



## Malachite Green Dye Removal Using the Seaweed *Enteromorpha*

R.JAYARAJ<sup>§</sup>, M. CHANDRA MOHAN, P. MARTIN DEVA PRASATH<sup>§\*</sup>  
and T. HIDHAYATHULLAH KHAN

<sup>§</sup>PG and Research Department of Chemistry  
TBML College, Porayar - 609307, Nagapattinam, Tamilnadu, India  
PG and Research Department of Chemistry  
Khadir Mohideen College Adirampattinam - 614 701, Tamilnadu, India  
*martinprasath@rediffmail.com*

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**Abstract:** Malachite green adsorption from an aqueous solution onto activated *Enteromorpha* carbon has been studied experimentally using batch adsorption method. Adsorption kinetics and equilibrium were investigated as a function of initial dye concentration, pH, contact time and adsorbent dosage. Kinetics studies indicated that the adsorption followed pseudo second order reaction. Equilibrium data was analyzed using Langmuir and Freundlich isotherm models. The adsorption capacity of *Enteromorpha* was found to be 94.74%. On the basis of experimental results and the model parameters, it can be inferred that the carbonaceous *Enteromorpha* is effective for the removal of malachite green from aqueous solution.

**Keywords:** Adsorption, *Enteromorpha*, Activated carbon, Malachite green dye, Kinetics, Equilibrium.

### Introduction

Dyes normally have a complex aromatic molecular structure which makes them more stable and more difficult to biodegrade<sup>1</sup>. Further dyes have synthetic origin. They are widely used in textiles, paper, rubber, plastics, leather, cosmetics, pharmaceuticals and food industries. At present there are more than 10,000 dyes which are commercially available<sup>2</sup>. Widespread use of dyes often poses pollution problems in the form of coloured waste water discharged into environmental water bodies. It not only affects aesthetic merit but also reduces light penetration and photosynthesis. Also, some dyes are either toxic or mutagenic and carcinogenic<sup>3</sup>. The conventional methods for treating dyes containing waste waters are coagulation and flocculation<sup>4</sup>, oxidation or ozonation<sup>5&6</sup>, membrane separation<sup>7</sup> and activated carbon adsorption<sup>8</sup>. But these technologies do not show considerable efficiency or economic advantage. Though activated carbon is the most popular and widely used dye

sorbent it has certain problems in its usage. The major drawback is its cost. Hence, there is a widespread awareness in using low cost, easily available biomaterials for the adsorption of dye colours. Many botanical materials of a very low price have directly been used as sorbent for dye adsorption from waste water<sup>9-20</sup>. Since India is a developing nation and a large producer of synthetic textile dyes, novel and economical treatment technologies of dye waste water are the need of the hour.

In the present study, a marine alga which is commonly and abundantly available in the Bay of Kodiyakkarai coast namely, *Enteromorpha* was selected as an adsorbent for the removal of Malachite green from aqueous solution.

## Experimental

*Enteromorpha* was collected from Kodiyakkarai coast in south east coast of India and sun dried. Dry biomass was cut with a knife into irregular shaped particles between 1 and 3 mm in size. The biomass was then washed with distilled water, filtered and finally dried overnight at 60 °C and crushed to an average size of 0-63  $\mu$  in a mortar and then activated by 0.1 M H<sub>2</sub>SO<sub>4</sub> for 24 h and finally carbonized and subsequently used for adsorption experiment.

### *Adsorbate solution*

A 25 ppm solution of malachite green dye was prepared by weighing accurately 25 mg of analar grade malachite green dye and dissolving in 1000 mL standard flask. It was made up to the mark with deionised water. The stock solution was further diluted with deionised water to desired concentration for obtaining the test solution.

### *Chemicals*

Analytical grade reagents were used for malachite green dye solution; ACS reagent grade concentrated hydrochloric acid, NaOH and pH buffer solutions were used to adjusted pH values of samples. In all experimental work, distilled demineralised water was used.

### *Batch mode adsorption studies*

The adsorption of MG dye on the *Enteromorpha* was studied by batch technique. A known weight of adsorbent (for example 50-350 mg of adsorbent) was equilibrated with 50 mL of dye solution of known concentration in a 250 mL reagent bottle in a mechanical shaker for a known period of time (30-180 min). After equilibrium, the suspension of the adsorbent was separated from solution by filtration using Whatman no. 41 filter paper. The concentration of dye remaining in solution was measured. The effect of some parameters, such as pH, concentrations, contact time and adsorbent dose on the adsorption was studied. The pH of the adsorptive solutions was adjusted using hydrochloric acid, sodium hydroxide and buffer solutions when required. The results of these studies were used to obtain the optimum conditions for maximum dye removal from aqueous solution.

## Results and Discussion

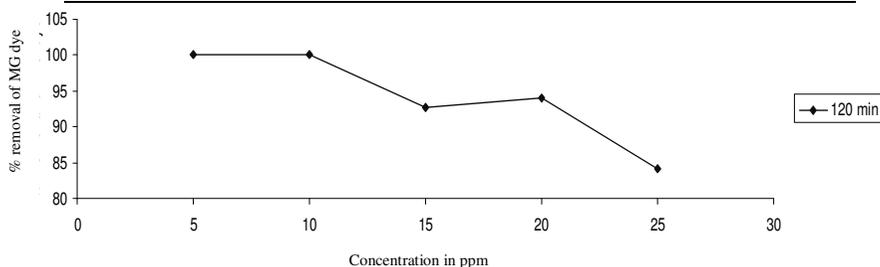
The results of the experiments carried out for the removal of malachite green dye from aqueous solution using *Enteromorpha* as adsorbent are discussed below.

### *Effect of initial concentration of dye*

The results for effect of initial concentration on percentage removal of dye using *Enteromorpha* is presented in Table 1. It can be seen from the Figure 1 that the percentage removal decreases with the increase in dye concentration. For *Enteromorpha* the percentage removal is 94.74% at the initial concentration of 25 mg/L for 250 mg of adsorbent dose and a contact time of 3 h.

**Table 1.** Effect of initial concentration of MG dye using *Enteromorpha* at 120 min

S.No	Initial concentration mg/L	% removal of MG dye
1.	5	100.0
2.	10	100.0
3.	15	92.60
4.	20	93.95
5.	25	84.2



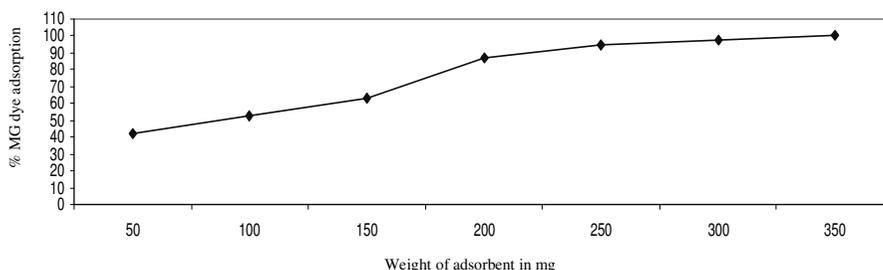
**Figure 1.** Effect of initial concentration on removal of MG dye

*Effect of adsorbent dose*

It is observed that there is a sharp increase in percentage removal with adsorbent dose for *Enteromorpha*. The results for adsorptive removal of MG dye with respect to adsorbent dose over the range of 50 - 350 mg shown Table 2 and Figure 2 indicate that the percentage removal of dye increases with adsorbent dose. The increase in percentage removal is due to the greater availability of the exchangeable sites or surface area. Moreover, the percentage of dye adsorption on adsorbent is determined by the adsorption capacity of the adsorbents.

**Table 2.** Effect of adsorbent dosage on removal of MG dye (Initial concentration: 25 ppm)

S.No	Adsorbent Dosage, mg	Optical Density		MG dye % of adsorption
		Before adsorption	After adsorption	
1.	50	0.38	0.22	42.11
2.	100	0.38	0.18	52.63
3.	150	0.38	0.14	63.16
4.	200	0.38	0.05	86.84
5.	250	0.38	0.02	94.74
6.	300	0.38	0.01	97.37
7.	350	0.38	0.00	100.0



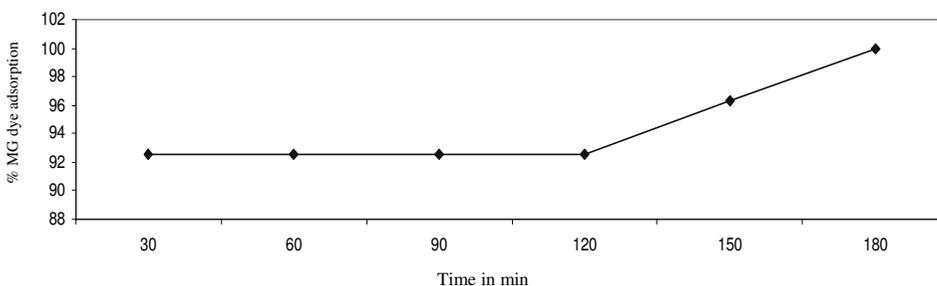
**Figure 2.** Effect of adsorbent dosage on removal of MG dye

### Effect of contact time

Figure 3 shows the variation in the percentage removal of MG dye with contact time on *Enteromorpha*. For varying initial dye concentration ranging from 5-25 mg/L, *Enteromorpha* showed the percentage removal of 94.74% at the contact time of 3 h. For the same concentration it was observed that the percentage removal was not increased with increase in contact time because equilibrium was attained. The optimal contact time to attain equilibrium with *Enteromorpha* was experimentally found to be about 3 h.

