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RESEARCH ARTICLE

OPTIMIZATION OF Cr AND Cu BIOSORPTION BY GREEN MARINE ALGAE *Caulerpa racemosa*Var. *Cylindracea* & *Ulva lactuca*

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Abstract

Biosorption potential of the *Caulerpa racemosa* var. *cylindracea* & *Ulva lactuca* (Chlorophyta) were studied in removal of toxic heavy metals such as chromium (Cr) & copper (Cu) from industrial reactive azo dyes effluents in batch mode. The experiments were carried out in ambient conditions at pH 7, 50 & 60 minutes of equilibrium time was obtained in *Caulerpa racemosa* & *Ulva lactuca* respectively. The maximum 20.23 % Cr and 42.91 % Cu removal was observed in *Caulerpa racemosa*. In *Ulva lactuca* 62.2 % Cr and 70.35 % Cu removal was observed. The biosorption yield towards Cu > Cr observed in both seaweed biomass. *Ulva lactuca* gives potential biosorption yield as compare to *Caulerpa racemosa*. .The data are well fitted by the Freundlich and Langmuir isotherms shows the favorable biosorption of dye effluent by green seaweed biomass. The data on the kinetic studies fitted well and shows the adsorption kinetics of dyes effluent by both green seaweed biomass followed the pseudo-second order model for biosorption of Cr and Cu, only pseudo first order model was observed in Cr treatment by *Ulva lactuca*. The SEM analysis shows the uneven surface and cells were damaged & swollen after treatment with effluent and FTIR study reveals the variation in functional groups and decrease in peak intensity indicates the participation of metal binding inside the cells of the biomass. Thus the present study indicates this biomass can be used as effective, eco friendly and low cost material in biosorption of highly polluted water containing heavy metals.

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Introduction:-

In recent years the pollution level is raised with increased human activities, the government and industries need to take action against pollution reduction at source and initiation for waste water cleanup. Among various pollutants dyes and heavy metals are very hazardous for living organisms and aquatic life if ingested inside the body they cause carcinogenic and mutagenic effect. At present there are various physical, chemical and biological process are

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available for treatment such as coagulation, flocculation, sedimentation, filtration, ionization, ozonation, ion-exchange, oxidation/reduction, reverse-osmosis etc. but these treatment technologies required high maintenance, high consumption of energy, high cost and toxic slurries generations. Therefore it is an urgent requirement to apply alternative treatment method which is efficient, eco-friendly and low cost [1].

Biological treatments are environment friendly and cost effective process applied using biological materials such as algae [2][3][4], living or non-living bacteria [5][6][7], yeast [8][9], fungi [10][11] and plants [12][13]. Biosorption is a process of removal of toxic heavy metals from the waste water using biological material which is alternative treatment technology involves biosorbent containing favorable functional groups and a solvent/liquid with dissolved sorbate group. Through various mechanisms the sorbate groups are attracted and bound with the sorbent and the sorbent possessing higher affinity towards the sorbate groups. The reaction continues till the equilibrium is developed between the adsorbent bound sorbate groups and the amount left in a solution [14]. Further metal sorption mechanisms using biosorbent occurs via chelation, ion-exchange, micro- precipitation, co-ordination, complexation etc [15]. The potential of seaweeds as biosorbents for removal of heavy metal has been studied by various scientists in recent years offers continuous availability and reusability of sorbent in numerous cycles. Brown and green seaweeds are studied most for the biosorption research [16][17]. Nasab *et al.*, 2017 [18] reported 53 to 80 % of metal removal efficiency for 0.1 to 0.5 g/l of biomass of *Gracillaria corticata.* Badescu et al., 2016 [19] investigated biosorption capacity of *Ulva lactuca* reached 29.63 mg Zn (II)/g of biomass which was further applied as fertilizer to improve soil quality. Amongst various heavy metals such as Cu(II), Ni(II), Cd(II), Pb(II) R.S. Praveen and K. Vijayraghavan, 2014 [20] studied highest metal ions affinity in aqueous solution as Pb>Cd >Cu >Ni by red algae *Kappaphycus alvarezii*. In brown seaweeds the cell wall is comprised of alginate and green & red algal cell wall is comprised of cellulose, carrageenans and agar [21] however the more research is required to study the potential of seaweeds in biosorption of metals

Therefore the present study investigates the potential of green algae *Caulerpa racemosa* and *Ulva lactuca* (Chlorophyta) in the biosorption of Cr and Cu as they are the largest tropical green algae with fastest growth rate [22]. Although seaweeds possess different commercial applications such as in food industry due to high carbohydrate and protein content in aquaculture waste water treatment as they uptake potassium, phosphorus, nitrogen for their growth and survival, thus successfully cleanse the aquaculture waste water. These seaweeds possess successful vegetative reproduction, high growth rate and having plastic morphology. Thus it is desirable to study the biosorption potential of green seaweeds as an alternative application. The present paper investigates the binding mechanisms and kinetics behind the biosorption of Cr and Cu by *Caulerpa racemosa* and *Ulva lactuca.*

Experimental:-

Sample collection & characterization of collected dyes effluents:-

The survey of industrial dyes manufacturing industrial units of Gujarat state, India has been carried out and untreated effluent samples of reactive dyes industries were selected for biosorption study. The selected effluent samples entitled as E1, E4 and E6 which were comprised of mixture of reactive red dyes, reactive yellow dyes and reactive black dyes respectively. E1collected from dyes manufacturing industrial units of Padra GIDC, Vadodara district; E4 collected from Vatva GIDC, Ahmadabad district and E6 collected from industrial unit at Kalamsar village, Khambhat taluka, Anand District. As shown in our previous study [23].

The effluent samples E1, E4 & E6 were comprised of mixture of chemical components and metals; physico chemical parameters were analyzed and indicated in previous research article. In the present study the effluent samples were analyzed by ICP-OES (Model- Optima 3300 RL, Make- Perkin Elmer) for determination of heavy metal concentration of Cr and Cu followed by standard methods of APHA-AWWA, 1985 [24]. These metals are toxic to aquatic life and living organisms if discharged without prior treatments into the water bodies. The concentration of heavy metals represented in Table-1.

Table 1:-Heavy metal concentration in effluent

Heavy Metal	Chromium (Cr) Ppm	Copper (Cu) ppm
E1	0.6573	-
E4	0.5179	16.865
E6	0.1376	16.048

(E1, E4 & E6 is reactive red dyes effluent, reactive yellow dyes effluent & reactive black dyes effluent respectively)

Seaweed collection & identification:-

The seaweed species *Caulerpa racemosa* var. *cylindracea* and *Ulva lactuca* (Chlorophyta) were collected from Beyt-dwarka near Okha coast, Gujarat, India (Longitude - 68°20´ E to 70°40´ E Latitude - 22°15´ N to 23°40´ N). The collected seaweeds immediately washed with seawater at source to remove unwanted debris, adhering sand particles and epiphytes then it was kept in icebox and immediately transferred to laboratory. The seaweed species washed three to four times with distilled water to remove surface salt and impurities. These seaweed species were identified at Fisheries department, Junagadh Agricultural University, Okha, Gujarat with method described by M. Umamaheswara Rao [25]. This seaweed biomass were dried by keeping it under sunlight and then crushed in mixture to get its powder form. These powdered biomasses of green seaweed were used in further study.

