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## Removal of Congo red Dye from Aqueous solution using Acid Activated Eco-Friendly Low Cost Carbon prepared from marine algae *Valoria bryopsis*

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**ABSTRACT**

*Activated carbon (AC) prepared from marine algae was found to be a potential adsorbent for Congo red dye for removal from aqueous solution. The AC was prepared from marine algae Valoria bryopsis by treatment with conc. $H_2SO_4$. The surface area of the AC and its properties were studied by scanning electron microscopy (SEM). Adsorptive removal of Congo red from aqueous solution onto AC has been studied under varying conditions of agitation time, metal ion concentration, adsorbent dose and pH to assess the kinetic and equilibrium parameters. Adsorption equilibrium was found to be reached in 180 min for 5 to 25 mg/L of Congo red concentrations. The Langmuir and Freundlich isotherm models were found to provide an excellent fitting of the adsorption data. For the Freundlich isotherm, high $r^2$ values were obtained (0.8460 to 0.6992) for Congo red concentration of 10 to 60mg/L, which indicated favorable adsorption of Congo red onto marine algae carbon. The adsorption capacity of Congo red was found to be 97.77%. The percent removal increased with increase in pH from 1 to 5. This adsorbent was found to be effective and economically attractive.*

**Keywords:** Activated carbon, Valoria bryopsis, Adsorption, Congo red.

## INTRODUCTION

The potable water used by every human being for drinking and cooking should be uncontaminated and pure. Thanks to the over-population, India is suffering from persistent demand for safe drinking water. Industries manufacturing dye and dye intermediates are the largest sector of chemical industries in India, since dyes are used in a variety of industries producing textiles, paints, pulp and paper. More than 80% of their production is utilized by the textile industries. A huge amount of water is necessary by these industries for the cleaning and washing purposes and they discharge highly coloured effluents containing different dyes. The presence of dyes and colour upsets the biological processes. Dyes are also carcinogenic and pose a major health hazard. Many investigators have studied the feasibility of inexpensive alternative materials like pearl millet husk, date pits, saw dust, buffing dust of leather industry, coir pith, crude oil residue tropical grass, olive stone and almond shells, pine bark, wool waste, coconut shell etc., as carbonaceous precursors for the removal of dyes from water and wastewater. The present study was undertaken to evaluate the efficiency of an acid activated carbon adsorbent prepared from marine algae for removal of congo red dye from aqueous solution. In order to design adsorption treatment systems, knowledge of kinetic and mass transfer processes is essential. The applicability of these processes was studied.

The dried marine algae valoria bryopsis were treated with concentrated sulphuric acid in the weight ratio of 1:1 (w/v) for eight hours and the resulting material was washed with double distilled water until a constant pH of the slurry was reached. The resulting black product was kept in muffle furnace maintained at 400$^o$ C for 8 hrs. It was then ground and the portion retained between 0 and 60 nm sieves was used in all the experiments.

## EXPERIMENTAL SECTION

### Adsorption Experiments

### Batch equilibration method

The adsorption experiments were carried out in batch process at 30, 40, 50 and 60 ˚C temperatures. A known weight of adsorbent material was added to 50 mL of the dye solutions with an initial concentration of 5 mg/L to 25 mg/L. The contents were shaken thoroughly using a mechanical shaker rotating with a speed of 120 rpm for three hours The solution was then filtered at preset time intervals and the residual dye concentration was measured.

**Table. 1. Effect of adsorbent dosage on removal of CR dye**

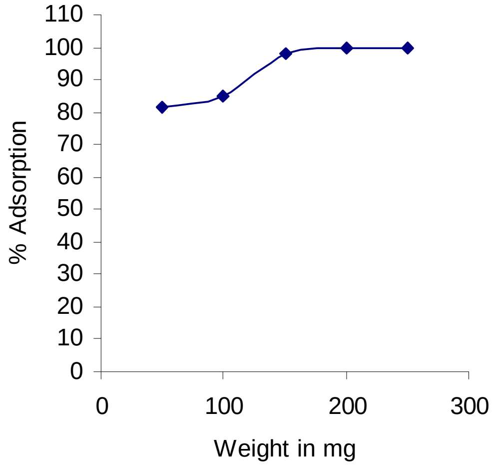
| S. No | Adsorbent dosage (mg) | CR % of adsorption |
|---|---|---|
| 1. | 50 | 81.48 |
| 2. | 100 | 85.19 |
| 3. | 150 | 97.77 |
| 4. | 200 | 100.0 |
| 5. | 250 | 100.0 |

### Effect of variable parameters :

### Dosage of adsorbent

The adsorption capacities for different doses of the adsorbent (namely 50,100,150,200 and 250mg) were determined at definite time intervals for the concentration range 50– 250 mg/L by keeping all other factors constant. The results are shown in Table1 and Figure1. It is apparent that the percentage removal of dye increases rapidly with increase in adsorbent dose, probably due to the greater availability of the exchangeable sites or the increased surface area.

