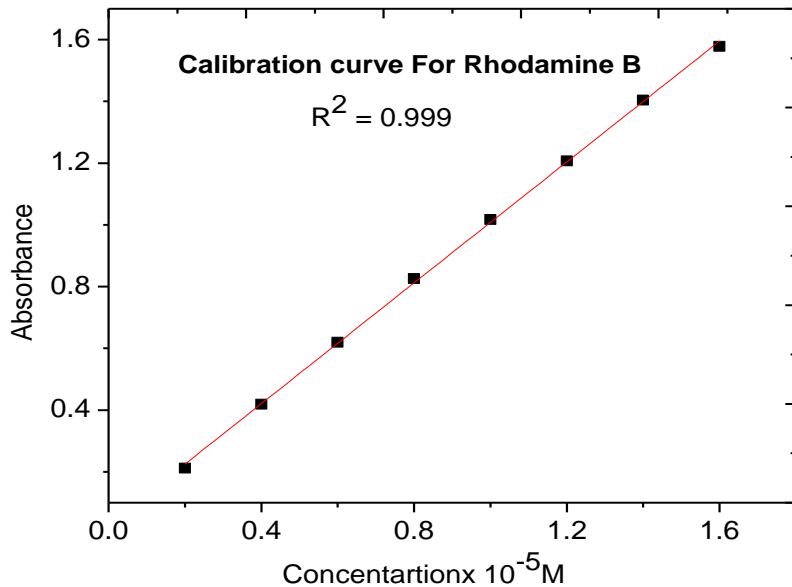


# 3. BET Analysis of PAC

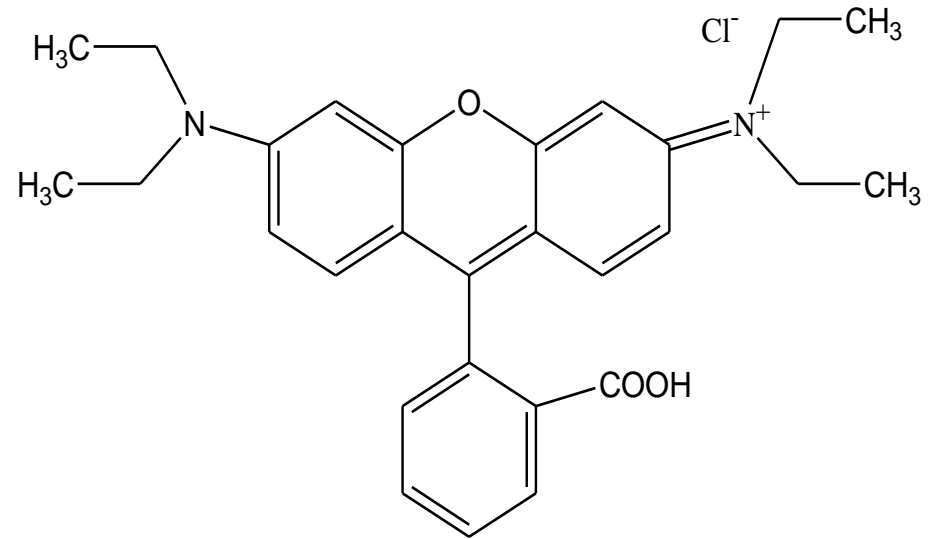


The BET surface area of the PAC is found to be 409.01m<sup>2</sup>/g. The Barret Joyner Halenda (BJH) pore size distribution indicates that the sample PAC has mesoporosity with pore diameter in the range of 2– 5 nm. The average pore diameter of PAC was found to be 4.3 nm which confirms the presence of mesopores.

# Adsorptive removal of Rhodamine B By PAC



**Calibration curve**



**Structure of the Rhodamine B**

Absorption maximum : 554nm  
Molecular formula :  $C_{28}H_{31}ClN_2O_3$   
Formula weight : 3479.02 g/mol

## Experimental procedure

Batch experiments were carried out in 100ml conical flasks with 50ml working solution of Rhodamine B (RB) with Activated carbon for 120 min in a temperature controlled shaker.