Heavy metal sorption by batch Expeiments:-

The batch experiment was carried out to determine dynamic biosorption of Cr & Cu from the dyes effluents by biomass of *Caulerpa racemosa* var. *cylindracea* and *Ulva lactuca*. The batch adsorption experiments were conducted by inoculating 2 g of seaweed biomass in 200 ml of dyes effluents in 500 ml of conical flask at pH 8. The experiments were performed in flask shaker at constant agitation speed of 80 rpm for better contact of surface area of the biomass and ion transfer at room temperature (28°C). The sample was taken at every 10 minutes of interval thus the experiment run time was prepared for 90 minutes and immediately filtered the adsorbent biomass with Whatman filter paper No. 40 to make effluent adsorbent free. The residual heavy metals in filtered effluent samples were analyzed by atomic absorption spectrophotometer (Make: shimadzu, Model: 1800). The equilibrium biosorption q_e (mg/g) was calculated by

$$q_e = \frac{(C\,o - C\,e)V}{W} \tag{1}$$

Where, Co and Ce are initial & equilibrium of dye effluent respectively; V & W are the volume (ml) & weight of the biomass (g). The concentration of Cr & Cu & adsorbed at time t as qt was calculated as per the equation (2) [26]:

$$q_t = \frac{(C\,o - C\,t)V}{W} \tag{2}$$

Where, Co is the initial concentration (ppm) and Ct is the heavy metal concentration (ppm) in filtrate effluent taken at time t; V is the volume (ml); & W is the weight (g) of the biomass taken as adsorbent. The heavy metal removal in percentage was determined by the following equation (3) [27]

$$\text{Biosorption yield (\%)} = \frac{Co - Ct}{Co} \times 100 \tag{3}$$

Heavy Metal Analysis:-

The effluent samples were taken for heavy metal analysis. The adsorbent free filtered effluent samples entitled as E1, E4 and E6 were digested with aqua-regia of HCl: HNO_3 (1:3 V/V) in hot plate and then diluted with double distilled water. These light yellow colored samples after digestion were analyzed for Cr & Cu by Atomic Absorption Spectroscopy (Make-Shimadzu, Model-AA 7000) where the computer desktop is attached with the instrument so the results were digitized and printed.

Scanning electron microscopy (SEM):-

The study of morphology of the seaweed biomass surface of *Caulerpa racemosa* var. *cylindracea* and *Ulva lactuca* were studied by Field Emission Gun-Scanning Electron Microscopy (Make: FEI Ltd., Model: Nova NanoSEM 450) for before and after treatment of effluents E1, E4 & E6.

Fourier Transform Infrared (FTIR) Analysis:-

The FT-IR spectra of dried untreated and treated seaweed biomass were taken with FT-IR spectrophotometer (Make: Perkin Elmer, U.S.A., Model: Spectrum GX). It was obtained by KBr disk method. The seaweeds samples were ground with mortar and pestle for 5 min after dried it by blow drier for 15-30 minutes. 2 mg of dried samples were taken with 200 mg of KBr (spectroscopic grade) were carried out with additional crushing and prepared pallets by hydraulic pallet press and the spectra were scanned between 4000 to 400 cm^{-1} range under ambient conditions.

Result and Discussion:-

In the present study, the Figure-1 indicates quantity absorbed in ppm as function of contact time by green seaweed biomass *Caulerpa racemesa* var. *cylindracea* and *Ulva lactuca* with the Cr and Cu. This study reveals that seaweed *Caulerpa racemosa* var. *cylindracea* and *Ulva lactuca* shows rapid absorption initially and reaches equilibrium at 50 minutes and 60 minutes time periods respectively; after that the absorption becomes constant and slowly decreased. This was occurred because of vacant space availability initially on the biomass surface therefore absorption becomes rapid as a result the concentration rise between adsorbate in the effluent and adsorbate on the seaweed biomass becomes higher. The process initially becomes rapid and reaches to equilibrium because of intra-particle diffusion in the cells of the biomass from bulk to surface and then it slowly decreased because of minimization of availability of vacant sites in surface of biomass and repulsive forces of molecules cause to slower down the absorption rate of reaction [27]. Thus biosorption process is dependent on attraction forces and diffusion process in the molecules and availability of vacant sites on the surface. Further similar works was reported by various scientists on heavy metals such as lead, chromium, copper, nickel, cadmium, cationic dyes [28][29][30][31][32][33][34].

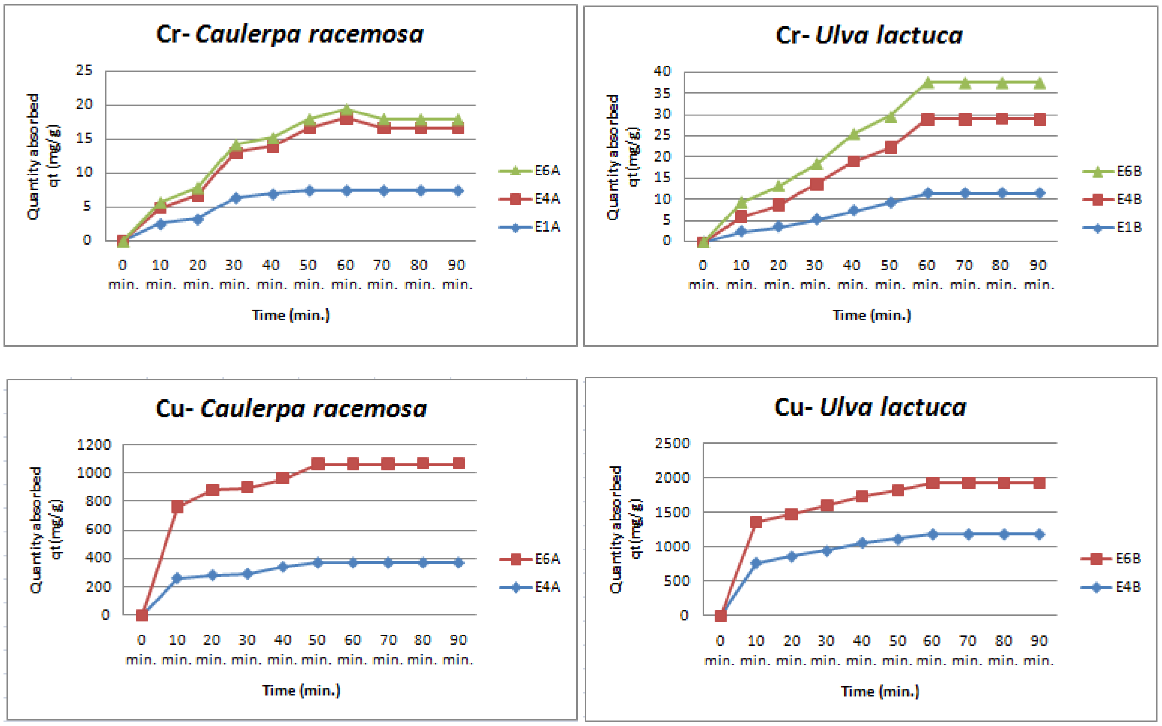


Figure1:-Biosorption capacity of green seaweed *Caulerpa racemosa* var. *cylindracea* and *Ulva lactuca* as function of contact time

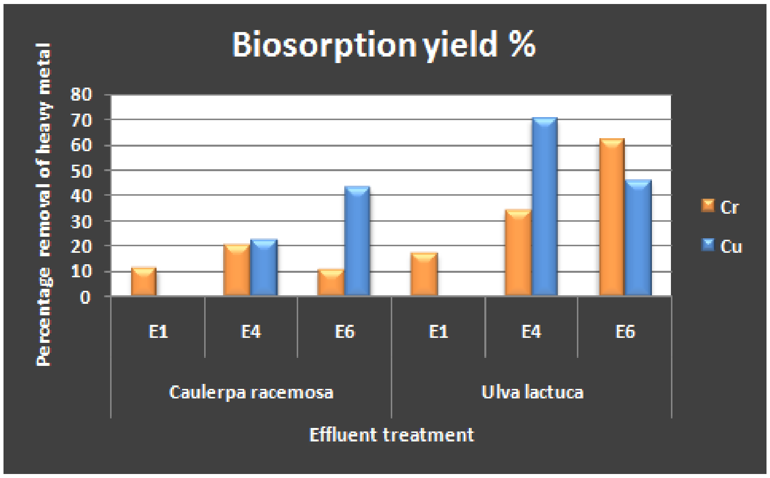


Figure 2:-Biosorption yield (%) of *Caulerpa racemosa* var. *cylindracea* and *Ulva lactuca*

Figure-2 indicates percentage removal of heavy metals by both seaweed biomass *Caulerpa racemosa* var. *cylindracea* and *Ulva lactuca* from the effluents E1, E4 & E6 for Cr and Cu. The maximum 20.23 % Cr removal and

42.91 % Cu removal was observed in *Caulerpa racemosa.* In *Ulva lactuca* 62.2 % Cr and 70.35 % Cu removal was observed. The biosorption of Cu is found maximum than Cr in both seaweed biomass. Many reports available on biosorption of metals under 250 minutes and 180 minutes time periods for green, red and brown seaweed biomass [35][36]. *Ulva lactuca* (B) shows higher affinity towards Cu > Cr and gives potential biosorption yield as compare to *Caulerpa racemosa.* The affinity towards metals is depending on ionic charge, ionic size and hydrolysis constant of the respective heavy metals [32][36][37].