**Table 3.** Effect of contact time on removal of MG dye (15 mg/L)

S. No	Contact time (t) minutes	Optical Density		MG dye % adsorption
		Before adsorption	After adsorption	
1.	30	0.27	92.59	0.02
2.	60	0.27	92.59	0.02
3.	90	0.27	92.59	0.02
4.	120	0.27	92.59	0.02
5.	150	0.27	96.30	0.01



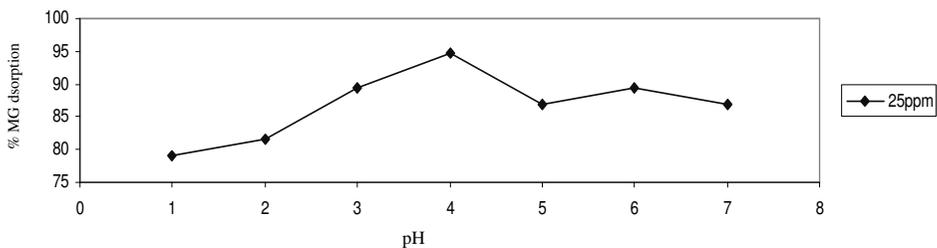
**Figure 3.** Effect of contact time on removal of MG dye (15 mg/L)

### Effect of pH

The pH is one of the most important parameter controlling uptakes of dye from wastewater and aqueous solutions. The effect of pH on adsorption of dye on *Enteromorpha* was studied at room temperature by varying the pH of dye solution from 1-7. It can be observed from the results shown in Table 4 and Figure 4 that the removal of dye by *Enteromorpha* was maximum at pH 4, other pH shows minimum adsorption.

**Table 4.** Effect of pH on removal of MG dye (contact time: 180 min)

S.No	pH	Optical Density		MG dye % of adsorption
		Before adsorption	After adsorption	
1.	1	0.38	0.08	78.95
2.	2	0.38	0.07	81.58
3.	3	0.38	0.04	89.47
4.	4	0.38	0.02	94.74
5.	5	0.38	0.05	86.84
6.	6	0.38	0.04	89.47
7.	7	0.38	0.05	86.84



**Figure 4.** Effect of pH on removal of MG dye

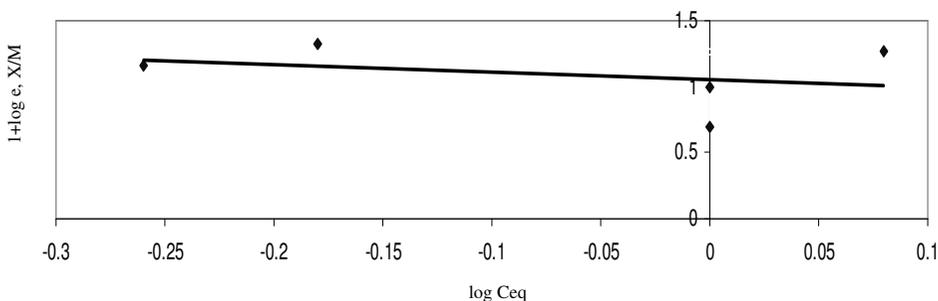
*Freundlich Isotherms*

Freundlich isotherm is  $\log q_e = \log K_f + 1/n \log C_e$

Where  $q_e$  is the amount of dye adsorbed per unit weight of adsorbent (mg/g),  $K_f$  is the measure of sorption capacity and  $1/n$  is sorption intensity;  $C_e$  is equilibrium concentration of residual dye in solution. Figure 5 shows the Freundlich adsorption isotherms for *Enteromorpha*. The straight line nature of the plots indicates that the process followed was of Freundlich adsorption type.

**Table 5.** Data for Freundlich plot (150 min)

S. No.	Initial Concentration, mg/L	MG dye eq, $C_{eq}$	$\log C_{eq}$	MG dye ad, 'x'	$\left(\frac{x}{m}\right), q_e \times 10^{-5}$	$\log_e \left(\frac{x}{m}\right)$	$1 + \log_e \left(\frac{x}{m}\right)$
1.	5	0.00	0.00	5.00	0.500	-0.30	0.70
2.	10	0.00	0.00	10.00	1.000	0.00	1.00
3.	15	0.55	-0.26	14.45	1.445	0.16	1.16
4.	20	1.21	0.08	18.79	1.879	0.27	1.27
5.	25	0.66	-0.18	23.03	2.303	0.32	1.32



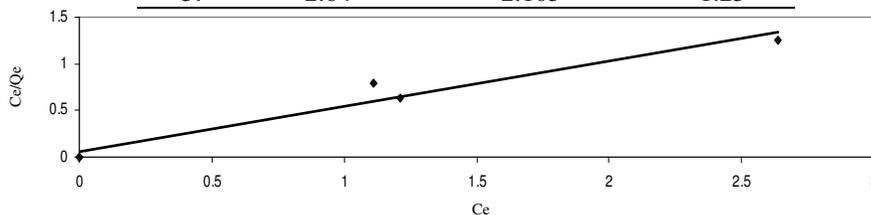
**Figure 5.** Data for Freundlich plot (150 min)

*Langmuir isotherm*

It is represented experimentally by the expression,  $\frac{P}{x/m} = \frac{1}{K_1 K_2} + \frac{P}{K_2}$  where  $K_1$  and  $K_2$  are proportionality constants,  $P$  - initial concentration ( $C_{eq}$ ),  $x/m$ - amount of dye adsorbed at equilibrium (mg/g),  $q_e$ . A plot of  $C_e/q_e$  versus  $C_e$  will give a straight line. The slope of this is  $1/K_2$  and intercept on the y - axis will give  $1/K_1 K_2$ . Figure 6 indicates adsorption of dye on *Enteromorpha* is best fit with Langmuir model and so we infer that it followed Langmuir adsorption isotherms.

**Table 6.** Data for Langmuir plot (120 min)

S. No.	MG dye eq	$\left(\frac{x}{m}\right), q_e \times 10^{-5}$	$\frac{C_e}{q_e}$
1.	0.00	0.500	0.00
2.	0.00	1.000	0.00
3.	1.11	1.389	0.80
4.	1.21	1.879	0.64
5.	2.64	2.105	1.25

**Figure 6.** Data for Langmuir plot (120 min)*Lagergren kinetics*

Lagergren also proposed kinetics for the adsorption. According to him, if a plot of time in minutes *versus*  $\log_{10}(q_e - q)$  gives a straight line and it follows the first order kinetics. If a plot of time in minutes *versus*  $t/q$  gives a straight line and it follows the pseudo second order kinetics.

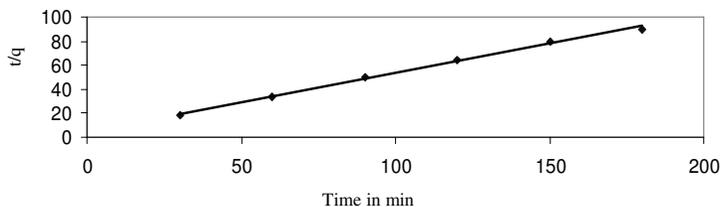
Where,

- $q_e$ –Maximum  $x/m$  value at maximum time
- $q$  –minimum  $x/m$  value at minimum time
- $x$ –amount of dye adsorbed
- $m$ –Mass of the adsorbent

Figure 7 indicated adsorption of dye on *Enteromorpha* gave the straight line, so it followed the pseudo second order.

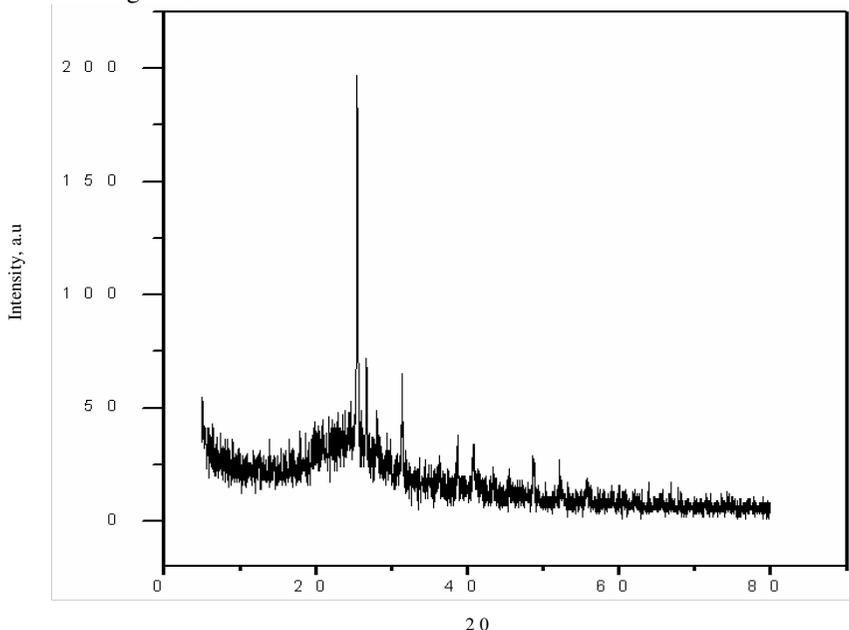
**Table 7.** Data for Lagergren plot (20 mg/L)

S. No	Contact time (t) minutes	MG dye ad 'X' $\mu\text{g}$	$\left(\frac{x}{m}\right)q \times 10^{-5}$	$q_e - q$	$t/q$
1.	30	16.36	1.636	0.364	18.34
2.	60	17.58	1.758	0.242	34.13
3.	90	18.18	1.818	0.182	49.50
4.	120	18.79	1.879	0.121	63.86
5.	150	18.79	1.879	0.121	79.83
6.	180	20.00	2.000	0.000	90.00

**Figure 7.** Data for Lagergren plot (20 mg/L)

*XRD study*

Further, the x-ray diffraction studies of the carbon prepared from the marine algae *Enteromorpha* were carried out using Rotoflux x-ray diffractometer 20KW / 20A, Model 10.61 with a microprocessor record. The XRD pattern of the carbonized marine algae is shown in the Figure 8.