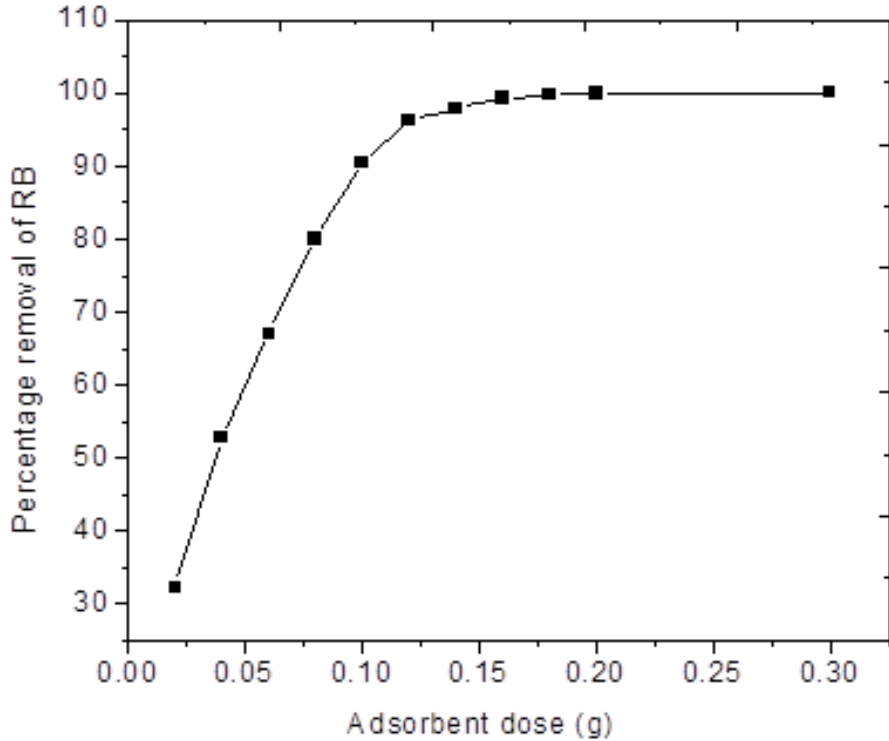
The solutions were centrifuged at 5000 rpm for 15 min and the absorbance of the supernatant solution was measured to determine the residual concentration at  $\lambda_{\max}$  554 nm by using UV – visible spectrophotometer.

$$\text{Percentage removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100$$

$$\text{Amount Adsorbed}(q_e) = (C_0 - C_e) \times \frac{V}{m}$$

where  $C_0$  and  $C_e$  (mol/L) are the initial and equilibrium concentrations of the dye respectively,  $V$ (L) is the volume of dye solution and  $m$ (g) is the mass of adsorbent used.

# 1. Effect of adsorbent dose

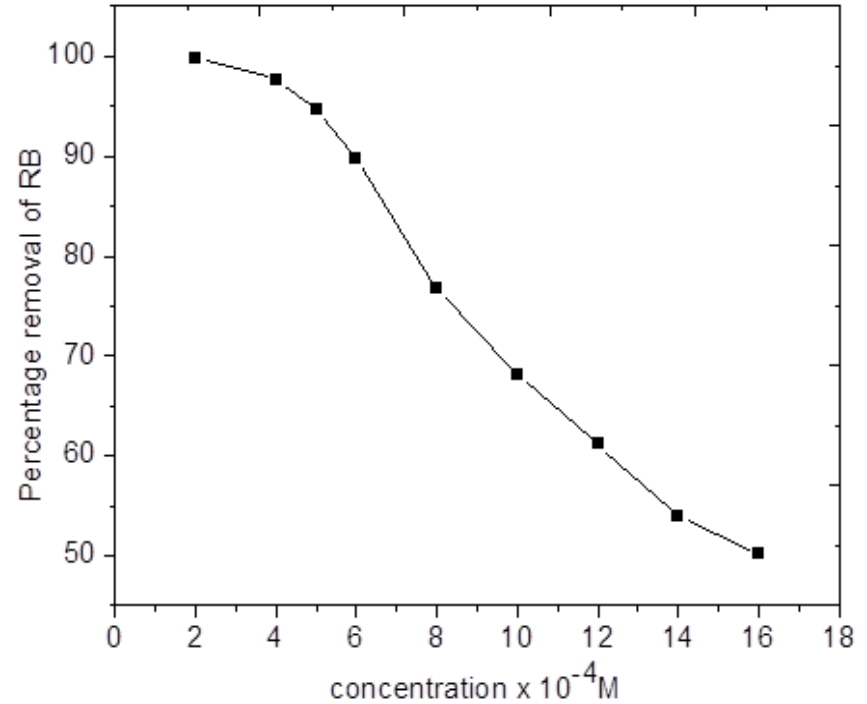


Effect of adsorbent dose on the removal of RB ( $6 \times 10^{-4}$  M), contact time 120 min.

The percentage adsorption of RB increases with increasing adsorbent mass. This is mainly due to increase in the active and vacuous areas over the surface of adsorbent.