Biosorption isotherms:-

The adsorption isotherms (Langmuir and Freundlich) used to derive wide range of sorbent concentration to study adsorption characteristics such as equilibrium concentration of adsorbate in the bulk and gain of metals onto the surface of adsorbent. The Langmuir and Freundlich isotherms have been applied in the present study; generally they are commonly used in the sorption study. These models have been successfully applied to explain the adsorption of metals [38][39][40]. The Langmuir equation [41] described in linerized form:

$$\frac{Ce}{Qe} = \frac{b}{Qo} + \frac{Ce}{Qo} \tag{4}$$

The Figure-3 (1,2,3,7,8,9) indicates the linear plot of specific adsorption (Ce/qe) against the equilibrium concentration (Ce) which indicates the adsorption follows Langmuir model. The values Q_m and b were presented in Table-2. The essential characteristics of the Langmuir isotherm can be expressed using constant separation factor RL which is indicated in the following equation [42]:

$$R_L = \frac{1}{1+bC0} \tag{5}$$

In the above equation the RL value indicates the character of adsorption to be either unfavorable (RL > 1), linear (RL = 1), favorable (0 <RL < 1), or irreversible (RL = 0).

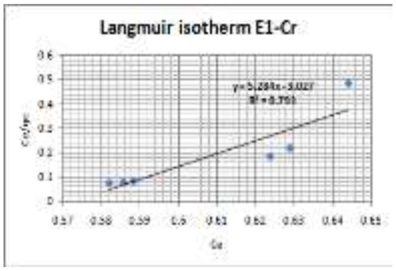
The Freundlich isotherm [43] is indicated by the following relation:

$$\ln Qe = \ln Kf + \frac{1}{n} \ln Ce \tag{6}$$

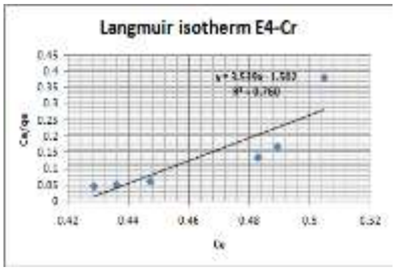
Where K_f and n are Freundlich constants; it can be determined by intercept and slope of the Figure-4 (4,5,6,10,11,12) which indicates the adsorption capacity and intensity respectively represented the values in Table-2.

Equillibrium studies:-

The values of Freundlich and Langmuir parameters are represented in Table-2. The plots of Langmuir isotherm and Freundlich isotherm shown in Fig-3 and Fig-4 for biomass of *Caulerpa racemosa* and *Ulva lactuca* which shows adsorption of heavy metals on the adsorbent biomass. The straight lines satisfactory describes Langmuir model for equilibrium adsorption process. The Langmuir and Freundlich model was found favorable for all the effluent samples and metals as indicated in Table-2 except in Cr by both the biomass and Cu by *Ulva lactuca* in E1 and E4 effluent respectively. The Freundlich isotherm indicates the equilibrium isotherm process. The Freundlich values indicate that the adsorption of metals onto the adsorbent biomass has high adsorption capacity with quite fast progression.



(1)



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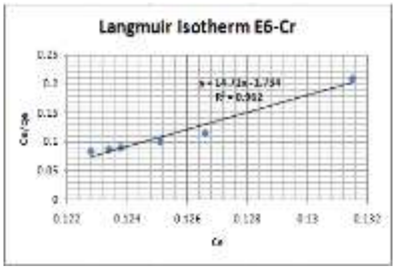
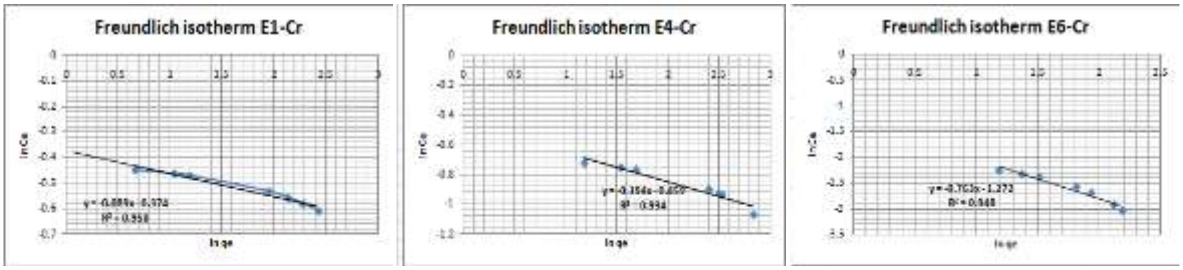
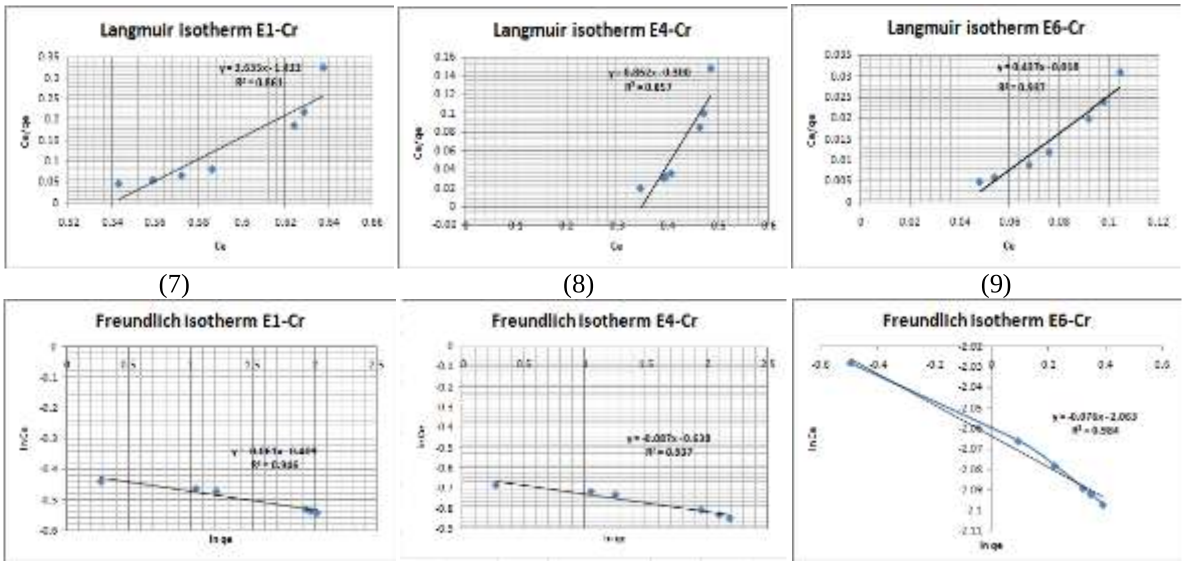


(3)



(4) (5) (6)

Figure-3:-Langmuir and Freundlich isotherm of Cr by *Caulerpa racemosa* (1-6).



(7) (8) (9)

(10) (11) (12)

Figure-4:-Langmuir and Freundlich isotherm of Cr by *Ulva lactuca* (7-12).