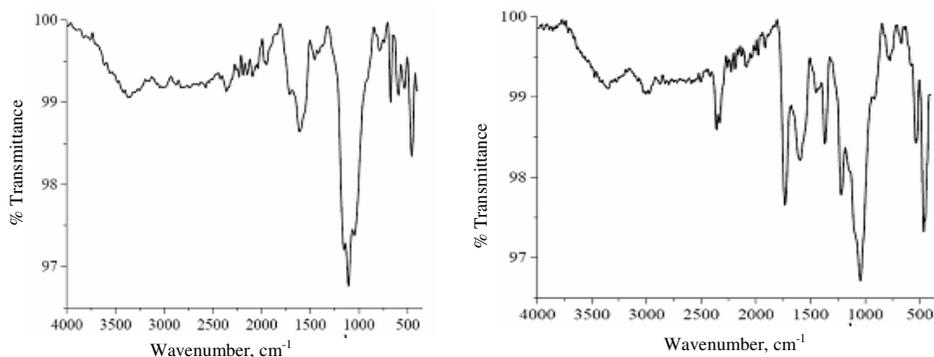
**Figure 8.** XRD Pattern of *Enteromorpha*

*IR study*

Fourier transform infrared spectroscopy (FTIR) was used to determine the vibration frequency changes in the functional groups of carbons. The spectra of carbon were measured within the range of 400-4000/cm wave number. Some fundamental FTIR frequencies of *Enteromorpha* observed for before and after adsorption are presented in Table 8. As can be inferred from Figure 8 that the adsorption frequencies are shifted to higher wave numbers with the adsorption of MG dye in *Enteromorpha*. From these findings it is presumed that the dye is incorporated within the adsorbent through interaction with the active functional groups.

**Table 8.** Some fundamental FTIR frequencies of *Enteromorpha* before and after adsorption

Possible assignments	Before adsorption of <i>Enteromorpha</i>	After adsorption of <i>Enteromorpha</i>
O-H stretching	3412.08	3500
C-H stretching	2924.09	3000
Quadrant & semi-circle stretching	1597.06	1600
C-H in plane ring bending	1099.43	1100
N-H bending	796.60	800
C-I Stretching	468.70	500



**Figure 9.** FTIR Spectrum of *Enteromorpha* before and after MG dye adsorption

## Conclusion

The present study showed that *Enteromorpha* can be used as an effective adsorbent for the removal of Malachite green dye from aqueous solution. The maximum adsorption capacity was obtained (94.74%) by using carbonaceous *Enteromorpha* at pH 4 with adsorbent dose of 250 mg and with agitation time of 180 minutes. The adsorption followed pseudo second order kinetics and data fitted the Langmuir and Freundlich adsorption isotherms. The data may be useful in designing and fabrication of an economic treatment plant for the removal of Malachite green dye from wastewaters.

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# Separation of Lead (II) Ions from Aqueous Solutions by Adsorption on Dolomite

Jeyasingh Thanaraj P., Martin Deva Prasath P.,\* Jayaraj R. and Thillai Natarajan S.

Post Graduate and Research Department of Chemistry, T.B.M.L. College, Porayar-609307, Tamil Nadu, INDIA

## Abstract

The presence of heavy metals in the environment has adverse effects on plants, animals and humans. Even a low concentration of lead in water is toxic to aquatic life. Lead affects the central nervous system, cardiovascular system and kidney function. The present study was aimed at the development of dolomite, a carbonate mineral, as the adsorbent for the removal of lead(II) ions by adsorption. Separation of lead(II) ions from aqueous solutions containing 10 to 200 mg dm<sup>-3</sup> of lead was studied. The effects of change in pH, adsorbent dosage, initial concentration of lead(II) ions, temperature and contact time were studied using batch method. The data were fed into various isotherm equations – Langmuir, Freundlich, Redlich-Peterson and Dubinin- Radushkevich and the best fit was envisaged. Thermodynamic parameters like changes in enthalpy, entropy and Gibbs free energy for the adsorption process were evaluated. Kinetics of the adsorption process was studied using Lagergren's first order, pseudo-second order, Elovich and Inter particle diffusion model rate equations and the rate constants and other parameters were deduced. Spectral studies (FTIR, XRD and SEM) were conducted on the adsorbent before and after the adsorption process and the data were analysed. Results show that the adsorption of lead(II) ions on dolomite is a spontaneous, endothermic process proceeding with increase in entropy.

**Keywords:** Adsorption, lead(II) ion, dolomite, Environmental pollution, Isotherms, Kinetics and Randomness.

## Introduction

Lead is widely used in storage batteries, plumbing, soldering, ammunition, bearings, printing and in petroleum, chemical, electrochemical, textile, paper and paint industries[1-3]. It is estimated that about five million tons of the metal are produced all over the world annually[4]. Lead contamination is a major environmental health hazard. The exhaust from automobiles contains oxides of lead which are potential air pollutants. These oxides are washed by rain and reach the soil. Tons and tons of effluents containing as much as 0.1 g dm<sup>-3</sup> of lead are released into water sources from many industries. Lead accumulates in the blood and in the bones and affects the

soft tissues. It is the culprit behind many health hazards such as anemia, and damage to kidney, lungs, brain and the central nervous system[7].

For the separation of heavy metals like lead from aqueous solutions, several techniques are in use. Some of them are precipitation & filtering, chemical oxidation, membrane separation, adsorption, ion exchange, solvent extraction, reverse osmosis, complex formation and distillation. Many of these processes are associated with disadvantages like high cost, low selectivity, incomplete removal, high energy requirements and generation of toxic slurries[6]. Adsorption methods are preferred because of their ease of operation, low maintenance costs and high efficiency[8]. The most efficient and widely used adsorbent is activated carbon but owing to its high cost, alternative cheap, readily available adsorbents are discovered through research. Clay minerals like Kaolinite[9,10], Bentonite[11,12] and Zeolite [13] have been successfully used as adsorbents. The present study makes use of the mineral dolomite (Calcium magnesium carbonate) as the adsorbent.

## Materials and methods

**Materials:** The dolomite used in this study was from M/s Loba Company, Mumbai. It has the composition as given by Table 1. It was crushed to fine powder in a mortar and sieved to get particles with diameter 0.63 mm or less and then dried in an air oven at 110°C.

**Lead(II) ion Solutions:** A stock solution of lead(II) ions containing 1000 mg dm<sup>-3</sup> of lead was prepared by dissolving accurate quantity of analar grade lead nitrate in deionized water. Solutions of desired concentrations were prepared by proper dilutions of this stock solution. The solution P<sup>H</sup> was adjusted to desired value with 0.1 M HCl and 0.1 M NaOH solutions.

**Batch adsorption studies:** The batch experiments were carried out in 250 cm<sup>3</sup> closed bottles kept in a mechanical shaker at 200 rpm. The effect of P<sup>H</sup> on the adsorption of lead(II) ions onto dolomite was studied by equilibrating the mixture containing 0.15 g of dolomite and 50 cm<sup>3</sup> of lead(II) ion solution containing 50 mg dm<sup>-3</sup> of lead at different P<sup>H</sup> values between 1 and 6. The optimum P<sup>H</sup> was determined as 5.0 and used throughout all adsorption experiments. The effect of adsorbent dosage was studied using dolomite ranging from 50 to 250 mg with 50 cm<sup>3</sup> lead(II) ion solution containing 50 mg dm<sup>-3</sup> lead. The optimum value for adsorbent dosage was determined as 150 mg and this value was used in all batch experiments. After the adsorption has reached equilibrium the mixture was centrifuged at 3500 rpm for 5 min and the supernatant

solution subjected to quantitative analysis. For kinetic studies equilibrium concentrations were determined at 10,20,30,40,50 and 60 min intervals and the data fit into various kinetic models. Metal ion solutions ranging from 10 to 60 mg dm<sup>-3</sup> were employed in the study of adsorption isotherms.

## Results and discussions

**Effect of P<sup>H</sup>:** The effect of P<sup>H</sup> on the adsorption of lead(II) ions onto dolomite is given in Fig.1. It was observed that the absorption capacity initially increased with increasing P<sup>H</sup> but decreased after P<sup>H</sup>=5. Under highly acidic conditions metal binding sites in the adsorbent were associated with H<sub>3</sub>O<sup>+</sup> ions which restricted approach of Pb<sup>2+</sup> ions due to electrostatic repulsion. With increasing P<sup>H</sup>, H<sub>3</sub>O<sup>+</sup> ions get replaced by neutral molecules or negative OH<sup>-</sup> ions, thereby facilitating approach of metal ions. Metal precipitation was found to occur at higher P<sup>H</sup> values.

**Effect of adsorbent concentration on metal removal:** The results of the experiment with varying adsorbent dosages is given in Fig.2. Adsorption was found to increase with increasing dosage of adsorbent since the number of metal binding sites would be increased. Maximum adsorption was found to occur with an adsorbent dosage of 200 mg or above.

**Effect of contact time on metal adsorption:** Fig.3 shows the removal of metal ions as a function of contact time. Maximum adsorption was found to occur with a contact time of 180 min. All the batch experiments were carried out for this period.

**Effect of temperature:** Batch adsorption experiments were carried out at four different temperatures namely 30,40,50 and 60°C with varying initial concentrations of metal ions: 50,100 and 200 mg dm<sup>-3</sup>. Increase in temperature was found to be associated with increase in the adsorption of metal ions onto the adsorbent which explains the endothermic nature of the adsorption process. Increase in temperature probably increases the number of metal-binding sites on the adsorbent. A maximum of 93.3% metal removal was found to occur at 60°C when the initial concentration of metal ion was 100 mg dm<sup>-3</sup>. The results are shown in Fig.4

**FTIR analysis:** The FTIR spectra of dolomite before and after adsorption are shown in Fig.5 a and 5b. The scanning electron microscope (SEM) pictures of dolomite before and after adsorption are

**SEM analysis:** The surface morphology of the dolomite 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 6). At such magnification, the dolomite particles showed rough areas of surface within which micropores were clearly identifiable.

**XRD analysis:** Further, the X-ray Diffraction Studies of the Dolomite were carried out using Rigaku corporation, Japan X-ray Diffractometer 40KV / 30mA, Model D/Max ULTIMA III. The before and after XRD pattern of the Dolomite is shown in the Figure 7a and 7b.