**Optimum dose was found to be 0.1 g.**

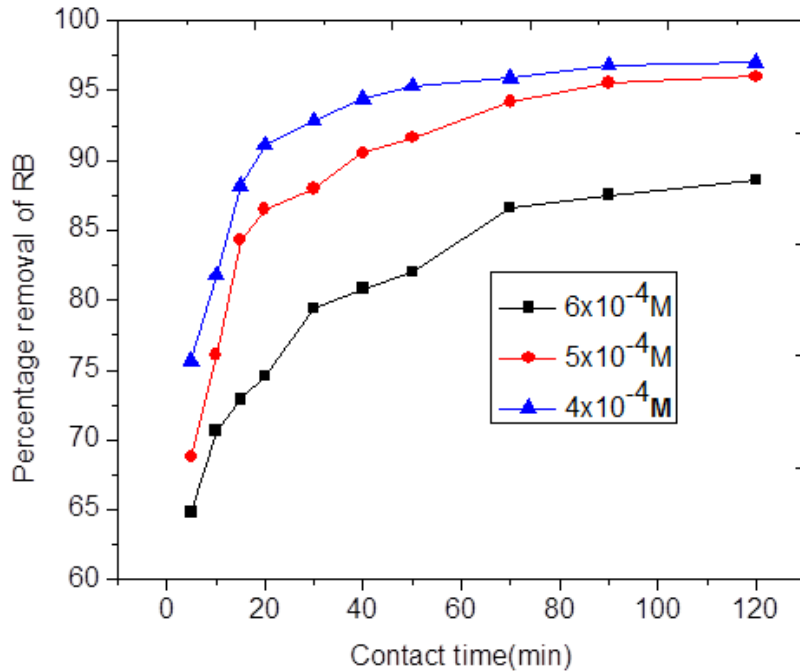
# 2. Effect of concentration



Effect of concentration for the removal RB by PAC (0.1g), contact time 120 min.

The percentage removal decreases with increase of RB concentration. At higher concentration, greater number of RB molecules would quickly saturate the binding sites found on the surface of PAC.

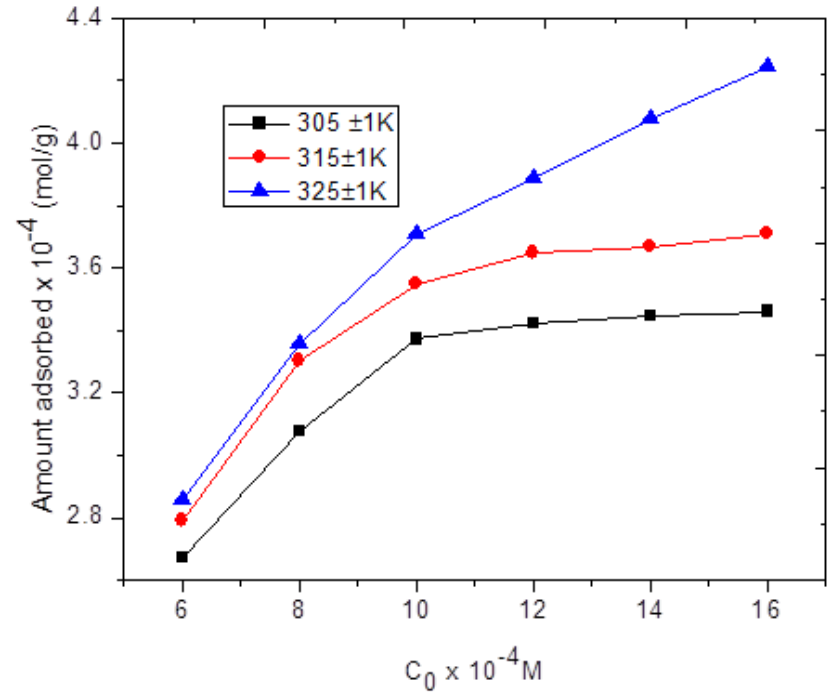
### 3. Effect of Contact time



Effect of contact time on the adsorption of RB by PAC (0.1g ) concentration  $4 \times 10^{-4}$ ,  $5 \times 10^{-4}$  M and  $6 \times 10^{-4}$  M.

As the contact time increases the percentage removal is increasing due to availability of active sites.

### 4. Effect of Temperature



Effect temperature for the removal of RB by PAC (0.1g) contact time 120min.

The removal of RB dye increases with increase in temperature. The positive effect of temperature on the adsorption of RB dye indicates that adsorption process is endothermic in nature.