Table 2:-Biosorption isotherm parameter in *Caulerpa racemosa* and *Ulva lactuca*

Isotherm	**Metal**	**Parameter**	**Value**					
			Caulerpa racemosa			***Ulva lactuca***		
			E1	**E4**	**E6**	**E1**	**E4**	**E6**
Langmuir Isotherm	Chromium	R2	0.793	0.760	0.962	0.861	0.857	0.937
		qmax(mg/g)	0.33	0.66	0.57	0.70	3.33	55.55
		B	5.29	0.42	0.11	1.85	2.87	24.27
	Copper	R2	-	0.981	0.992	-	0.968	0.977
		qmax(mg/g)	-	4.60	29.41	-	166	29.41
		B	-	0.08	6.80	-	3.03	6.80
Freundlich Isotherm	Chromium	R2	0.946	0.937	0.984	0.958	0.934	0.948
		KF	16.39	11.49	13.15	11.23	5.15	1.31
		N	2.44	1.56	0.48	2.67	2.17	0.78
	Copper	R2	-	0.981	0.992	-	0.968	0.977
		KF	-	4.58	1.86	-	0.75	1.84
		N	-	0.25	0.17	-	0.09	0.17

Sorption kinetics:-

Percentage removal of heavy metals was monitored with time. The kinetics of metals shows rapid binding of dyes molecules to the biosorbent during the first few minutes, followed by a slow increase upto equilibrium stage reached in 50 to 60 minutes for both seaweed biomass, no change was observed for further increase in equilibrium time upto 90 minutes. This rapid process occurred because of vacant sites available in the biosorbent at the initial stage. The kinetic study was modeled by the pseudo first and second order equation models. The pseudo first order model as Lagergren's first order equation is known to explain the adsorption rate depended on adsorption capacity. The Lagergren's first-order rate equation in linear form is as follows [44]:

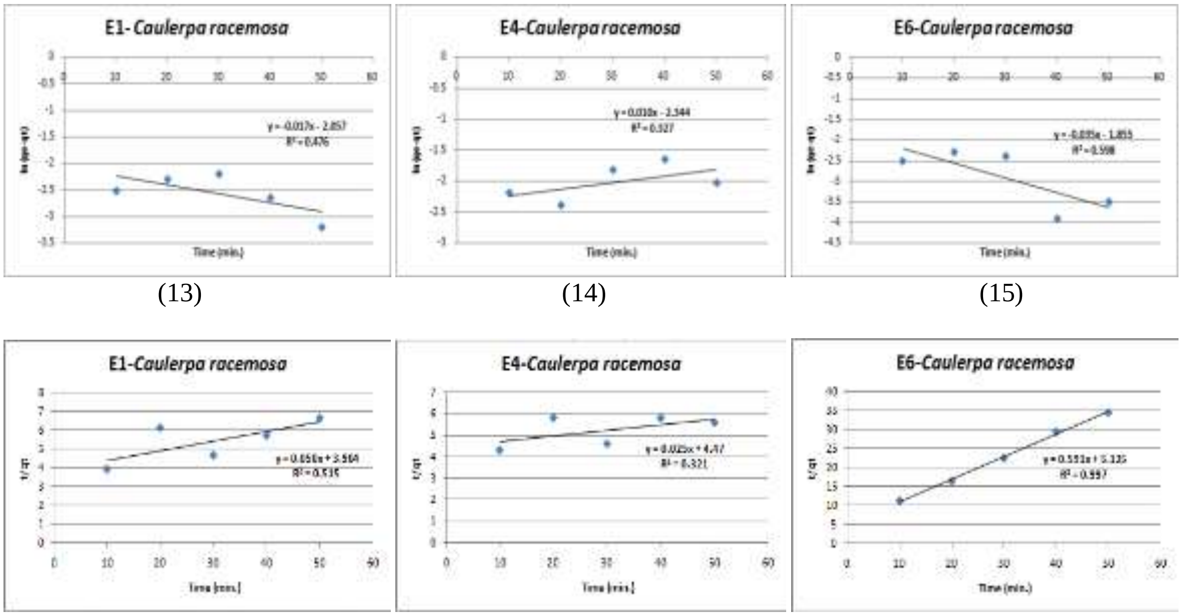
$$\ln(qe - qt) = \ln(qe - K_1 t) \tag{7}$$

The pseudo second order model in linerized form is given by the Ho [45] is:

$$\frac{t}{qt} = \frac{1}{K_2 qe^2} + \frac{1}{qe} t \tag{8}$$

Where, the K is pseudo-second order rate constant for adsorption (g/mg/time) & q_e & q_t were the content of metals (mg/g) adsorbed at equilibrium & time t respectively. The linear plot of t vs t/qt was obtained which indicates the kinetic data fitted best in pseudo-second order model.

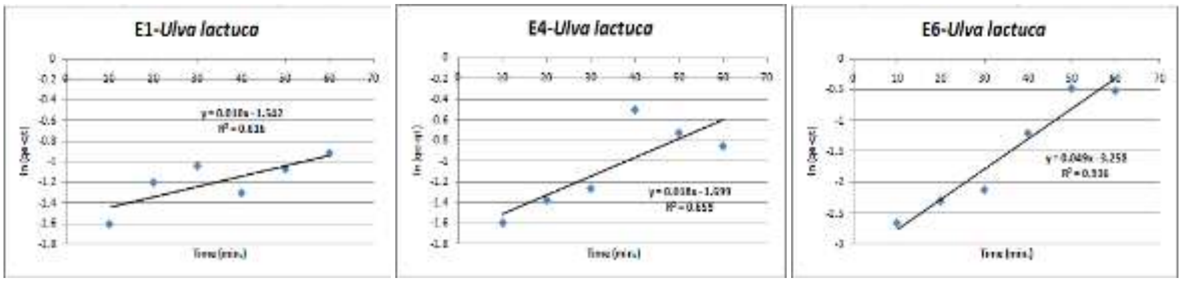
The linear plot of ln (qe-qt) Vs t for pseudo-first order reaction and t/qt vs t for pseudo-second order reaction of the adsorption of metals onto *Caulerpa racemosa* and *Ulva lactuca* are shown in the Fig-5-8. The correlation coefficients are closer to the correlation coefficient of second-order kinetics than the pseudo-first order kinetics which suggests that the pseudo second order model followed by both the biomass, only pseudo first order model was observed in Cr treatment by *Ulva lactuca.*



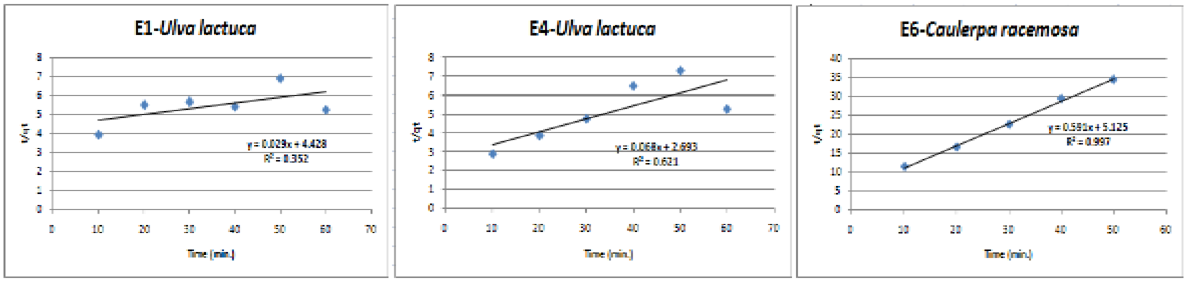
(13) (14) (15)

(16) (17) (18)

Figure-5:-Pseudo-first order & Pseudo-second order plot for Cr by *Caulerpa racemosa* (13-18).

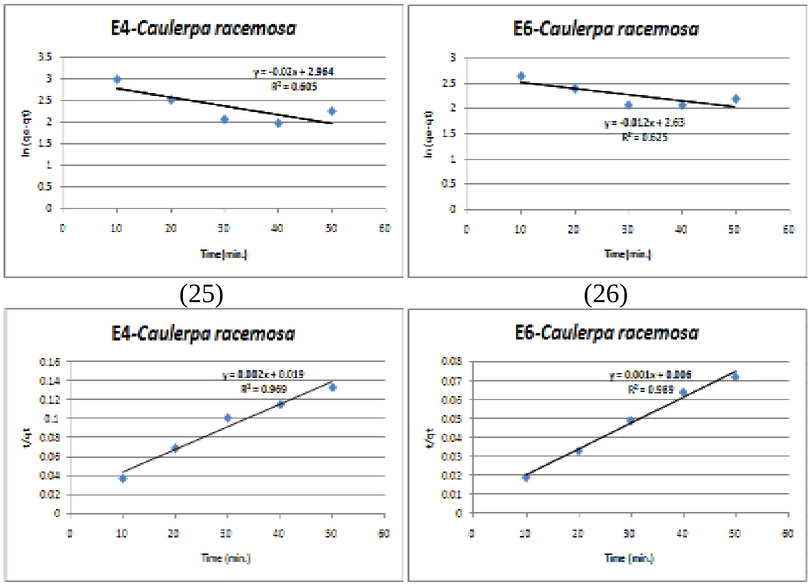


(19) (20) (21)



(22) (23) (24)