**Figure.1. Effect of adsorbent dosage on removal of CR dye**



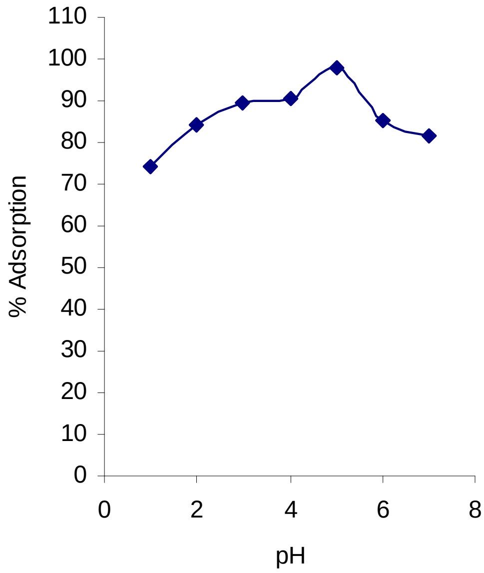

### Initial concentration of dye

Experiments were conducted with different initial concentrations of dyes ranging from 5 to 25 mg/L. All other factors were kept constant.

### Contact time

The effect of contact time on the removal of the dye in a single cycle was determined by keeping particle size, initial concentration, dosage, temperature, pH and concentration of other ions constant. For varying initial dye concentrations ranging from 5 to 25 mg/L. As much as 97.77% of the dye was found to be removed with a contact time of 3 hours.

**Figure.2.Effect of pH on removal of Congo red using Valoria bryopsis**



## pH
Adsorption experiments were carried out at pH 1,2,3,4,5,6,and 7. The acidic and alkaline pH of the media was maintained by adding the required amounts of dilute hydrochloric acid and sodium hydroxide solutions. The parameters like particle size of the adsorbents, dye concentration, dosage of the adsorbent, temperature and concentration of other ions were kept constant while carrying out the experiments. The pH of the samples were maintained using a portable pH meter, Systronics make. The pH meter was calibrated with 4.0 and 9.2 buffers. . Figure 2 shows the effect of pH on dye removal efficiencies of Valoria bryopsis. It can be observed that the removal of dye by Valoria bryopsis was maximum at pH 5.

## Temperature
The adsorption experiments were performed at four different temperatures namely, 30, 40, 50 and 60˚C in a thermostat attached with a shaker, Hasthas make. The constancy of the temperature was maintained with an accuracy of ± 0.5 ºC.

## Desorption studies
Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye. The effect of various reagents used for desorption were studied. The results with water, acetic acid , 0.1M Hydrochloric acid are presented in the Table-2. Desorption increases with increase in the acidly of the desorbing medium. It is higher in hydrochloric acid than in acetic acid. This could be due to the increased solubility of congo red in acidic medium.

**Table.2.Desportion of Valoria bryopsis**

| Adsorbate | % Desorption | | |
|---|---|---|---|
| Valoria bryopsis | $H_2O$ | ACOH | HCl |
| | 30.72 | 65.78 | 82.42 |

**Table.3. First order parameters for the adsorption of Congo red using Valoria bryopsis at 30°C**

| Adsorbate | Mg/l | Equilibrium uptake mg/g | | $k_1$ | $r^2$ |
|---|---|---|---|---|---|
| | | $q_{e\,(I)}$ | $q_{e\,(exp)}$ | | |
| Valoria bryopsis | 10 | 3.3333 | 2.4424 | 0.02108 | 0.9847 |
| | 20 | 6.6666 | 8.9186 | 0.02799 | 0.9828 |
| | 30 | 9.9999 | 9.9991 | 0.01594 | 0.9094 |

**Table.4. Pseudo second order parameters for the adsorption of Congo red using Valoria bryopsis at 30°C**

| Adsorbate | Mg/l | Equilibrium uptake mg/g $q_e$ | $k_2$ | $r^2$ |
|---|---|---|---|---|
| Valoria bryopsis | 10 | 3.4674 | 0.01550 | 0.9670 |
| | 20 | 4.5335 | 0.08977 | 0.9302 |
| | 30 | 10.5203 | 0.01773 | 0.5256 |

## Adsorption Kinetics
Kinetics of the adsorption process was studied by measuring the percentage adsorption at different time intervals namely 10,20,30,40,50 and 60 min and the data fed into four kinetic

models – first order, pseudo – second order, Elovich and the intraparticle diffusion( Tables 3,4,5 & 6). The values of rate constants and adsorption capacities were measured.