**Kinetics of adsorption:** Kinetics of adsorption is a characteristic responsible for the efficiency of adsorption. Since the initial sorption rate plays a crucial role, adsorption was measured at time intervals 10,20,30,40, 50 and 60 min and kinetics of the process was studied making use of four models namely Lagergren's first order, Pseudo second order, Elovich and Inter particle diffusion.

The Lagergren's first order rate equation can be written as

$$\text{Log}(q_e - q_t) = \text{log} q_e - k_1 t / 2.303 \quad (1)$$

Where  $q_e$  and  $q_t$  are the amounts of lead(II) ions adsorbed (mg g<sup>-1</sup>) at equilibrium and at time  $t$  and  $k_1$  is the Lagergren's first order rate constant (in min<sup>-1</sup>). Values of  $k_1$  and  $q_e$ , calculated from the slope and y- intercept, respectively, of the plot of  $\text{log}(q_e - q_t)$  against  $t$  are given in Table 2. The pseudo-second order kinetics can be expressed by the rate equation,

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (2)$$

where  $q_e$  and  $q_t$  are the amounts of lead(II) ions adsorbed (mg g<sup>-1</sup>) at equilibrium and at time  $t$ ;  $k_2$  is the second order rate constant (mg<sup>-1</sup>min<sup>-1</sup>). Values of  $k_2$  and  $q_e$ , calculated from plots of  $t/q_t$  against  $t$ , are given in Table 2.

The Elovich model can be expressed as

$$q_t = 1/\beta \ln \alpha \beta + 1/\beta \ln t \quad (3)$$

Where  $\alpha$  refers to initial adsorption rate and  $\beta$  is the desorption constant. Both  $\alpha$  and  $\beta$  can be calculated from the slope and y-intercept of the plot of  $q_t$  vs  $\ln t$ .

The inter particle diffusion model of kinetics can be stated as the rate equation,

$$q_t = k_p \cdot t^{1/2} \quad (4)$$

where  $k_p$  is the rate constant for the diffusion process and  $c$  is a constant.

The kinetics parameters are given in Table 2.

Considering the R<sup>2</sup> values the data best fits the Lagergren's first order model and the inter particle diffusion

**Adsorption isotherms:** The adsorption isotherms are one of the promising data to get an idea of the mechanism of adsorption. Four adsorption isotherms are selected in this study namely the Langmuir, Freundlich, Redlich-Peterson (R-P) and Dubinin-Radushkevich (D-R) isotherms. The Langmuir adsorption isotherm assumes that adsorption

takes place at specific homogeneous sites on the adsorbent and that a single layer is adsorbed. The linearized Langmuir isotherm can be represented by the equation [5]:

$$C_e/q_e = 1/q_0 K_L + C_e/q_0 \quad (5)$$

Where  $q_e$  is the adsorption capacity ( $\text{mg g}^{-1}$ ) for lead(II) ions on the adsorbent at equilibrium,  $C_e$  is the equilibrium lead(II) ion concentration ( $\text{mg dm}^{-3}$ ) in the solution,  $q_0$  is the monolayer adsorption capacity ( $\text{mg g}^{-1}$ ) of the adsorbent and  $K_L$  is the Langmuir adsorption constant ( $\text{dm}^3 \text{g}^{-1}$ ) which is related to the free energy of adsorption. The plot of  $C_e/q_e$  vs  $C_e$  gives a straight line with a slope of  $1/q_0$  and the intercept of  $1/q_0 K_L$ .

The Freundlich isotherm is an empirical equation used to describe heterogeneous systems and can be represented by equation [6]:

$$\log q_e = \log K_F + 1/n \log C_e \quad (6)$$

Where  $K_F$  ( $\text{dm}^3 \text{g}^{-1}$ ) and  $n$  (without dimension) are Freundlich isotherm constants, indicating the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively. The Redlich-Peterson adsorption isotherm can be stated by the equation [7]:

$$\log C_e/q_e = \log B_R + \beta \log C_e \quad (7)$$

Where  $C_e$  denotes the concentration of lead(II) ions in solution at equilibrium,  $q_e$  represents the adsorption capacity of the adsorbent,  $\beta$  is the desorption constant and  $B_R$  is called Redlich-Peterson isotherm constant.

The Dubinin-Radushkevich (D-R) isotherm is more general than the Langmuir isotherm in that it does not assume a homogeneous surface or constant adsorption capacity. The linearised form of the D-R isotherm equation is

$$\log q_e = \log q_0 - \beta \varepsilon^2/2.303 \quad (8)$$

Where  $q_0$  is the theoretical saturation capacity,  $\beta$  is a constant ( $\text{mol}^2 \text{kJ}^{-2}$ ) related to the mean free energy of adsorption per mole of the adsorbate and  $\varepsilon$  is called the Polanyi potential and is equal to  $RT \ln(1+1/C_e)$  where  $R$  is the gas constant (in  $\text{J K}^{-1} \text{mol}^{-1}$ ) and  $T$  is the temperature in Kelvin.

Table 3 gives the Langmuir, Freundlich, R-P and D-R isotherm parameters for the adsorption of lead(II) ions on dolomite at a constant temperature of  $30^\circ\text{C}$ .

The essential feature of the Langmuir isotherm can be expressed by means of  $R_L$ , a dimensionless constant referred to as the separation factor or equilibrium parameter which can be expressed as

$$R_L = 1/(1+K_L C_0) \quad (9)$$

Where  $C_0$  is the initial concentration of lead(II) ions. The  $R_L$  values calculated for this study are given in Table 3. The adsorption process will be favourable if the  $R_L$  values lie in between 0 and 1 [18].  $R_L$  values given in Table 3 very well lie in this range and hence the adsorption process was favourable. The parameter  $K_L$  obtained from Langmuir isotherm is actually the equilibrium constant for the adsorption process and hence can be used to determine the Gibbs free energy change of the process as per the equation,

$$\Delta G = -RT \ln K_L \quad (10)$$

The Freundlich constant  $n$  is a measure of the deviation from linearity of the adsorption. If the value of  $n$  lies above unity it indicates physisorption. In the present study, as shown by Table 3,  $n$  lies between 2.27 and 2.80 and hence adsorption of lead(II) ions onto dolomite is purely a physical process involving weak van der Waals forces.

**Thermodynamic parameters:** The equilibrium constant ( $\text{dm}^3 \text{g}^{-1}$ ) for the adsorption process is a valuable parameter since it measures the extent of adsorption at the given temperature and pressure. It is calculated using the formula,

$$K_a = (C_0 - C_e)V/m \quad (11)$$

Where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations ( $\text{mg dm}^{-3}$ ) of lead(II) ions,  $V$  is the volume of lead(II) ion solution ( $\text{dm}^3$ ) used and  $m$  is the mass (g) of the adsorbent employed.

From the value of equilibrium constant ( $K_a$ ), changes in enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ) and Gibbs free energy ( $\Delta G$ ) can be calculated using the following equations:

$$\Delta G = -RT \ln K_a \quad (12)$$

$$\ln K_a = -\Delta G/RT = \Delta S/R - \Delta H/RT \quad (13)$$

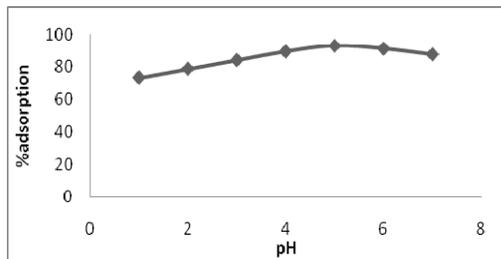
A plot of  $\ln K_a$  vs  $1/T$  gives a straight line with the slope  $-\Delta H/R$  and intercept  $\Delta S/R$ .

The results are given in Table 4. Free energy changes have a negative sign indicating that the adsorption is spontaneous. Enthalpy changes on the other hand are positive underlying the endothermic nature of the adsorption process. Entropy changes are positive since randomness increases due to adsorption. A free energy change between 0 and  $-20 \text{ kJ/mol}$  and an enthalpy change below  $80 \text{ kJ/mol}$  indicates physisorption [17]. A view of Table 4 will show that adsorption of lead(II) ions on dolomite is a physical process governed by weak hydrophobic and van der Waals forces. This is desirable since the adsorbent can be reused after desorption.

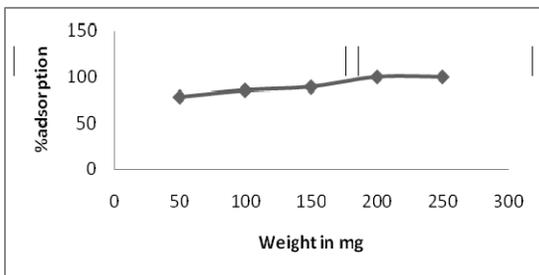
**Conclusions**

The research carried out in this study indicates that dolomite can be used as a good adsorbent for the removal of lead(II) ions from aqueous solutions. The following results have been obtained:

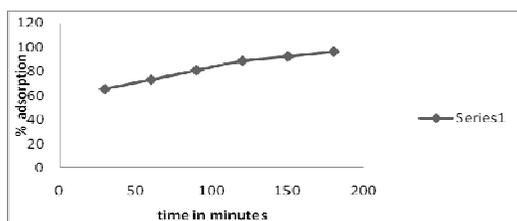
- (1) The functional groups on dolomite were determined using FTIR spectrophotometer.
- (2) Scanning electron microscope (SEM) pictures before and after adsorption clearly show the filling of voids in the adsorbent.
- (3) The structure of the adsorbent is not very much changed due to adsorption as shown by X-ray diffraction studies which confirms physisorption.
- (4) Batch studies suggest that maximum (92.86%) metal removal occurs at  $P^H=5.0$ .
- (5) Adsorption follows Freundlich isotherm model as shown by  $R^2$  values.
- (6) Lagergren's first order kinetics and inter particle diffusion can be applied to calculate rate constants and adsorption capacities.
- (7) Thermodynamic parameters indicate a feasible, physical, spontaneous and endothermic adsorption process .