# Adsorption isotherms

## Freundlich Adsorption Isotherm

$$\log(q_e) = \log(K_f) + \frac{1}{n} \log(C_e)$$

where  $q_e$  (mol/g) is the amount of dye adsorbed at equilibrium,  $C_e$  (mol/L) is the equilibrium dye concentration in solution,  $K_f$  (mol/g) and  $n$  are constants.

## Dubinin- Radushkevich adsorption isotherm

$$\ln(q_e) = \ln(Q_m) - K\varepsilon^2$$
$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right)$$
$$E = \frac{1}{\sqrt{(2K)}}$$

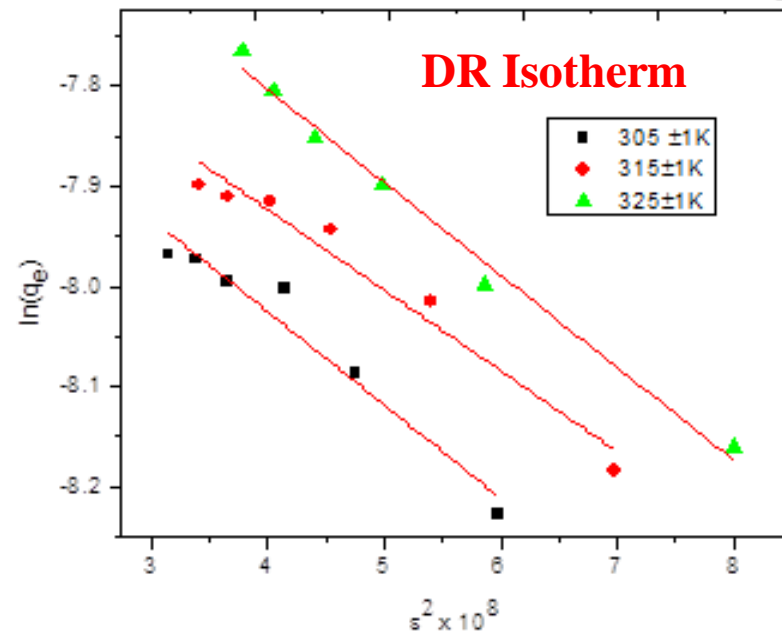
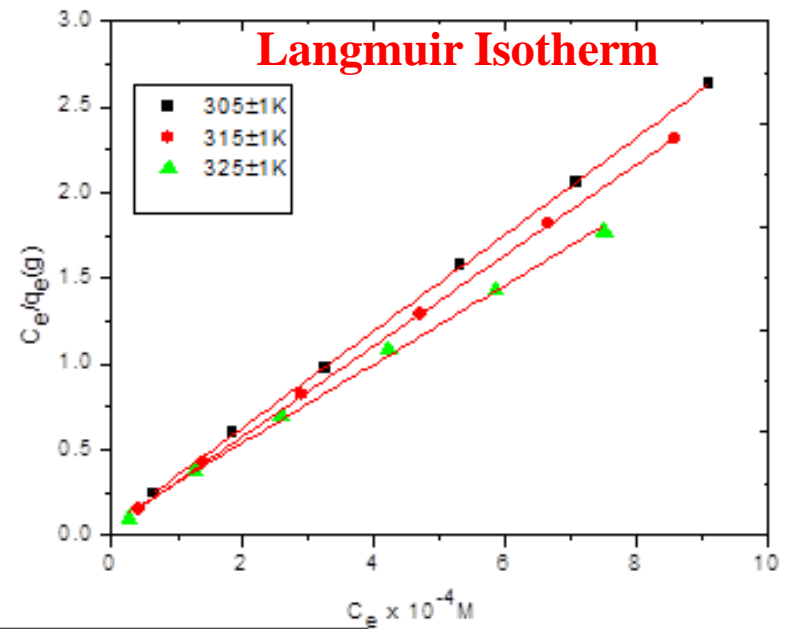
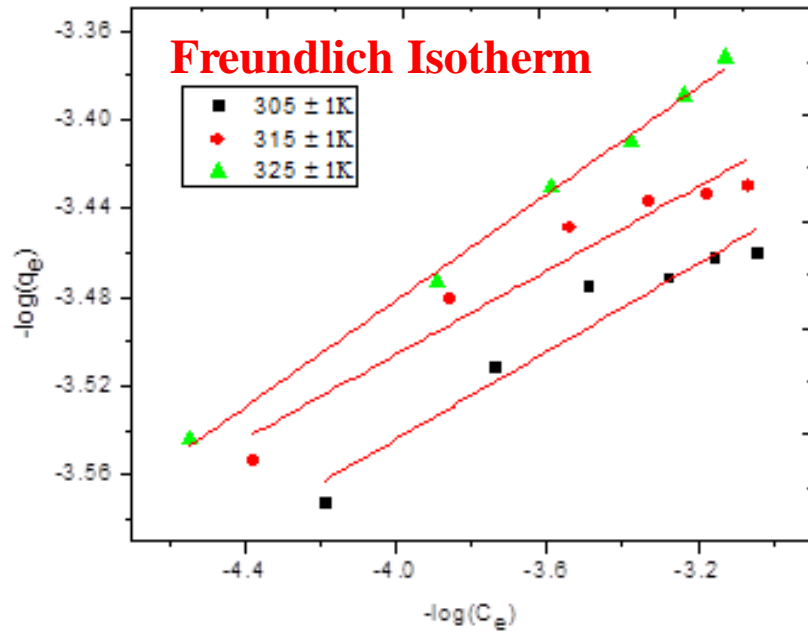
where  $K$  (mol<sup>2</sup>/KJ<sup>2</sup>) is constant related to the adsorption constant, and  $\varepsilon$  is the Polanyi potential and  $E$  is mean free energy of sorption (kJ/mol), **If  $E < 8$ , then it is due to physical adsorption ,**  
**If  $E$  is 8 to 16 then the adsorption takes place via ion exchange and  $E > 16$  then the adsorption is due to chemical nature.**