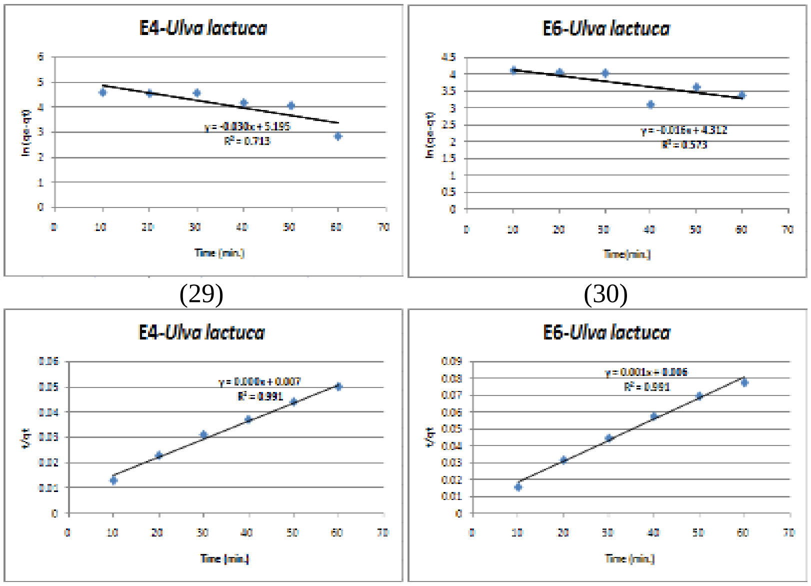
Figure 6:-Pseudo-first order & Pseudo-second order plot for Cr by *Ulva lactuca* (19-24).



(25) (26)

(27) (28)

Figure 7:-Pseudo-first order & Pseudo-second order plot for Cu by *Caulerpa racemosa* (25-28).



(29) (30)

(31) (32)

Figure 8:-Pseudo-first order & Pseudo-second order plot for Cu by *Ulva lactuca* (29-32)

The Image-1 and Image-2 represents untreated original seaweed biomass of *Caulerpa racemosa* and *Ulva lactuca* respectively and E1, E4 and E6 represents after effluent treatment images. This study shows that before exposure of the effluent the surface of the biomass cells were found smooth and uniform, having certain dimensions, after the exposure of effluent the surface of the biomass represents uneven surface and the cells were found swollen and damaged which represents the accumulation of dyes functional groups inside the surface of cells and linked with their functional groups. The heavy metals and component structures occupies the free binding sites inside the cell wall which exchange cations represents strong cross linking of the metals and complexes due to ion exchange mechanism [46].

The recorded spectra give information regarding functional groups variations for before and after treatment with effluent containing heavy metals (Fig-9 to 16). The FTIR spectrum of the biomass indicates distinct and various adsorption peaks represents the existence of functional group such as O-H alcohol, N-H amino salt, C=N oxime/imine, S=O sulfate, S=O sulfonic acid, C-O aliphatic ether, C-O primary alcohol, C-O vinyl ether, O-H carboxylic acid, P-C organo-phosphorus compound, C-O alkyl aryl ether, C-H alkane, C=C alkane disubstituted (cis), C-F fluro compound, C-O primary alcohol, C-O secondary alcohol, C-O tertiary alcohol, N-O nitro compound, C-O aromatic ester, S=O sulfonamide, S=O sulfoxide found in *Caulerpa racemosa* and *Ulva lactuca.* These bands are resulted due to the participation of functional groups of seaweed in the adsorption of heavy metals such as Cr & Cu. The comparison of the each spectrum with its original spectrum before treatment indicates decrease in intensity of bands and band shifts reported in Table-3. The IR spectra of *Caulerpa racemosa* and *Ulva lactuca* indicates minor changes in the peaks frequencies because of the binding with heavy metals & dyes effluent functional groups resulted in decline in adsorption frequencies. These binding taken places due to presence of active sites of the biomass. Thus the analytical study of FTIR indicates the presence of ionizabe functional groups inside the biomass which has ability to interact with cations and other functional groups [47][48][49]. Thus it can be concluded that functional groups play very important role in the removal of cations and breakdown or transformation of the molecules of the dyes effluent.

Table 3:- Functional group assignment in *Caulerpa racemosa*

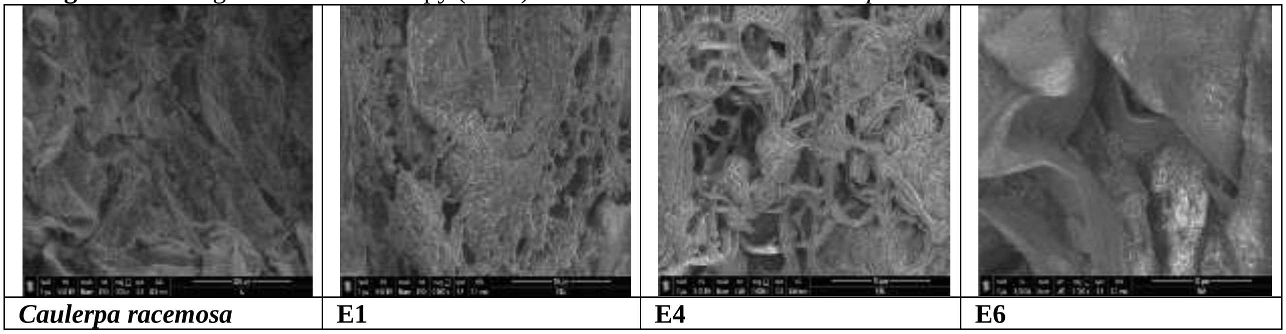
Caulerpa racemosa	**Adsorption bands (cm^{-1})**			**Assignment**
E1-effluent	Initial	Final	Difference	
	3426.95	3426.83	0.12	O-H stretching alcohol, bonded
	2924.16	2923.50	0.66	N-H stretching amine salt bonded
	1651.27	1656.90	(-5.63)	C=N imine/oxime, associated
	1651.27	1644.96	6.31	C=N imine/oxime, associated
	1543.79	1545.84	(-2.05)	N-O stretching nitro
	1455.14	1415.99	39.15	P-C aromatic organo-phosphorus compound, S=O stretching sulfate, S=O stretching sulfate, O-H bending alcohol, O-H bending carboxylic acid
	1245.26	1246.26	(-1)	C-N amine stretching
	1166.82	1139.71	27.11	S=O sulfonic acid anhydrous hydrate, C-O stretching eliphatic ether
	1029.11	1030.03	(-0.92)	C-O strtching vinyl ether
E4-effluent	3426.95	3428.58	(-1.63)	O-H stretching alcohol, bonded
	2923.50	2925.75	(-2.25)	N-H stretching amine salt bonded
	1651.27	1642.70	8.57	C=N imine/oxime, associated
	1543.79	1551.03	(-7.24)	N-O stretching nitro
	1455.14	1410.94	44.2	P-C aromatic organo-phosphorus compound, O-H bending carboxylic acid, O-H bending alcohol, S=O stretching sulfate, S=O stretching sufonyl chloride
	1245.26	1247.59	(-2.33)	C-N amine stretching
	1166.82	1080.45	86.37	S=O sulfonic acid anhydrous hydrate, C-O stretching eliphatic ether
	1029.11	1029.48	(-0.17)	C-O stretching vinyl ether, C-O stretching alkyl aryl ether
E6-effluent	3426.95	3428.02	(-1.07)	O-H stretching alcohol, bonded

	2923.50	2925.75	(-2.25)	N-H stretching amine salt bonded
	1651.27	1641.42	9.85	C=N imine/oxime, associated
	1455.14	1407.74	47.4	P-C aromatic organo-phosphorus compound, O-H bending carboxylic acid, O-H bending alcohol, S=O stretching sulfate, S=O stretching sufonyl chloride,
	1245.26	1244.35	0.91	C-N amine stretching
	1166.82	1205.06	(-38.24)	S=O sulfonic acid anhydrous hydrate, C-O stretching eliphatic ether
	1029.11	1029.29	(-0.18)	C-O stretching vinyl ether, C-O stretching alkyl aryl ether