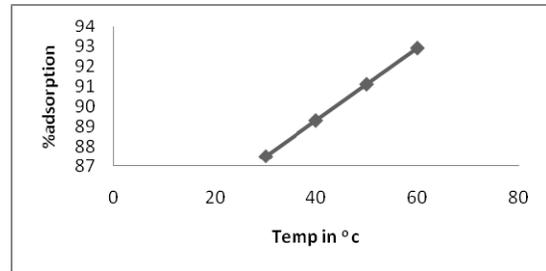
**Fig.1. Percentage adsorption of Pb<sup>2+</sup> on dolomite as a function of P<sup>H</sup> at 30<sup>0</sup>C**



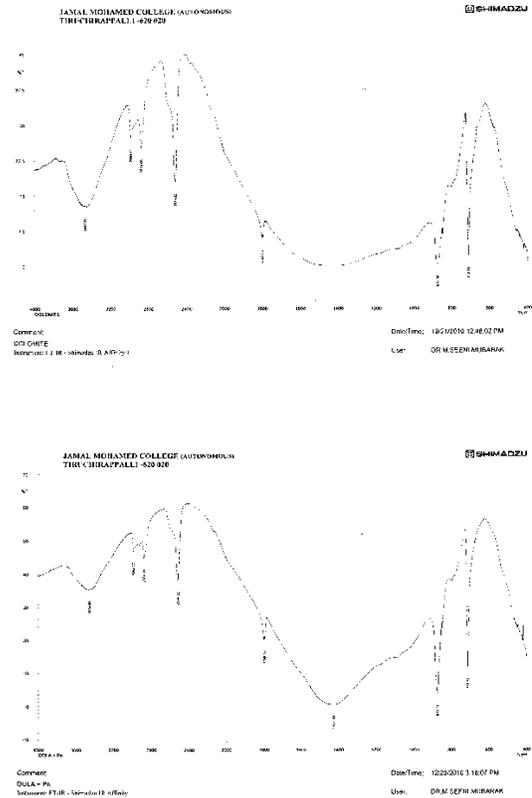
**Fig.2. Effect of adsorbent dosage on the adsorption of lead on dolomite**



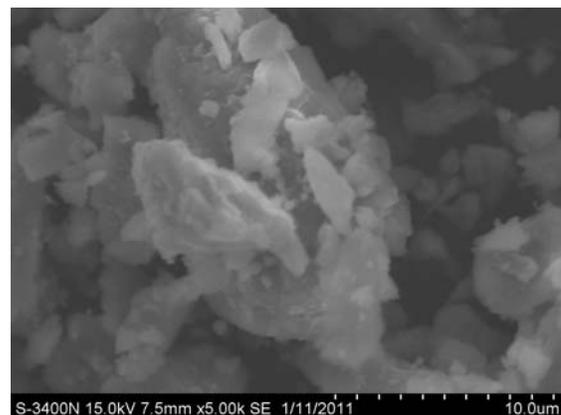
**Fig.3. Effect of contact time on the removal of lead**



**Fig.4. Effect of temperature on removal of lead**



**Fig 5: FTIR spectrum of dolomite a. before adsorption b. after adsorption**



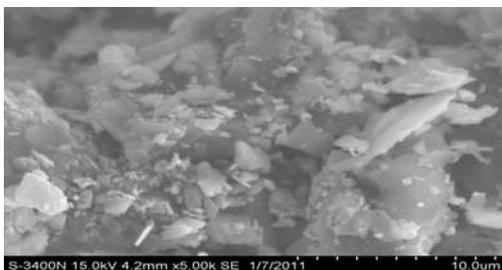


Fig. 6a and 6b. The vacant sites in the first picture are found to be filled with metal ions in the second.

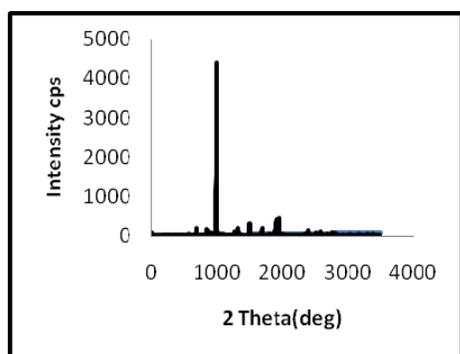
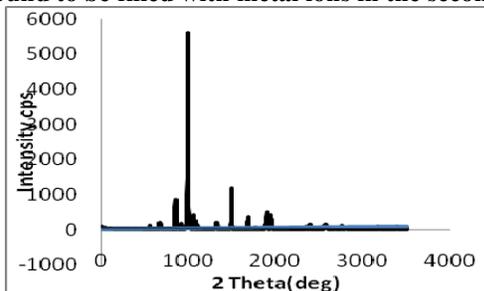


Fig.7a and 7b. The x-ray diffraction picture of the adsorbent before and after adsorption is given in Fig.7.

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**Table 1**  
**Chemical Composition of Dolomite**

Species	Percentage	Species	Percentage	Species	Percentage
CaCO <sub>3</sub>	54.35	CaO	30.41	Ca	
MgCO <sub>3</sub>	45.65	MgO	21.86	Mg	13.18
		CO <sub>2</sub>	47.73	C	13.03
				O	52.06
Total	100	Total	100	Total	100

**Table 2**  
**Kinetics parameters for the adsorption of lead on dolomite at 300C**

Lagergren's first order model

q <sub>e</sub> (mg g <sup>-1</sup> )	K <sub>1</sub> (min <sup>-1</sup> )x10 <sup>2</sup>	R <sup>2</sup>
3.4075	1.7920	0.9890
6.3140	2.7287	0.9318

Pseudo-second order model

q <sub>e</sub> (expt)(mg g <sup>-1</sup> )	K <sub>2</sub> (g mg <sup>-1</sup> min <sup>-1</sup> )x 10 <sup>3</sup>	R <sup>2</sup>
10.9863	1.320	0.8436
9.7099	1.609	0.9891

Elovich model

A	β	R <sup>2</sup>
0.1441	1.1328	0.9485
0.4421	0.4549	0.9671

Inter particle diffusion model

k <sub>p</sub> (mg g <sup>-1</sup> min <sup>-1/2</sup> )	C (mg g <sup>-1</sup> )	R <sup>2</sup>
0.3706	-0.6869	0.9803
0.8951	-1.1043	0.9401

**Table 3**

**Isotherm parameters for the adsorption of lead(II) ions on dolomite at 30<sup>0</sup>C.**

Langmuir isotherm

K <sub>L</sub> (dm <sup>3</sup> g <sup>-1</sup> )	q <sub>o</sub> (mg g <sup>-1</sup> )	B <sub>L</sub> (dm <sup>3</sup> mg <sup>-1</sup> )	R <sup>2</sup>
9.9438	19.9919	0.4974	0.9430
5.1372	28.1397	0.1826	0.9522

Freundlich isotherm

1/n	n	K <sub>F</sub>	R <sup>2</sup>
0.3565	2.8049	7.3770	0.9586
0.4669	2.2686	6.2334	0.9999

Redlich-Peterson isotherm

β	B <sub>R</sub>	R <sup>2</sup>
0.6435	0.1368	0.9853
0.4229	0.1964	0.9404

Dubin-Radushkevich isotherm

B	q <sub>o</sub>	R <sup>2</sup>
0.1707	13.249	0.9307
0.5509	14.563	0.9710

**Table 4**  
**Thermodynamic parameters for the adsorption of lead(II) ions on dolomite**

C <sub>0</sub> (mg dm <sup>-3</sup> )	ΔG(mean) (kJ/mol)	ΔH (kJ/mol)	ΔS (J/K/mol)	R <sup>2</sup>
50	- 3.0367	17.247	63.753	0.9896
100	- 2.9368	22.686	80.535	0.9406
200	- 2.5824	11.312	43.671	0.9324



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## **The removal of heavy metal chromium (VI) from aqueous solution by using marine algae *Gracilaria edulis***

**S. Thillai Natarajan\*, R. Jayaraj\*, P. Jeyasingh Thanaraj and P. Martin Deva Prasath\***

*PG and Research Department of Chemistry, TBML College, Porayar, Nagapattinam, Tamilnadu, India*

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### **ABSTRACT**

*The preparation of activated carbon (AC) from marine algae is a promising way to produce a useful adsorbent for Chromium (VI) removal from aqueous solution. The AC was prepared using marine algae *Gracilaria edulis* with conc.  $H_2SO_4$  and physico-chemical properties of AC were investigated. The specific surface area of the activated carbon was determined and its properties studied by scanning electron microscopy (SEM). Adsorptive removal of Chromium(VI) from aqueous solution onto AC prepared from marine algae 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 obtained in 180min for 10 to 50 mg/L of Chromium(VI) concentrations. The Langmuir, Freundlich and DKR equilibrium isotherm models were found to provide an excellent fitting of the adsorption data. In Freundlich equilibrium isotherm, the  $r^2$  values obtained were in the range of 0.2 to 1 (0.9698 to 0.7204) for Chromium(VI) concentration of 10 to 60mg/L, which indicates favorable adsorption of Chromium(VI) onto marine algae carbon. The adsorption capacity of Chromium(VI) was 98.37%. The percent removal maximum in pH1. This adsorbent was found to be effective and economically attractive.*

**Keywords:** Activated carbon, *Gracilaria edulis*, Enthalpy, Adsorption, Chromium(VI) removal.

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### **INTRODUCTION**

Water is essential for survival. But today about 200 million people in India do not have access to safe drinking water due to water pollution. Any change in physical, chemical or

biological properties of water is known as water pollution. Heavy metal is important role of water pollution. The heavy metals are continuously released into the aquatic eco system from natural process such as volcanic activity and weathering of rocks. The effluents from mining, ore processing, metal processing, metal polishing, cleaning, paint manufacturing and battery manufacturing industries and acid rain contribute for the increasing metal loads in the water bodies. The heavy metal contamination of the water system is responsible for serious diseases and death. Chromium is one of the few metallic elements found in the earth's crust. Large number of important alloys contains chromium as the principle element. Environmental pollution due to chromium arises from industrial and agricultural operations. Chromium has broad industrial applications, such as alloy industries, paper and pulp; basic steel works foundries and petroleum refining industries. Chromium is a trace element that is drinking water essential for most animals, including humans of that iron metabolism and maintenance of blood vessels. Eye irritation has been reported by factory workers exposed to chromium dust. Hence it is essential to remove Chromium from industrial wastewater before discharging in to natural water sources to meet National Regulatory Standards as well as to protect public health. Conventional treatment methods for heavy metals containing waste water, chemical precipitation, Ferrite treatment system, sulphate precipitation, solvent extraction, evaporation, xanthate process etc., but due to operational demerits and the treatment cost is high. The need for cost effective and economic removal of toxic heavy metals from waste water resulted in a research for non-conventional materials and methods. Several low cost adsorbents include sawdust, orange peel, almond husk, parthenium etc. The objective of the present study is to be prepare and characterize quality evaluate the efficiency of using sago waste carbon as an adsorbent for the removal of Chromium. The adsorption study was carried out systematically involving various parameters such as pH, agitation and adsorption dose.