## Langmuir Adsorption Isotherm

$$\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{1}{Q_m} C_e$$
$$R_L = \frac{1}{1 + K_L C_0}$$

where  $q_e$  (mol/g) and  $C_e$  (mol/L) are the amount of dye adsorbed per unit weight of adsorbent and the concentration of the dye solution at equilibrium. The constant  $Q_m$  (mol/g) is the adsorption capacity and  $K_L$  (L/mol) is the Langmuir equilibrium constant.

# Adsorption Isotherms



## Adsorption isotherm parameters

<b>Rhodamine B – PAC system</b>				
Adsorption parameters	Isotherm	Temperature(K)		
		305	315	325
<b>Langmuir adsorption isotherm</b>				
<b><math>Q_m</math> (mol/g)</b>		<b><math>3.551 \times 10^{-4}</math></b>	<b><math>3.778 \times 10^{-4}</math></b>	<b><math>4.344 \times 10^{-4}</math></b>
$K_L$ (L/mol)		$4.16 \times 10^4$	$5.673 \times 10^4$	$5.974 \times 10^4$
<b><math>R^2</math></b>		<b>0.999</b>	<b>0.999</b>	<b>0.999</b>
$R_L$		0.038	0.028	0.053
<b>Freudlich adsorption isotherm</b>				
1/n		0.098	0.094	0.119
<b><math>K_f</math> (mol/g)</b>		<b><math>7.095 \times 10^{-4}</math></b>	<b><math>7.441 \times 10^{-4}</math></b>	<b><math>9.948 \times 10^{-4}</math></b>
$R^2$		<b>0.920</b>	<b>0.926</b>	<b>0.995</b>
<b>DR- adsorption isotherm</b>				
$Q_m$ (mol/g)		$4.7446 \times 10^{-4}$	$4.994 \times 10^{-4}$	$5.903 \times 10^{-4}$
$K$ (mol <sup>2</sup> /KJ <sup>2</sup> )		$0.093 \times 10^{-8}$	$0.080 \times 10^{-8}$	$0.092 \times 10^{-8}$
<b><math>E</math> (kJ/mol)</b>		<b>23.183</b>	<b>24.933</b>	<b>23.269</b>
$R^2$		<b>0.945</b>	<b>0.952</b>	<b>0.986</b>