Table 4:- Functional group assignment in *Ulva lactuca*

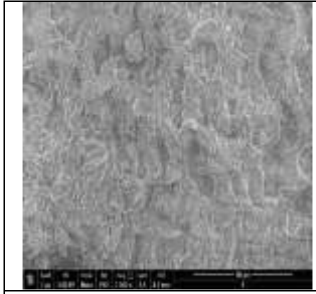
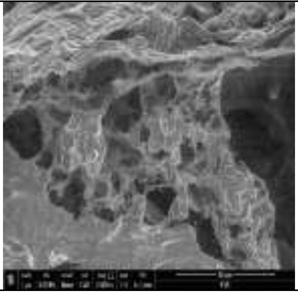
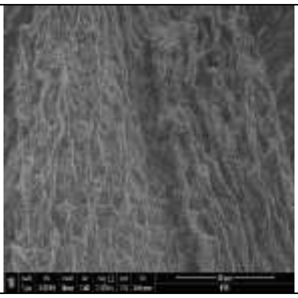
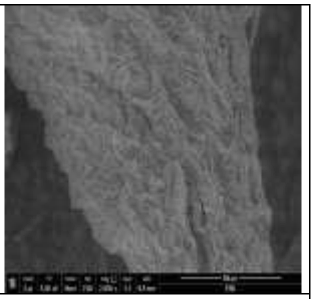
Ulva lactuca	**Adsorption bands (cm^{-1})**			**Assignment**
E1-effluent	Initial	Final	Difference	
	3415.81	3428.28	-12.47	O-H alcohol stretching free
	2926.48	2925.39	1.09	O-H carboxylic acid stretching, N-H stretching amine salt, C-H alkane stretching
	1643.81	1635.39	8.42	C=N imine/oxime stretching, C=C alkane disubstiuted (cis)
	1442.51	1422.84	19.67	O-H bending carbocylic acid, C-F fluro compound
	1101.62	1055.64	45.98	C-O aliphatic ether stretching, C-O secondary alcohol stretching, C-O alkyl aryl ether stretching, C-N amine stretching, C-O vinyl ether stretching
E4-effluent	3415.81	3427.31	(-11.5)	O-H alcohol stretching free
	2926.48	2925.21	1.27	O-H carboxylic acid stretching, N-H stretching amine salt, C-H alkane stretching
	1643.81	1633.52	10.29	C=N imine/oxime stretching, C=C alkane disubstuted (cis)
	1442.51	1421.37	21.14	O-H bending carbocylic acid, C-F fluro compound
	1101.62	1055.99	45.63	C-O aliphatic ether stretching, C-O secondary alcohol stretching, C-O alkyl aryl ether stretching, C-N amine stretching, C-O vinyl ether stretching
E6-effluent	3415.81	3426.24	(-10.43)	O-H alcohol stretching free
	2926.48	2928.03	(-1.55)	O-H carboxylic acid stretching, N-H stretching amine salt, C-H alkane stretching
	1643.81	1631.97	11.84	C=N imine/oxime stretching, C=C alkane disubstuted (cis)
	1442.51	1422.31	20.2	O-H bending carbocylic acid, C-F fluro compound
	1101.62	1055.63	45.99	C-O aliphatic ether stretching, C-O secondary alcohol stretching, C-O alkyl aryl ether stretching, C-N amine stretching, C-O vinyl ether stretching

Image 1:-Scanning electron microscopy (SEM) of Untreated & Treated *Caulerpa racemosa*



Caulerpa racemosa **E1** **E4** **E6**

Image 2:-Scanning electron microscopy (SEM) of Untreated & Treated *Ulva lactuca*