## EXPERIMENTAL SECTION

### Adsorbent Material

The raw material dried *Graciliria edulis* was treating with concentrated sulphuric acid in a weight ratio of 1:1(w/v) for 12 hrs and the resulting materials was washed with distilled water until a constant pH of the slurry was reached. The resulting black product was kept in muffle furnace maintained at 400<sup>0</sup> C for 8 hrs, followed by ground and the portion retained between 0 – 60 sieves was used in all the experiments.

### Adsorption dynamic experiments

#### Batch equilibration method

The adsorption experiments were carried out in a batch process at 30, 40, 50 and 60 °C temperatures. The 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. The solution was then filtered at preset time intervals and the residual dye concentration was measured.

**Effect of variable parameters:****Dosage of adsorbents**

The various doses of the adsorbents are mixed with the dye solutions and the mixture was agitated in a mechanical shaker. The adsorption capacities for different doses were determined at definite time intervals by keeping all other factors constant.

**Initial concentration of dye**

In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of dyes ranging from 10 to 60 mg/L. All other factors have kept constant.

**Contact time**

The effect of period of contact on the removal of the dye on adsorbent in a single cycle was determined by keeping particle size, initial concentration, dosage, pH and concentration of other ions constant.

**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 and concentration of other ions have kept constant while carrying out the experiments. The pH of the samples was determined using a portable pH meter, Systronics make. The pH meter was calibrated with 4.0 and 9.2 buffers.

**Temperature**

The adsorption experiments were performed at four different temperatures viz., 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  $\pm 0.5$  °C.

**RESULTS AND DISCUSSION****Effect of contact time and initial dye concentration**

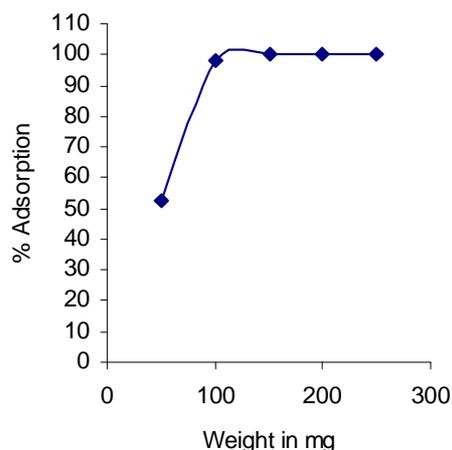
The experimental results of adsorptions of at various concentrations (10,20,30,40 and 50 mg/L) with contact time, the equilibrium data were reveals that, percent adsorption decreased with increase in initial metal concentration, but the actual amount of dye adsorbed per unit mass of carbon increased with increase in metal concentration. It means that the adsorption is highly dependent on initial concentration of metal. It is because of that at lower concentration, the ratio of the initial number of metals to the available surface area is low subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of metal is dependent upon initial concentrations. Equilibrium have established at 180 minutes for all concentrations. Figure 1 reveals that the curves are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the metals on the carbon surface.

**Effect of adsorbent dose**

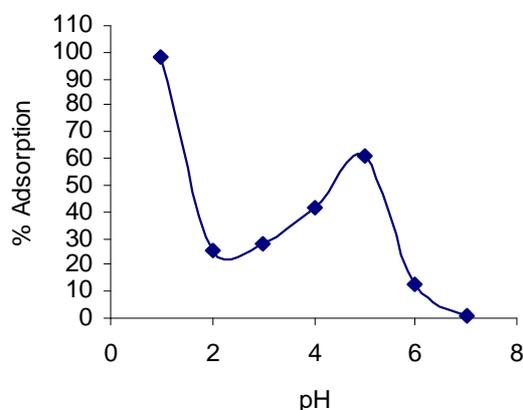
The results for adsorptive removal of Chromium (VI) dye with respect to adsorbent dose are shown in fig 2 over the range of 50 – 250 mg. The percentage removal of metal is seen to increase with adsorbent dose from fig 2. It is observed that there is a sharp increase in percentage removal with adsorbent dose for *Graciliria edulis*. It is apparent that the percentage removal of metal increases rapidly with increase in the dose of the adsorbents due to the greater availability of the exchangeable sites or surface area. Moreover, the percentage of metal adsorption on adsorbent is determined by the adsorption capacity of the adsorbents.

**Table. 1. Effect of adsorbent dosage on removal of Cr(VI)**

S. No	Adsorbent dosage (mg)	Cr(VI) % of adsorption
1.	50	52.61
2.	100	98.37
3.	150	100.00
4.	200	100.00
5.	250	100.00

**Figure.1. Effect of adsorbent dosage on removal of Cr(VI)****Table.2. Effect of pH on removal of Cr(VI) using *Graciliria edulis***

S. No	pH	Cr(VI) % of adsorption
1.	1	98.37
2.	2	25.41
3.	3	28.10
4.	4	41.17
5.	5	60.78
6.	6	13.07
7.	7	00.65

Figure.2.Effect of pH on removal of Cr(VI) using *Graciliria edulis*

### Effect of pH

The pH is one of the most Important parameter controlling uptake of metal from waste water and aqueous solutions. Figure 4 shows the effect of pH on metal removal efficiencies of *Graciliria edulis*. The effect of pH on adsorption of metal on *Graciliria edulis* was studied at room temperature by varying the pH of solution from 1- 7. The results are shown in fig 4. It can be observed that the removal of metal by *Graciliria edulis* was maximum at pH 1, other pH shows minimum adsorption

### Adsorption Kinetics :

The kinetic behavior as Four rate equations reported in the literature namely, first order model pseudo – second order model, Elovich model and the intraparticle diffusion model are shown below.

Table.3. First order parameters for the adsorption of Cr(VI) using *Graciliria edulis* at 30°C

Adsorbate	Mg/l	Equilibrium uptake mg/g		$k_1$	$r^2$
		$q_e (t)$	$q_e (exp)$		
Graciliria edulis	10	5.0000	4.8479	0.07454	0.9143
	20	10.000	7.1928	0.04506	0.7117
	30	15.000	12.7145	0.02547	0.9418

Table.4. Pseudo second order parameters for the adsorption of Cr(VI) using *Graciliria edulis* at 30°C

Adsorbate	Mg/l	Equilibrium uptake mg/g	$k_2$	$r^2$
		$q_e$		
Graciliria edulis	10	6.4265	0.01064	0.9792
	20	12.9855	0.004221	0.9147
	30	17.2613	0.002192	0.9145

**Table.5. Elovic parameters for the adsorption of Cr(VI) using Graciliria edulis at 30°C**

Adsorbate	Mg/l	$\alpha$	$\alpha \beta_E$	$\beta_E$	$r^2$
Graciliria edulis	10	0.8419	0.5486	0.6510	0.9213
	20	0.4431	0.4232	0.3115	0.8461
	30	1.3328	0.3344	0.2506	0.9243

**Table.6. Intraparticle diffusion for the adsorption of Cr(VI) using Graciliria edulis at 30°C**

Adsorbate	Mg/l	a	$k_{id}$	$r^2$
Graciliria edulis	10	0.4427	18.6899	0.8788
	20	0.5271	13.1829	0.8023
	30	0.5064	10.5978	0.9382

**Equilibrium studies :**

Freundlich Plot I, & II, Langmuir plot I & II, DKR plot I & II three isotherm values calculated and each isotherm parameter values are calculate from different concentrations like 10mg/L, 20mg/L, 30mg/L, 40mg/L and 50mg/L at contact time of 180 minutes.