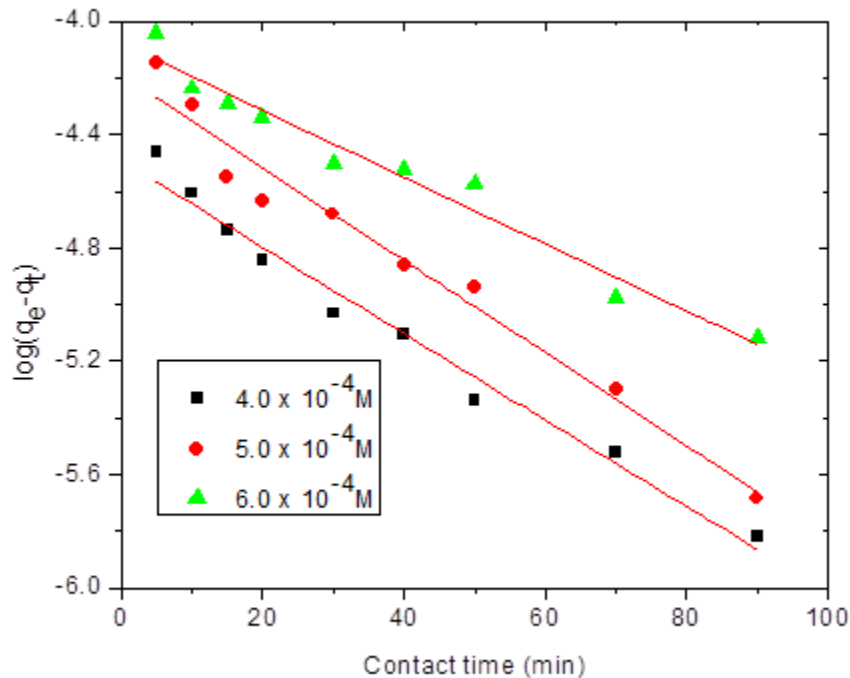


# Adsorption Kinetics

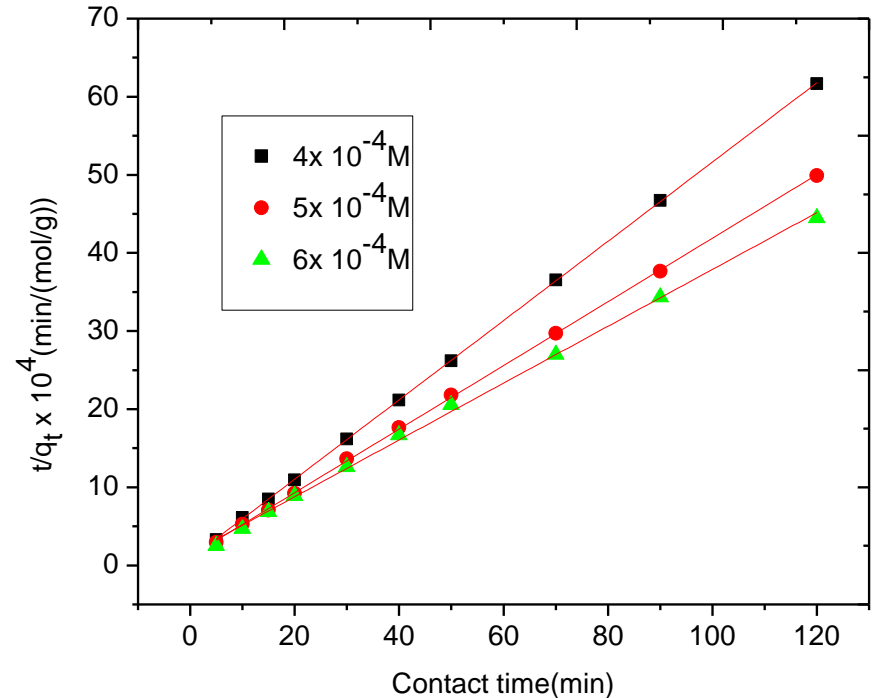
$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

where  $q_e$  and  $q_t$  are the adsorption capacity at equilibrium and at time  $t$ , respectively (mol/g),  $k_1$  is the rate constant of pseudo-first-order adsorption (L/min) and  $k_2$  is the pseudo second order rate constant (g/mol min).



**Pseudo first order**



**Pseudo second order**

# Thermodynamic parameters

$$\Delta G^0 = -RT \ln K_L$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\Delta H^0 = -R \frac{T_2 T_1}{T_2 - T_1} \ln \frac{K_{L1}}{K_{L2}}$$

where  $K_L$ ,  $K_{L1}$  and  $K_{L2}$  are the Langmuir constants at different temperatures,  $R$  is the universal gas constant (8.314 J/mol/K) and  $T$  is the Kelvin temperature