			
Ulva lactuca	**E1**	**E4**	**E6**

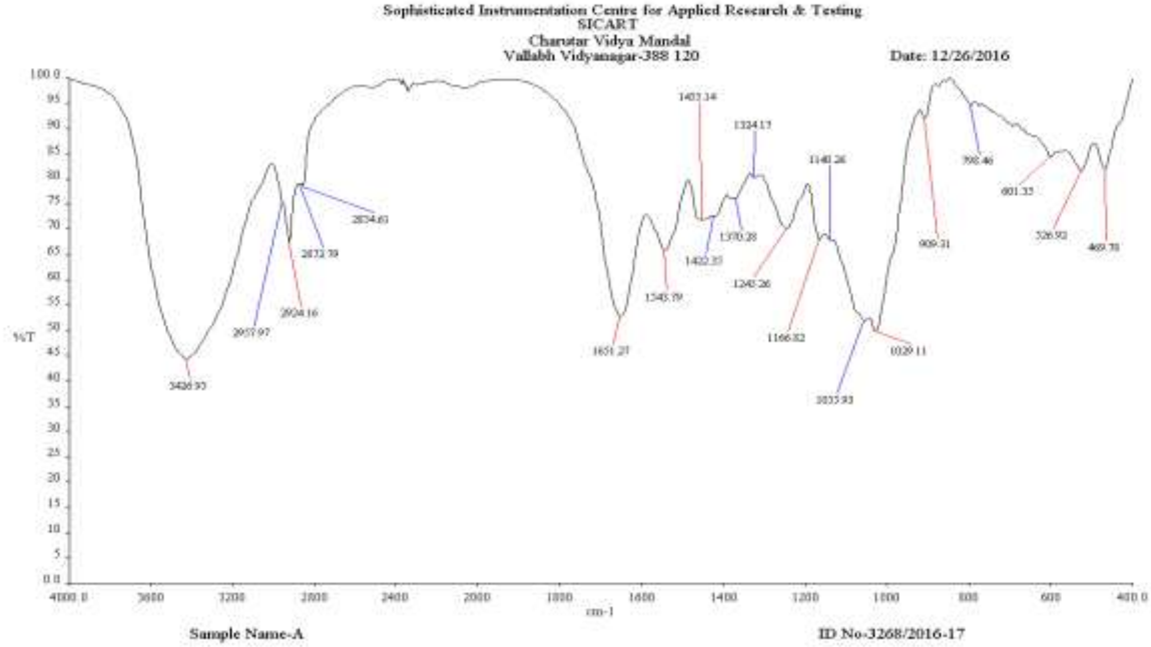


Figure 9:- FTIR of *Caulerpa racemosa*

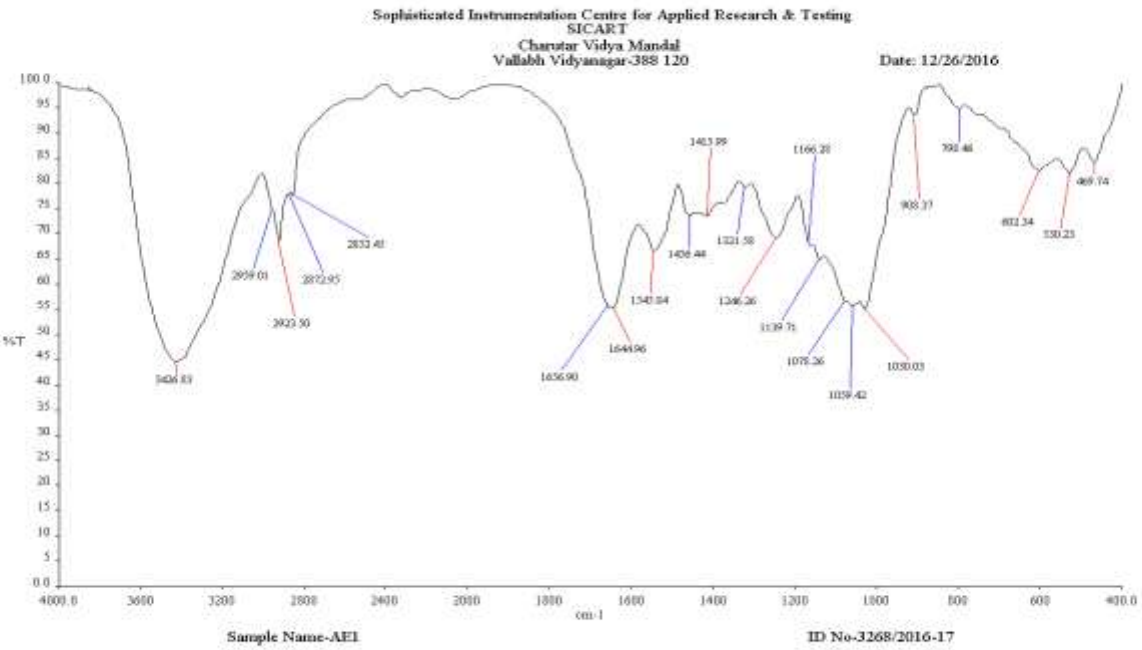


Figure 10:- FTIR of *Caulerpa racemosa* after treatment with E1effluent

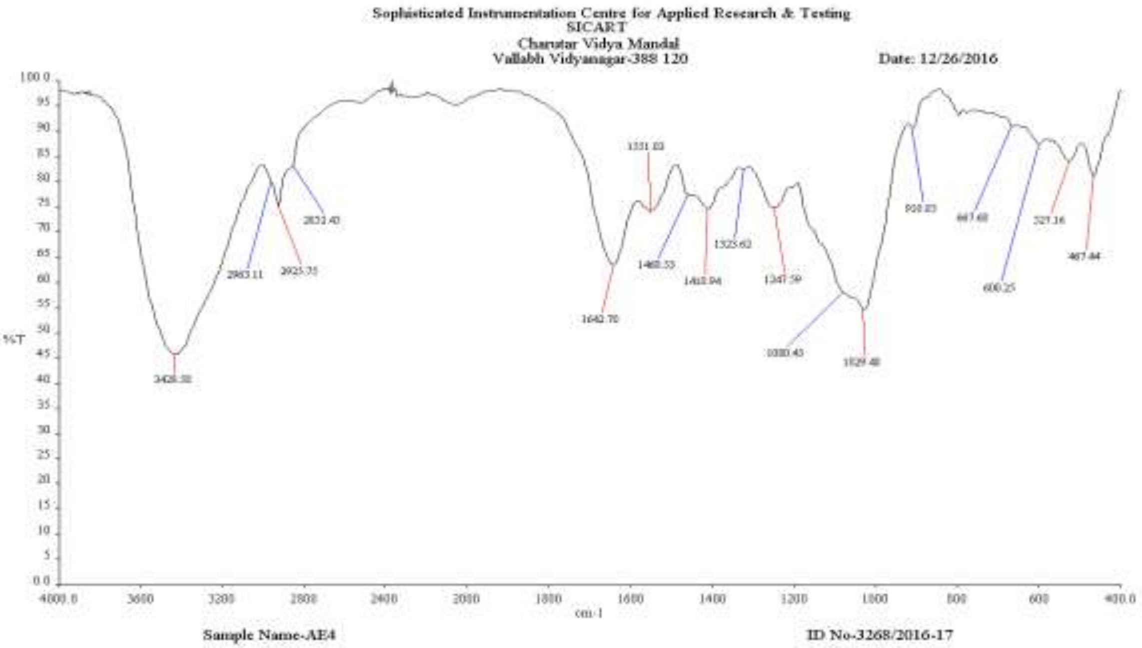


Figure11:- FTIR of *Caulerpa racemosa* after treatment with E4 effluent

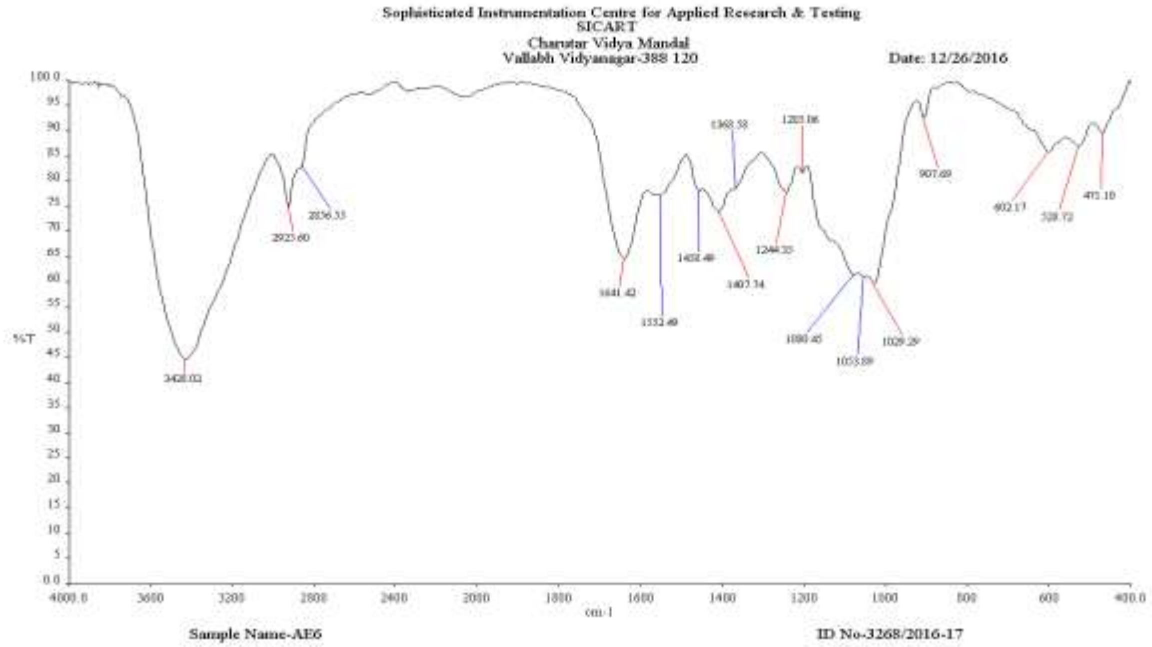


Figure-12:- FTIR of *Caulerpa racemosa* after treatment with E6 effluent.