**Table.7. Isotherm parameters for the adsorption of Cr(VI) using Graciliria edulis at 30°C****Langmuir plot**

Adsorbate	Model	Model parameters			
		$K_L$	$b_L$	$q_0$	$r^2$
Graciliria edulis	Langmuir plot- I	71.8442	2.4030	29.8946	0.7204
	Langmuir plot- II	111.3338	4.4778	24.8658	0.9354

**Freundlich plot**

Adsorbate	Model	Model parameters			
		$K_F$	$1/n$	n	$r^2$
Graciliria edulis	Freundlich plot -I	18.0507	0.3740	2.6735	0.9725
	Freundlich plot -II	13.8597	0.2533	3.9478	0.9698

**DKR plot**

Adsorbate	Model	Model parameters			
		$\epsilon^2$	$\beta$	$q_0$	$r^2$
Graciliria edulis	DKR plot-I	16.9007	22.3326	0.02531	0.9452
	DKR plot-II	14.2610	20.6125	0.01704	0.8612

**Effect of temperature :**

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

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

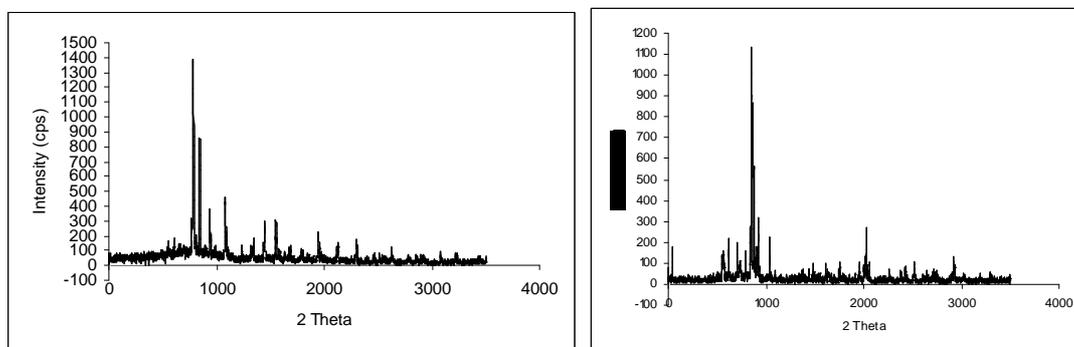
Where  $K_C$  is the equilibrium constant for the distribution of Nickel between the liquid and solid phase.  $T$  is absolute Temperature.  $K$  and  $R$  the gas constant, Van't Hoff plot were constructed for each system and  $\Delta H$  and  $\Delta S$  were calculated from the slope and intercept of the plots respectively .

**Table.8. Thermodynamic parameters for the adsorption of Cr(VI) using Graciliria edulis**

Adsorbate	Mg/l	- $\Delta G$ KJ / mol				$\Delta H$ KJ / mol	$\Delta S$ J/mol
		30°C	40°C	50°C	60°C		
Graciliria edulis	50	8.5869	9.4680	10.5658	13.9828	53.4471	201.5039
	100	5.6164	6.2984	7.4676	8.1601	37.6109	139.9223
	150	4.2978	4.7701	5.2009	5.9251	13.8356	59.4293

### XRD Study

Further, the Xray Diffraction Studies of the carbon prepared from the marine algae Graciliria edulis were carried out using Rigaku corporation, Japan X-ray Diffractometer 40KV / 30mA, Model D/Max ULTIMA III . The before and after adsorption are shows in fig .3 . It is evident from the figure that there is no appreciable change in the spectra adsorbent after adsorption. This may be due to the fact that adsorption dosen't alter the chemical nature of the surface of the adsorbent i.e. the adsorption forces in present case is of physical in nature. The XRD pattern of the adsorbent before and after adsorption are given in fig.4 which supports the adsorption process.

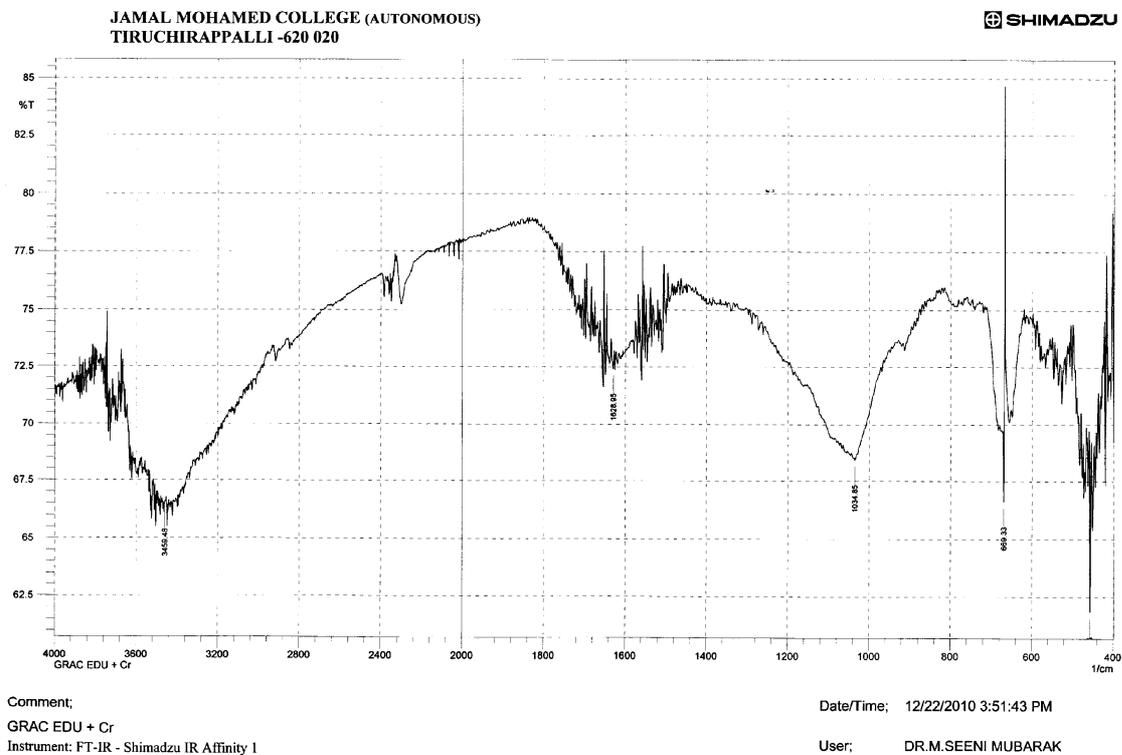
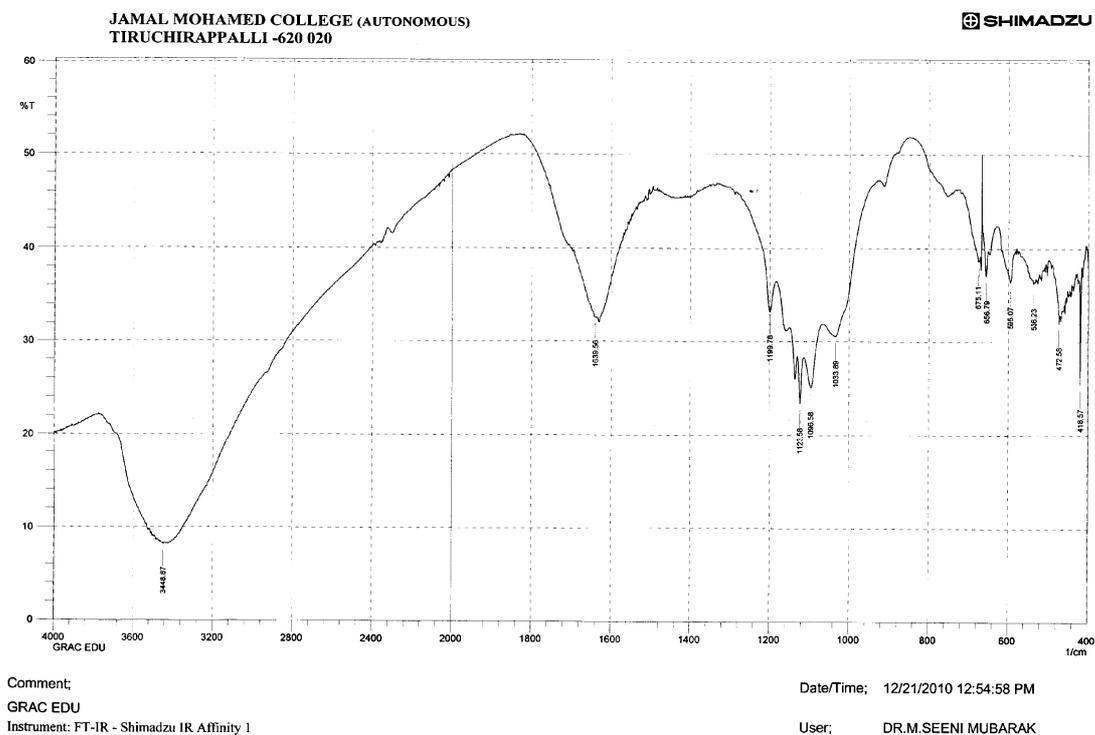


**Figure 3. XRD Pattern of Graciliria edulis before and after adsorption of Chromium(VI)**

### IR Study

Fourier transform infrared spectroscopy (FTIR) was used to Shimadzu Fourier transform infrared spectroscopy determine the vibration frequency changes in the functional groups of carbons. The spectras of carbon were measured within the range of 400 -4000/cm wave number. Some fundamental FTIR frequencies of Graciliria edulis observed for before and after adsorption are presented in table 12 . As can be inferred from Figure 5 that the adsorption frequencies are shifted to higher wave numbers with the adsorption of chromium in Graciliria edulis. From these findings it is presumed that the dyes is incorporated within the adsorbent through interaction with the active functional groups.

