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

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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*, Entalphy, 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**

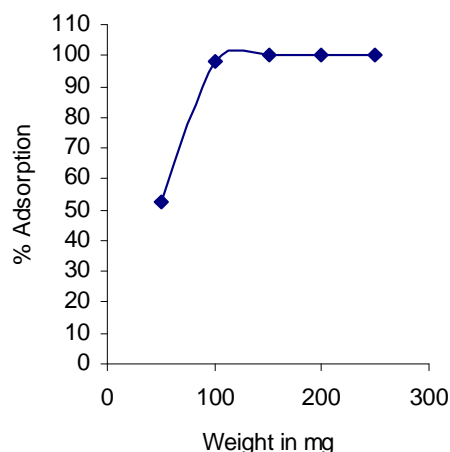
The experimental results of adsorptions of at various concentrations (10,20,30,40 and 50 mg/L) with contact time, the equilibrium data were reveals that, percent adsorption decreased with increase in initial metal concentration, but the actual amount of dye adsorbed per unit mass of carbon increased 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**

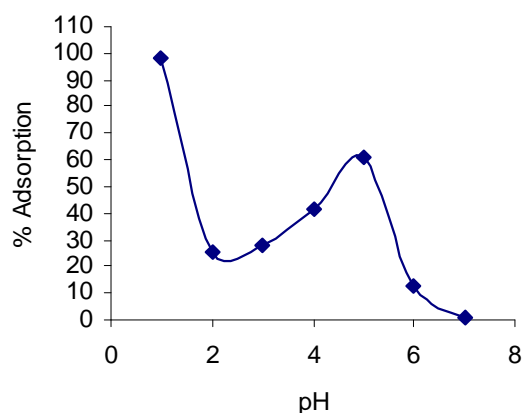
The results for adsorptive removal of Chromium (VI) dye with respect to adsorbent dose are shown in fig 2 over the range of 50 – 250 mg. The percentage removal of metal is seen to increase with adsorbent dose from fig 2. It is observed that there is a sharp increase in percentage removal with adsorbent 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		$k_1$	$r^2$
		$q_e (t)$	$q_e (exp)$		
<i>Graciliria edulis</i>	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	$k_2$	$r^2$
		$q_e$		
<i>Graciliria edulis</i>	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 ( $\Delta S$ )

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

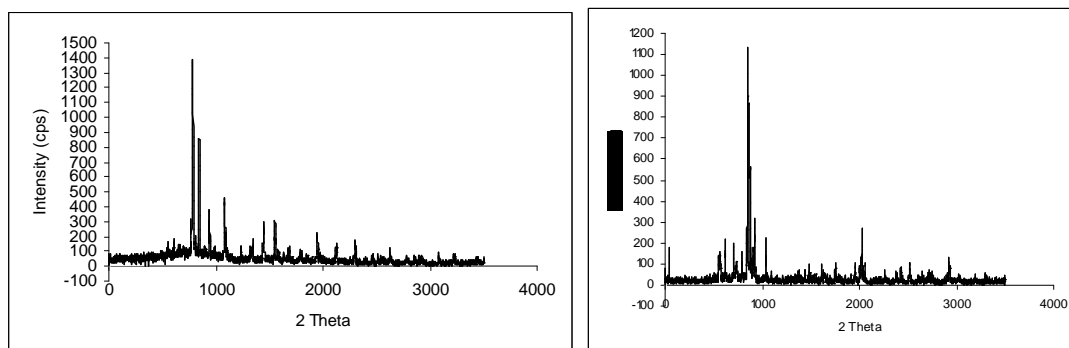
Where  $K_C$  is the equilibrium constant for the distribution of Nickel between the liquid and solid phase.  $T$  is absolute Temperature.  $K$  and  $R$  the gas constant, Van't Hoff plot were constructed for each system and  $\Delta H$  and  $\Delta S$  were calculated from the slope and intercept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