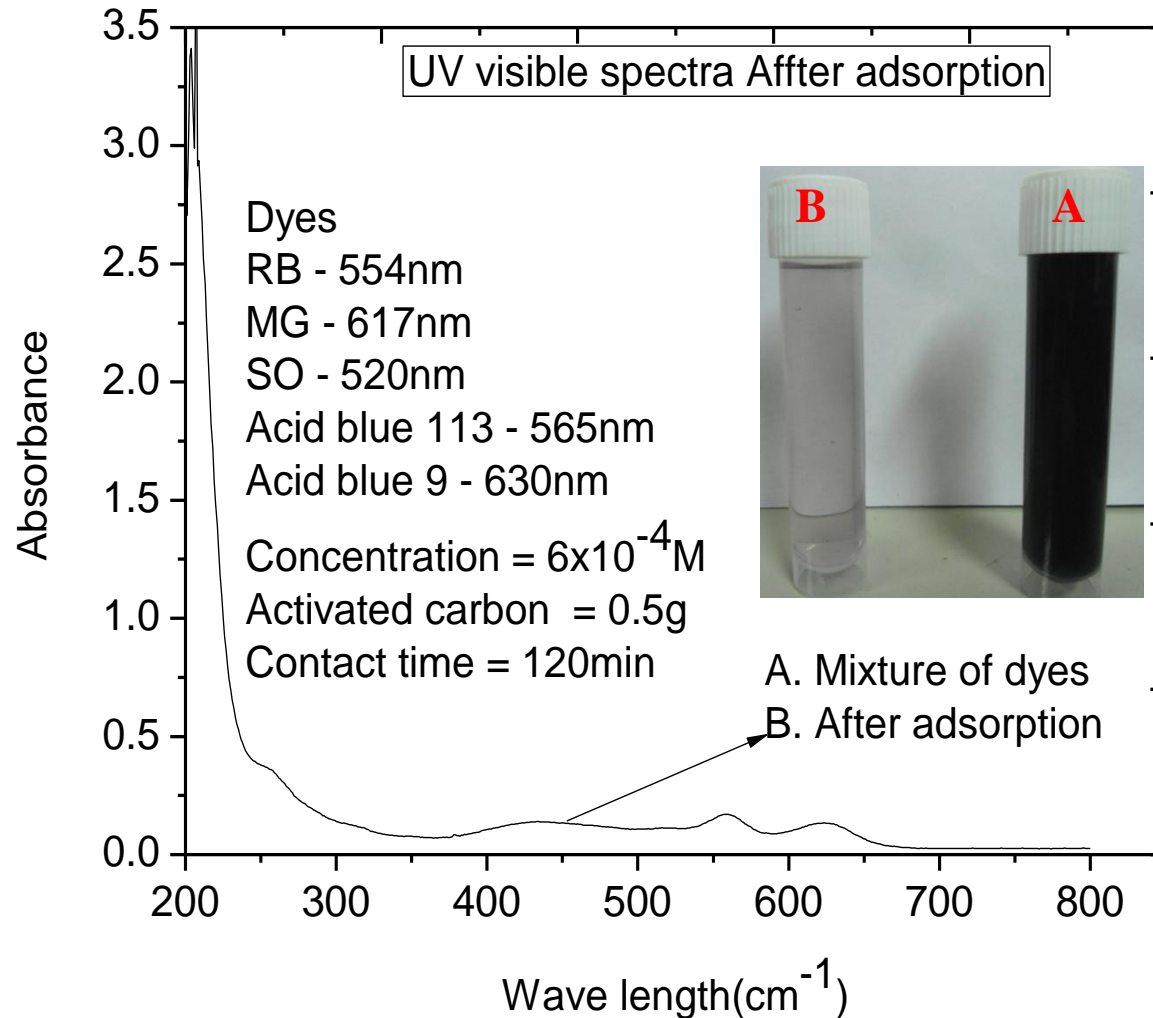
Temperature (K)	$\Delta G^0$ (kJ/mol)	$\Delta H^0$ (kJ/mol)	$\Delta S^0$ (J/mol/K)
305	-26.970	24.776	169.659
315	-28.666		
325	-29.716		

# Desorption studies

- The desorption studies are necessary to elucidate the nature of adsorption mechanism and to regenerate the adsorbent.
- RB adsorbed on PAC was desorbed by Ethanol, Acetone, 0.1N Acetic acid and 0.1N NaOH respectively.
- The maximum desorption occurred with Ethanol as the desorbing medium. This strongly suggests that chemisorption might be the major mode of dye removal by the adsorbent.

<b>Desorbing reagent</b>	<b>Desorption (%)</b>
Ethanol	79.005
Acetone	49.893
0.1N Acetic Acid	2.411
0.1N NaOH	3.344