**Table.5. Elovic parameters for the adsorption of Congo red using Valoria bryopsis at 30°C**

| Adsorbate | Mg/l | A | $\alpha\ \beta_E$ | $\beta_E$ | $r^2$ |
|---|---|---|---|---|---|
| Valoria bryopsis | 10 | 0.6699 | 1.1258 | 1.6804 | 0.5667 |
| | 20 | 0.1169 | 0.04164 | 0.3558 | 0.9671 |
| | 30 | 0.4544 | 0.2174 | 0.4785 | 0.7406 |

**Table.6. Intraparticle diffusion for the adsorption of Congo red using Valoria bryopsis at 30°C**

| Adsorbate | Mg/l | A | $k_{id}$ | $r^2$ |
|---|---|---|---|---|
| Valoria bryopsis | 10 | 0.4086 | 2.7346 | 0.9748 |
| | 20 | 1.0859 | 1.5907 | 0.9285 |
| | 30 | 1.7099 | 2.5375 | 0.8499 |

**Table.7. Isotherm parameters for the adsorption of Congo red using Valoria bryopsis at 30°C**
**Langmuir plot**

| Adsorbate | Model | Model parameters | | | |
|---|---|---|---|---|---|
| | | $K_L$ | $b_L$ | $q_o$ | $r^2$ |
| Valoria bryopsis | Langmuir plot- I | 20.2015 | 3.5454 | 5.6977 | 0.9956 |
| | Langmuir plot- II | 10.0994 | 1.0847 | 9.3135 | 0.9152 |

**Freundlich plot**

| Adsorbate | Model | Model parameters | | | |
|---|---|---|---|---|---|
| | | $K_F$ | 1/n | n | $r^2$ |
| Valoria bryopsis | Freundlich plot -I | 4.9430 | 0.5224 | 1.9142 | 0.8460 |
| | Freundlich plot -II | 11.0773 | 0.8007 | 1.2488 | 0.6992 |

**DKR plot**

| Adsorbate | Model | Model parameters | | | |
|---|---|---|---|---|---|
| | | $\varepsilon^2$ | $\beta$ | $q_o$ | $r^2$ |
| Valoria bryopsis | DKR plot-I | 9.5113 | 0.04916 | 5.0470 | 0.9437 |
| | DKR plot-II | 9.2830 | 0.01454 | 2.3858 | 0.9992 |

## Adsorption Isotherms :

The results of adsorption experiments from Table . 7 were fed into three different isotherm equations- Freundlich, Langmuir and Dubinin-Kaganer-Radushkevich. Various parameters involved were calculated.

## Thermodynamic Parameters:

Van't Hoff equation in the following form, was used to calculate the thermodynamic parameters such as Gibb's free energy change ( $\Delta G$), enthalpy change ($\Delta H$) and entropy change ($\Delta S$) were listed in Table. 8 :

**Table.8. Thermodynamic parameters for the adsorption of Congo red using Valoria bryopsis**

| Adsorbate | Mg/l | - ΔG KJ / mol | | | | ΔH KJ / mol | ΔS J/mol |
|---|---|---|---|---|---|---|---|
| | | $30^{o}$c | $40^{o}$c | $50^{o}$c | $60^{o}$c | | |
| Valoria bryopsis | 25 | 6.7786 | 8.0696 | 9.0377 | 11.2059 | 30.1877 | 67.9890 |
| | 50 | 4.7217 | 6.8044 | 7.3967 | 10.2660 | 47.2116 | 170.2338 |
| | 100 | 4.4523 | 5.6028 | 6.9021 | 8.8586 | 36.8785 | 135.7409 |