**Figure 4. FTIR Spectrum of Graciliria edulis before and after Chromium(VI) adsorption**

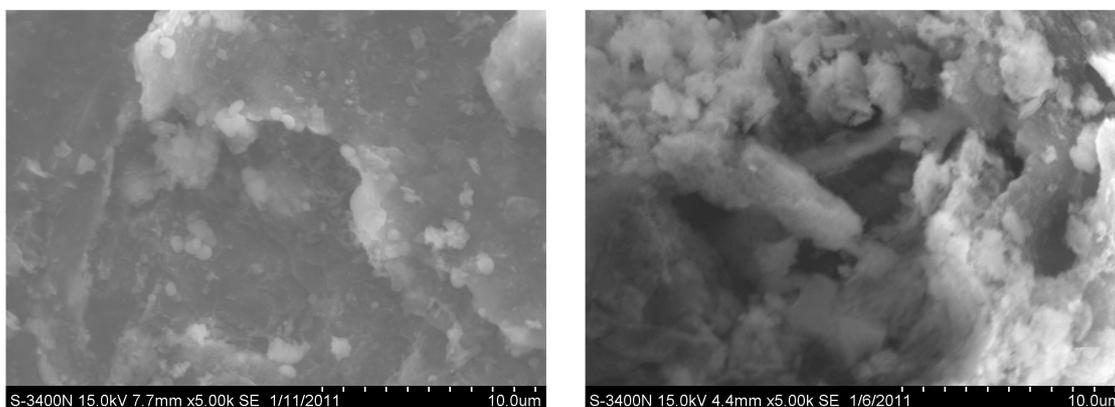


**Table 9. Some fundamental FTIR frequencies of *Graciliria edulis* before and after adsorption**

Possible assignments	Before adsorption of <i>Graciliria edulis</i>	After adsorption of <i>Graciliria edulis</i>
O-H stretching	3448.87	3459.48
Quadrant & semi-circle stretching	1639.56	1628.95
C-H in plane ring bending	1096.58	1034.85
N-H bending	675.11	669.33
C-I Stretching	472.58	462.56

**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 within which micropores were clearly identifiable.

**Figure 5. SEM micrograph of *Graciliria edulis* before and after Chromium(VI) adsorption****CONCLUSION**

The experimental data correlated reasonably well by the Langmuir, Freundlich and DKR adsorption isotherms and the isotherm parameters were calculated. The low as well high pH value pay the way to the optimum amount of adsorption of the dye. The amount of Chromium(VI) adsorbed decreased with increasing ionic strength and increased with increase in temperature. The values of  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  results shows that the carbon employed has a considerable potential as an adsorbent for the removal of Chromium(VI).

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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***

**R. Jayaraj, P. Jeyasingh Thanaraj, S. Thillai Natarajan and P. Martin Deva Prasath**

*PG and Research Department of Chemistry, TBML College, Poraya, Nagapattinam, Tamilnadu, India*

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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.

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**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 *Valoniopsis* 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° 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.

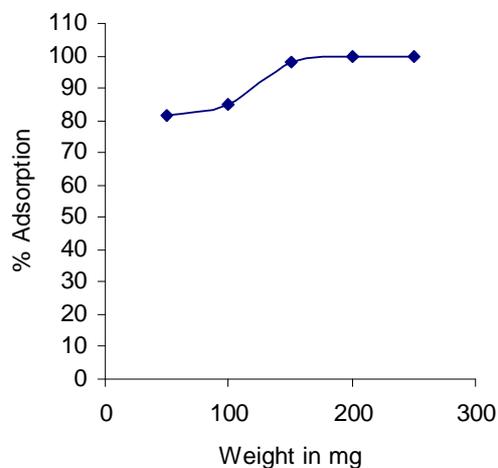
**Table. 1. Effect of adsorbent dosage on removal of CR dye**

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

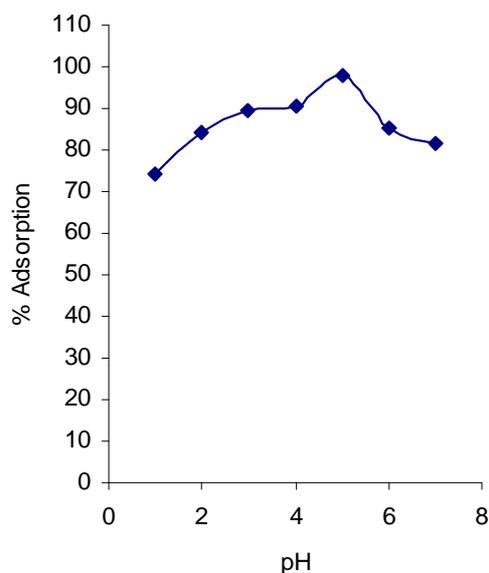
The adsorption capacities for different doses of the adsorbent (namely 50,100,150,200 and 250mg) were determined at definite time intervals for the concentration range 50– 250 mg/L by keeping all other factors constant. The results are shown in Table1 and Figure1. It is apparent that the percentage removal 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 Valeria 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  $\pm 0.5$  °C.

**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 acidity 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.Desorption of Valoria bryopsis**

Adsorbate	% Desorption		
	H2O	ACOH	HCl
Valoria bryopsis	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		$k_1$	$r^2$
		$q_e (l)$	$q_e (exp)$		
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	$k_2$	$r^2$
		$q_e$		
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			
		$K_L$	$b_L$	$q_0$	$r^2$
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			
		$\varepsilon^2$	$\beta$	$q_0$	$r^2$
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**

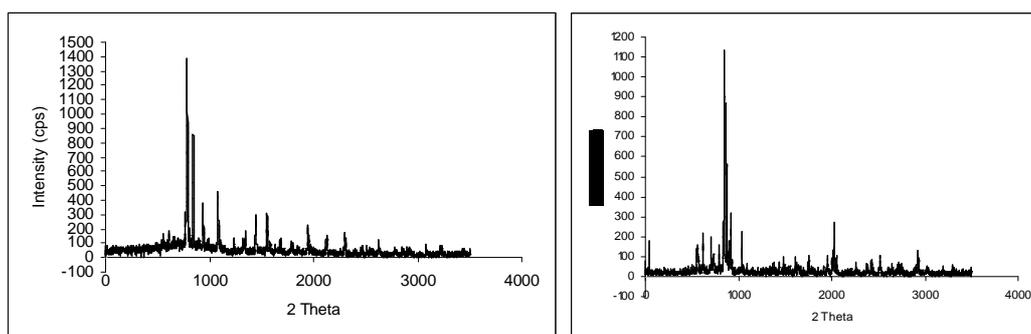
Adsorbate	Mg/l	- $\Delta G$ KJ / mol				$\Delta H$ KJ / mol	$\Delta S$ J/mol
		30°c	40°c	50°c	60°c		
Valoria bryopsis	25	6.7786	8.0696	9.0377	11.2059	30.1877	67.9890
	50	4.7217	6.8044	7.3967	10.2660	47.2116	170.2338
	100	4.4523	5.6028	6.9021	8.8586	36.8785	135.7409

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

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:**

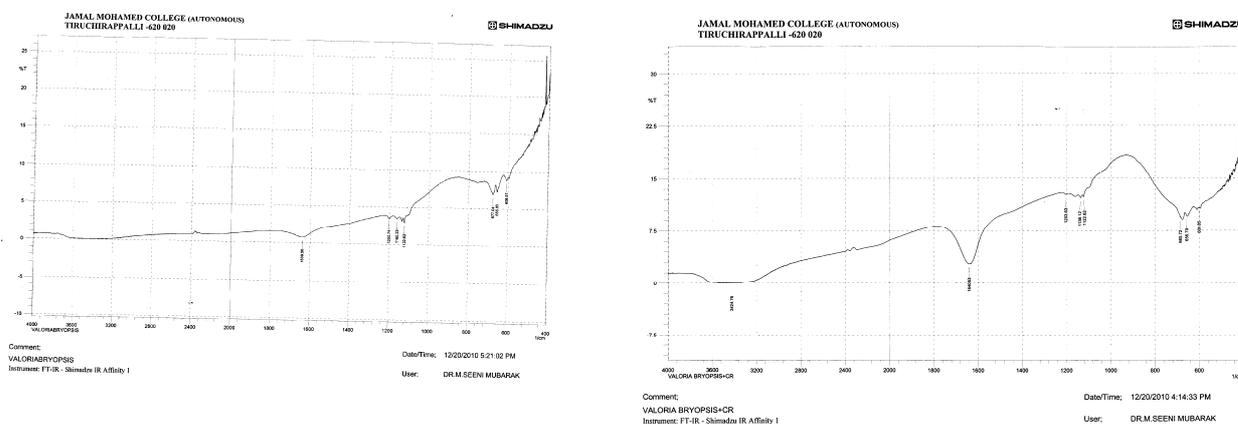
Xray Diffraction Studies of the carbon prepared from the marine algae were carried out using Rigaku corporation, Japan X-ray Diffractometer 40KV / 30mA, Model D/Max ULTIMA III . The XRD pictures taken before and after adsorption are shown in fig .3 It is evident from the figure that there is no appreciable 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  $\text{cm}^{-1}$  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.

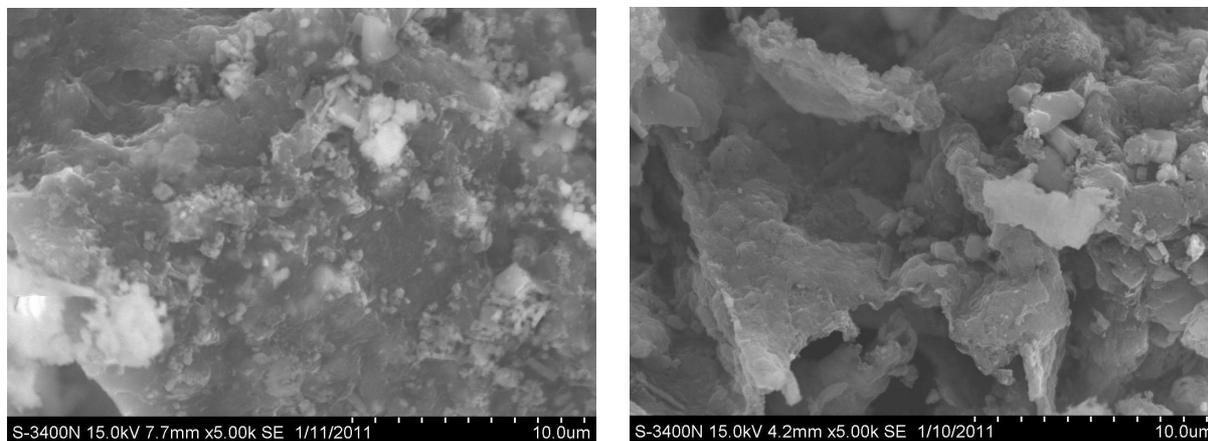
**Figure 4. FTIR Spectrum of Valoriya bryopsis before and after congored dye adsorption**



### 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 $\times$  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  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  show that the carbon employed has a considerable potential as an adsorbent for the removal of congo red dye.

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