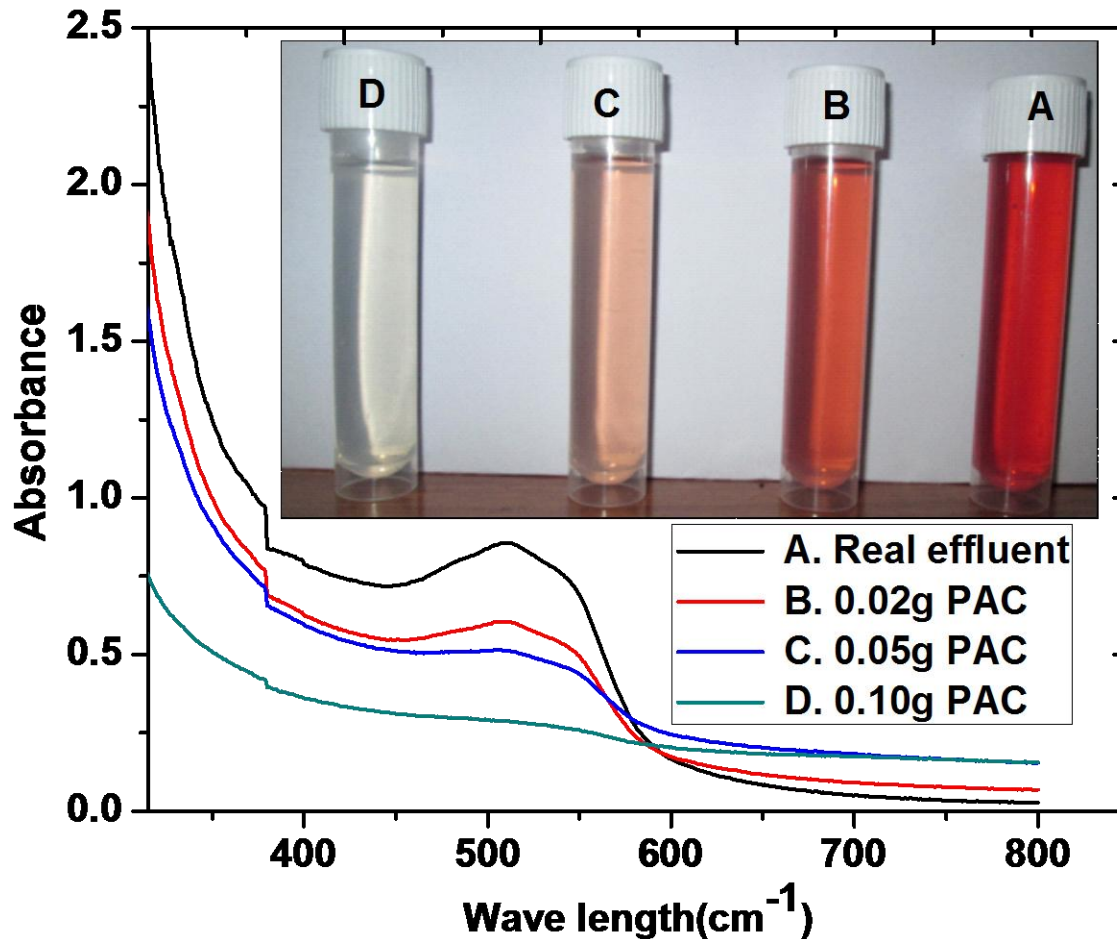
# Adsorptive removal of mixture of dyes (Cocktail of dye solution) with Activated carbon



- A cocktail of dye solution was prepared by mixing  $6 \times 10^{-4}$  M of each Malachite green, Rhodamine B, Safranin O, Acid blue 113 and Acid blue 9 and tested for adsorptive removal by using Activated carbon.
- 100% removal was seen except Acid blue 9 and acid blue 113.

# Removal of color from Real textile effluent with PAC

The real effluent was collected from a textile industry in Thirupur. Experiments were carried out to remove the dyes from the effluent (50ml) with 0.02g, 0.05g and 0.1g of activated carbon contacted for 1hrs.



- COD : 6060mg – **720mg**
- BOD: 1800mg – **300mg**

# Conclusions

- ❖ The Langmuir monolayer adsorption capacity of RB dye - PAC system was estimated as  $3.551 \times 10^{-4}$  mol/g.
- ❖ The mean free energy of sorption (E) value was found to be 24.933kJ/mol, indicating that chemisorption might be the major mode in the adsorption of RB.
- ❖ The adsorption kinetics of RB dye with PAC followed the pseudo second order kinetics
- ❖ The negative values of  $\Delta G^\circ$  and the positive value of  $\Delta H^\circ$  indicated the process is spontaneous and endothermic in nature. It is due to high positive value of  $\Delta S^\circ$  and entropy driven process.
- ❖ The desorption studies suggest that 79% of the dyes can be recovered from the adsorbent.
- ❖ The PAC effectively removes Rhodamine B from aqueous solution. Also the PAC can be efficiently used for the adsorptive removal of dyes from real effluents from the dye industries.





THANK  
YOU