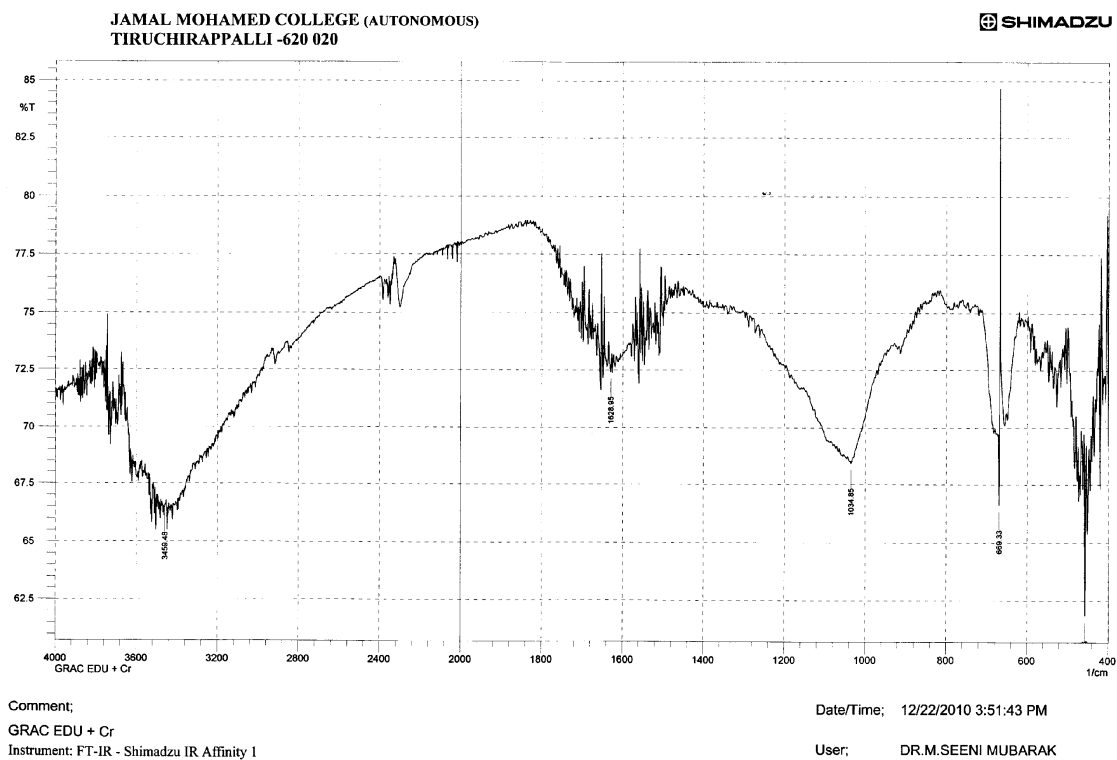
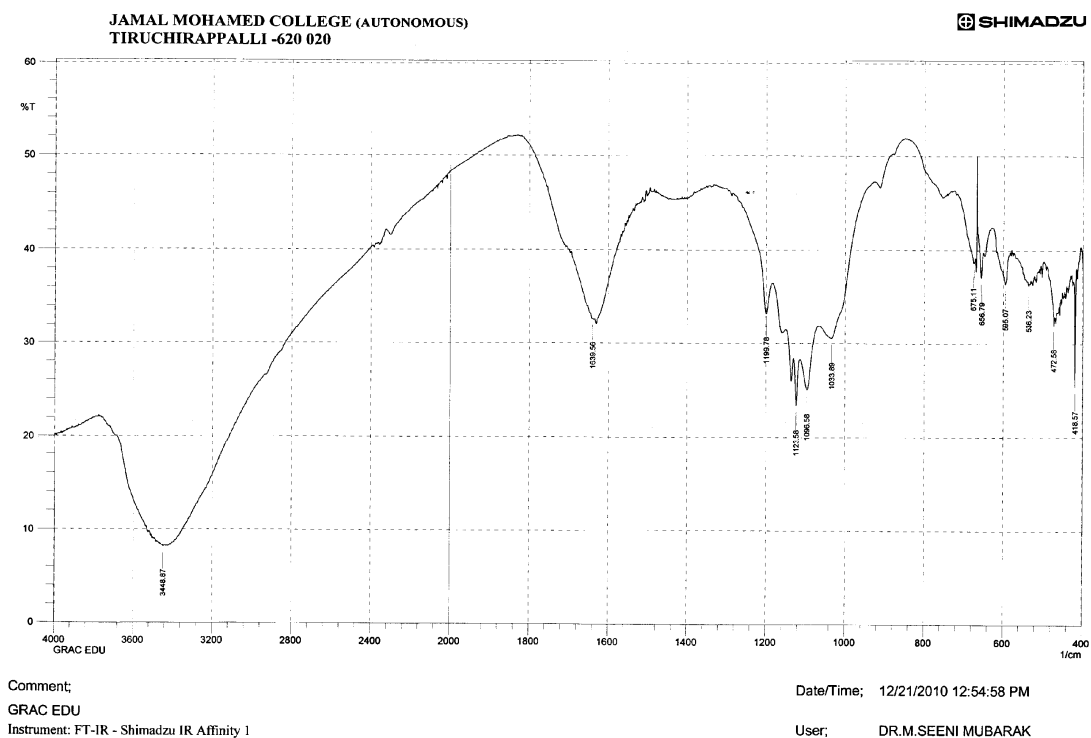


**Figure 3. XRD Pattern of Graciliria edulis before and after adsorption of Chromium(VI)**

### 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**



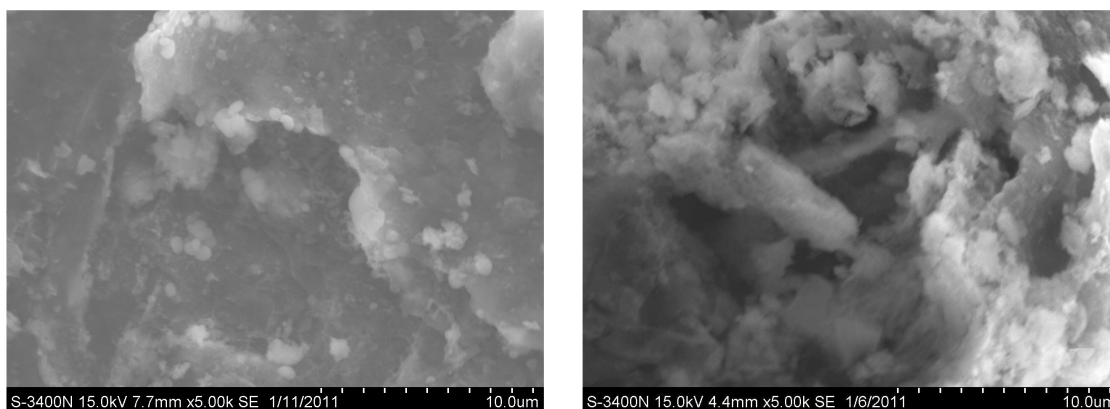


**Table 9.** Some fundamental FTIR frequencies of *Graciliria edulis* before and after adsorption

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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