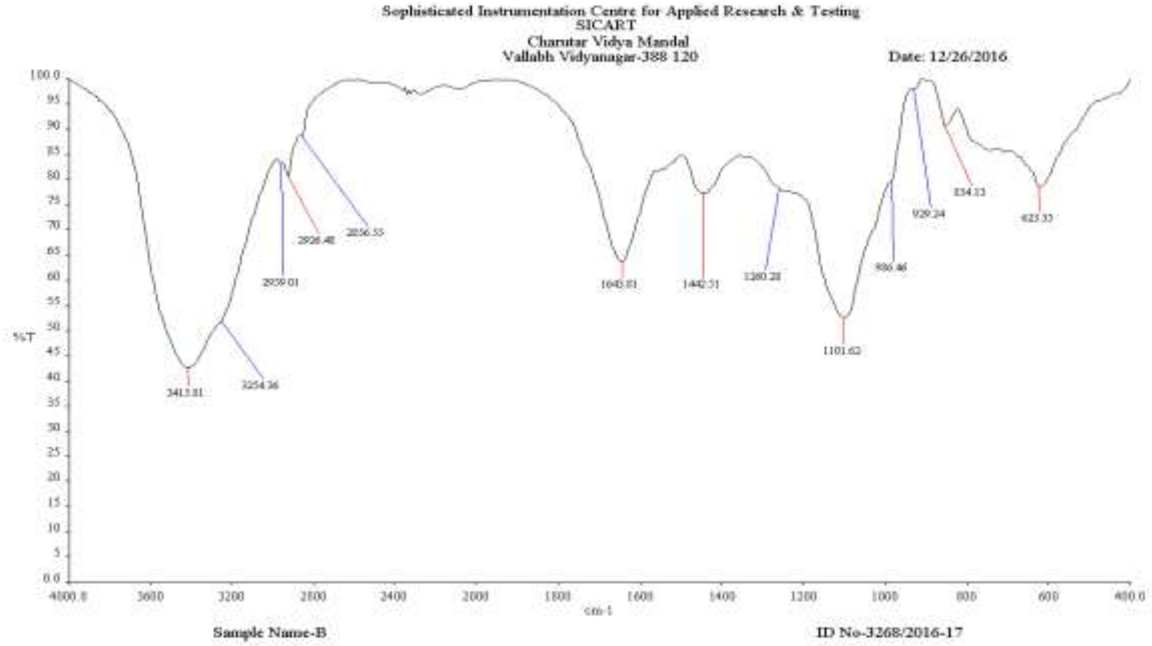


Figure 13:- FTIR of *Ulva lactuca*

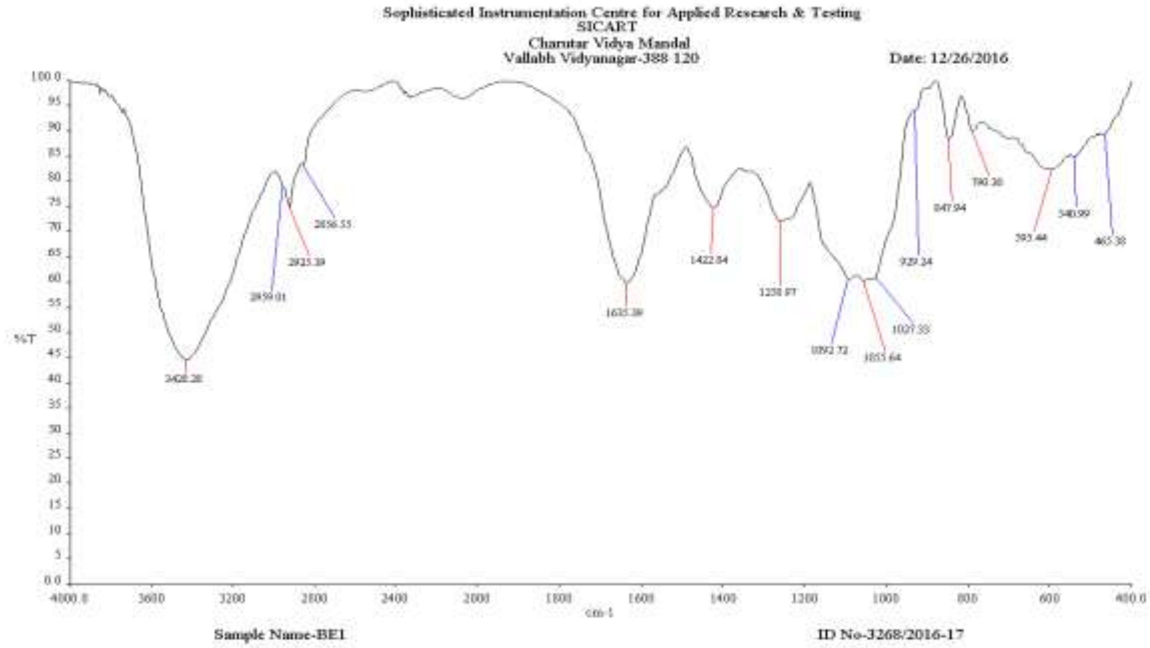


Figure14:- FTIR of *Ulva lactuca* after treatment with E1 effluent

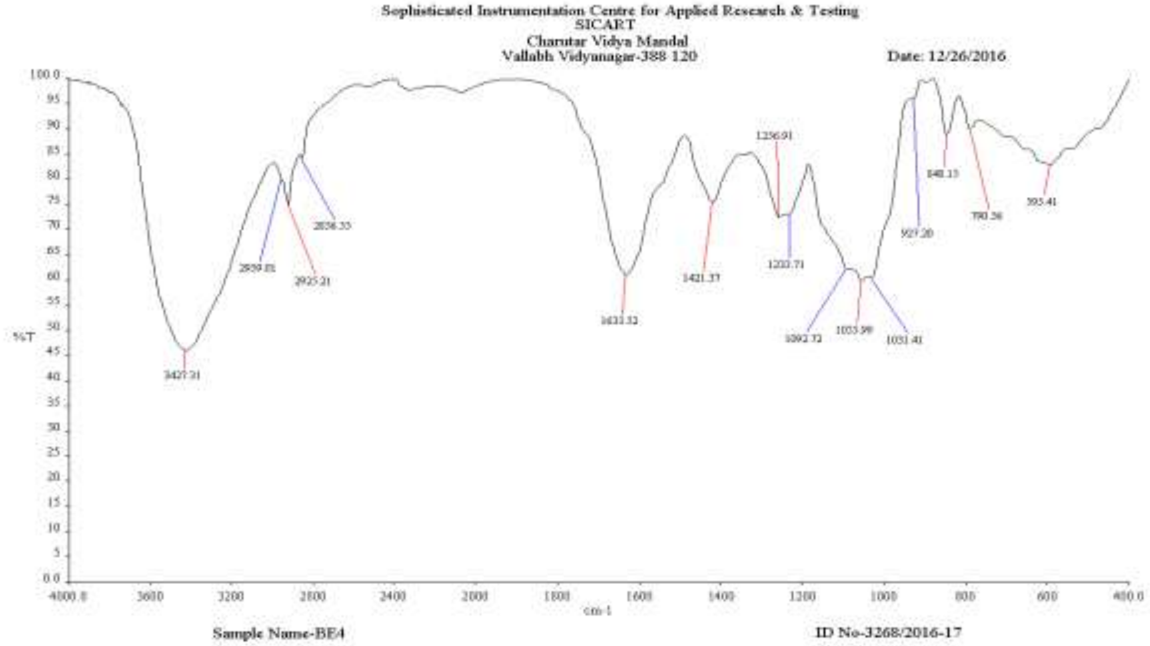


Figure15:- FTIR of *Ulva lactuca* after treatment with E4 effluent

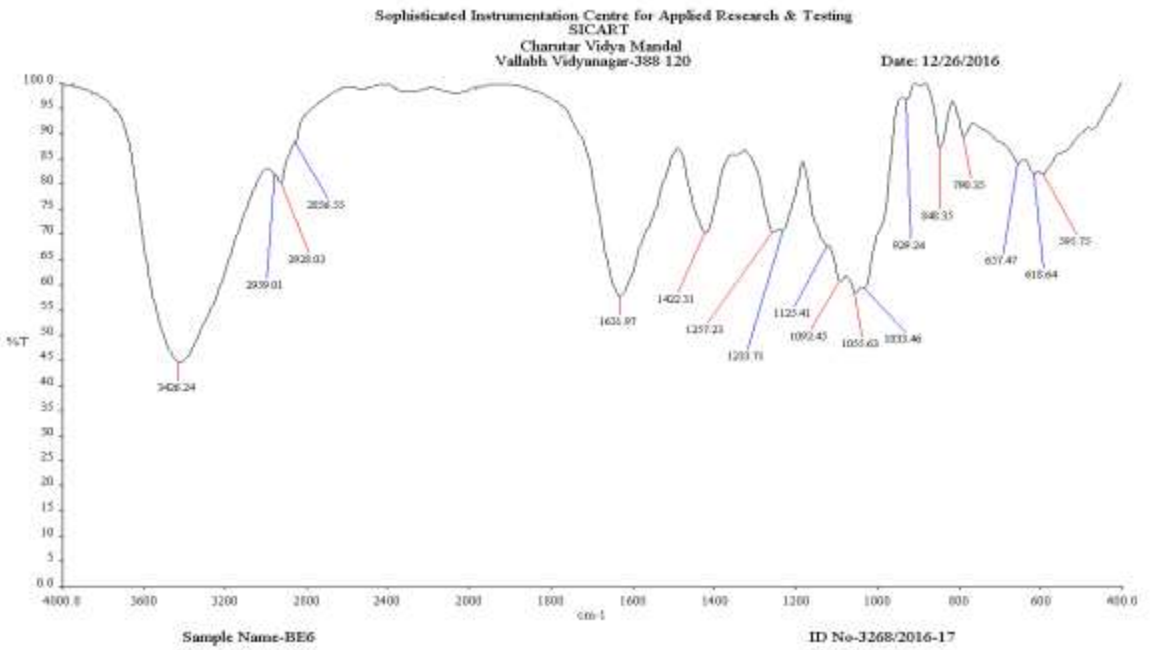


Figure 16:- FTIR of *Ulva lactuca* after treatment with E6 effluent

Conclusion:-

The present study concludes that green seaweed biomass of *Caulerpa racemosa* var. *cylindracea* and *Ulva lactuca* has high biosorption capacity for heavy metals. The biosorption of Cu is found maximum than Cr in both seaweed biomass. *Ulva lactuca* shows higher affinity towards Cu > Cr and gives potential biosorption yield as compare to *Caulerpa racemosa.* The highest 20.23 % Cr removal and 42.91 % Cu removal was observed in *Caulerpa racemosa* and in *Ulva lactuca* 62.2 % Cr and 70.35 % Cu removal was observed. The data are well fitted by the Freundlich and Langmuir isotherms show the favorable biosorption of dye effluent by green seaweed biomass. The data on the kinetic studies fitted well and shows the adsorption kinetics of dyes effluent by both green seaweed biomass followed the pseudo-second order model for biosorption of Cr and Cu, only pseudo first order model was observed in Cr treatment by *Ulva lactuca.* The SEM and FTIR analysis indicates the uneven surface, cells were damaged & swollen after treatment with effluent and the variation in functional groups, and decrease in peak intensity indicates the participation of metal binding inside the cells of the biomass. Thus the study indicates considerable potential of green seaweed biomass as biosorbent for the removal of heavy metal from effluent which can be applicable on field level.

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