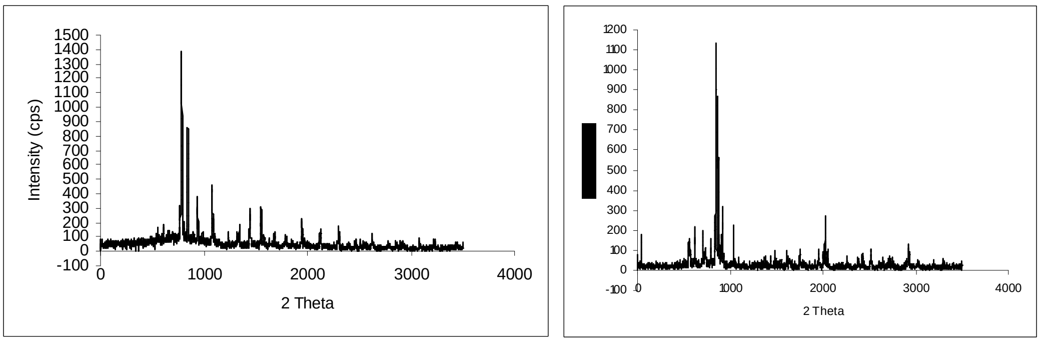
$$\text{Log}K_c = \left(\frac{\Delta S}{2.303\,R}\right) - \left(\frac{\Delta H}{2.303\,RT}\right)$$

Where $K_C$ is the equilibrium constant for the adsorption process, T is absolute Temperature and R, the gas constant, Vant Hoff plot were constructed for each system and $\Delta H$ and $\Delta S$ were calculated from the slope and intercept of the plots respectively .

### XRD Study:

Xray Diffraction Studies of the carbon prepared from the marine algae were carried out using Rigaku corporation, Japan X-ray Diffractometer 40KV / 30mA, Model D/Max ULTIMA III . The XRD pictures taken before and after adsorption are shown in fig .3 It is evident from the figure that there is no appreciable change in the spectra. This may be due to the fact that adsorption did not alter the chemical nature of the surface of the adsorbent i.e. the adsorption is physical in nature.

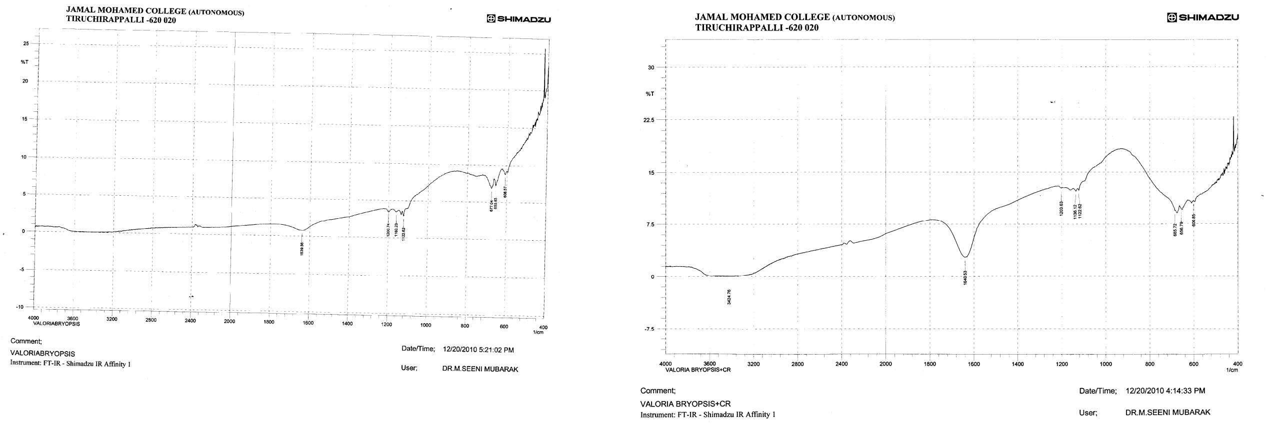
**Figure 3. XRD Pattern of Valoria bryopsis before and after adsorption of congored dye**




## IR Study:

Fourier transform infrared spectroscopy (FTIR) was used to determine the functional groups on the carbon surface. The spectra were measured within the range of 400 -4000 cm-1 in a Shimadzu spectrophotometer. Some fundamental FTIR frequencies of the adsorbent, before and after adsorption, are presented in table 10 As can be inferred from Figure 4 the absorption frequencies are shifted to higher wave numbers with the adsorption of congo red. From these findings it is presumed that the dye was incorporated onto the adsorbent through interaction with the active functional groups.

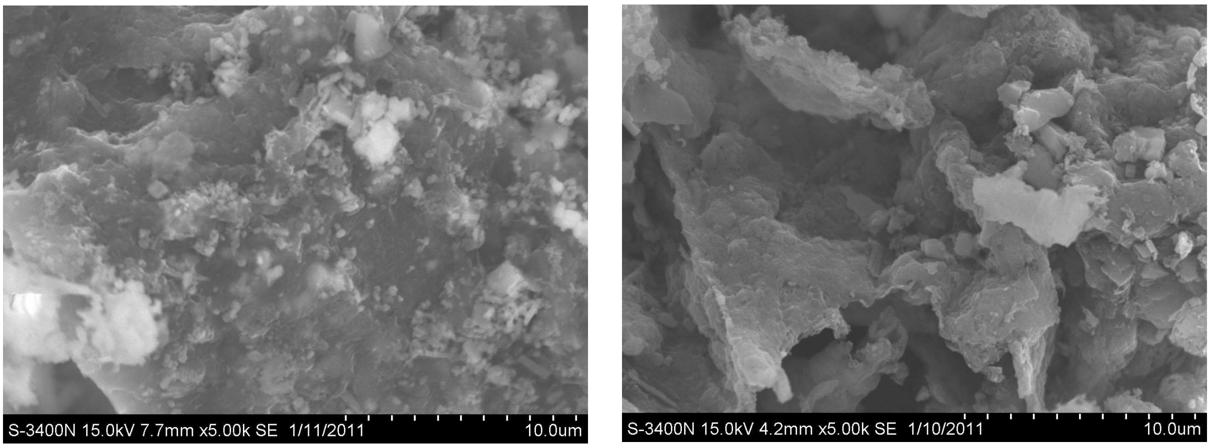
**Figure 4. FTIR Spectrum of Valoriya bryopsis before and after congored dye adsorption**




## SEM analysis:

The surface morphology of the activated carbon was examined using scanning electron microscopy (SEM), the corresponding SEM micrographs being obtained using at an accelerating voltage of 15 kV (Hitachi SE 900) at 5000× magnification (Figure 5). At such magnification, the activated carbon particles showed rough areas of surface on which micro pores were clearly identifiable.

**Figure 5. SEM micrograph of Valoria bryopsis before and after congored dye adsorption**




## CONCLUSION

The experimental data correlated reasonably well with the Langmuir, Freundlich and DKR adsorption isotherms. Adsorption of the dye is not favoured at around neutral pH. The amount of congo red dye adsorbed decreased with increasing ionic strength and increased with increase in temperature. The values of ΔH°, ΔS° and ΔG° show that the carbon employed has a considerable potential as an adsorbent for the removal of congo red dye.

## REFERENCES

[1] King P, Parasanna Kumar V and Prasad V S R K, *Journal of Industrial Pollution Control* **(2005)**, 21(1), 155-162
[2] Matheickal J T, Leela lyengar and Venkobachar C, *Kes. J. Canda* **(1991),** 26, 187
[3] Selvarani K, Ph D., **(2000)** Thesis, Regional Engineering College, Thiruchirapalli.
[4] Jia Y F and Thomas K K, *Langmuir* **(2002),** 18, 470-478.
[5] Namasivayam C, Muniasamy N, Gayathri K, Rani M and Renganathan K, *Biores Technol*, **(1996),** 57, 37.
[6] Namasivayam C and Yamuna R T, *Environ Pollution*, **(1995),** 89, 1.
[7] Langmuir I, *J Amer Chem Soc*, **(1998)**, 40, 1361.
[8] Freundlich H, *Phys Chemie*, **(1906),** 57, 384.
[9] Krishna D G and Bhattacharyya G, *Appl Clay Sci*, **(2002),** 20, 295.
[10] 10. Arivoli S, Viji Jain M and Rajachandrasekar T *Mat Sci Res India*, **(2006),** 3, 241-250.
[11] Arivoli S and Hema M *Intern J Phys Sci*., **(2007),** 2, 10-17.
[12] Arivoli S, Venkatraman B R, Rajachandrasekar T and Hema M *Res J Chem Environ*., **(2007),** 17, 70-78.
[13] Arivoli S, Kalpana K, Sudha R and Rajachandrasekar T *E-J Chem*, **(2007),** 4, 238-254.
[14] Renmin Gong, Yingzhi Sun, Jian Chen, Huijun Liu and Chao yang (**2005**), *Dyes and Pigments*, 67, 179.
[15] Vadivelan V, Vasanthkumar KJ *Colloid Interf Sci*, **(2005),** 286, 91.
[16] Weber W J**(1967),** Principle and Application of Water Chemistry, Edited by Faust S D and Hunter J V Wiley, New York.
[17] Yupeng Guo, Jingzhu Zhao, Hui Zhang, Shaofeng Yang, Zichen Wang and Hongding Xu **(2005),** *Dyes and Pigments*, 66, 123-128.